

## THE USE OF CHEMISTRY FOR THE SYNTHESIS OF INORGANIC-ORGANIC HYBRID MATERIALS

H. Schmidt

Fraunhofer-Institut für Silicatforschung, Würzburg,  
Fed. Rep. Germany

The combination between inorganic and organic polymeric materials on nanometer scale depends strongly on methods for synthesizing inorganic polymeric networks suitable to the thermal stability of organic materials. The sol-gel process as a "soft-chemistry" method has been proved to be a proper tool for building up inorganic network with incorporated organic components. Examples for chemical synthesis and material applications are given.

### 1. Introduction

The combination of different types of materials for achieving novel properties has always been of high interest, since in many cases the properties of the basic materials do not meet special requirements for application. Therefore, numerous examples can be given: Laminated automotive wind screens, fiber reinforced or filled polymers, corrosion protected steel surfaces, or various other types of composites. The composites are generally characterized by the fact, that the two (or more) basic types of materials have to be combined by mechanical processes before or during the processing or the moulding step. Exceptions are gas phase deposited films on substrates, where the material synthesis step takes place during the coating procedure or the formation of crystals in glasses to produce glass ceramics. Only in the latter case, the composite unit size can cover the range of "microscopic" dimensions, whereas the other examples (and that is true for the majority of the real composites) cover the range of "macroscopic" composites. Generally,

the preparation of composites based on mechanical procedures limits the unit size, since handling or even preparation of nanosized particles or fibers is rather difficult or even impossible. Thus, for the generation of microcomposites, chemistry orientated in-situ processes seem to be a more suitable tool. Numerous processes are known which can produce very small units, like crystallisation from solvents or melts, condensation from the gas phase, or growth processes of amorphous materials by condensation reactions from solution or from the gas phase. The task for the synthesis of microcomposites is to use those processes in combination with other (known) material synthesis processes in order to develop new materials.

A combination of special interests are very often materials with extremely different basic properties like metals and polymers or ceramics and polymers. Especially ceramics and polymers are not only very different in properties but also in their production technologies.

The basic "construction principles" for inorganic polymers like glasses are network forming units like the  $[\text{SiO}_4]^{4-}$  tetrahedron or analogous components which are linked to a three-dimensional network by sharing corners. The properties defined by this principle are well known: Hardness, brittleness, high temperature processing, high Tg values, and low free volumes. Almost the opposite can be observed in organic polymers. For example, in hydrocarbons, the structure building units are  $\equiv\text{C}-\text{C}\equiv$ ,  $\equiv\text{C}-\text{O}-$  or  $\equiv\text{C}-\text{N}=\text{}$  groupings which are linked together to polymeric chains by chemical (not melting) processes and a linear chain is formed in the first step which has to be crosslinked to get three-dimensional networks. As a result, the polymers usually are soft, low temperature processing is possible, and the desired elastic or thermoplastic properties can be achieved. The free volume is high due to the organic chain movement, and Tg's generally are low. Figure 1 compares the Tg regimes of the two groups of polymers based on the Cp consideration. There might be an overlap with very special compositions.

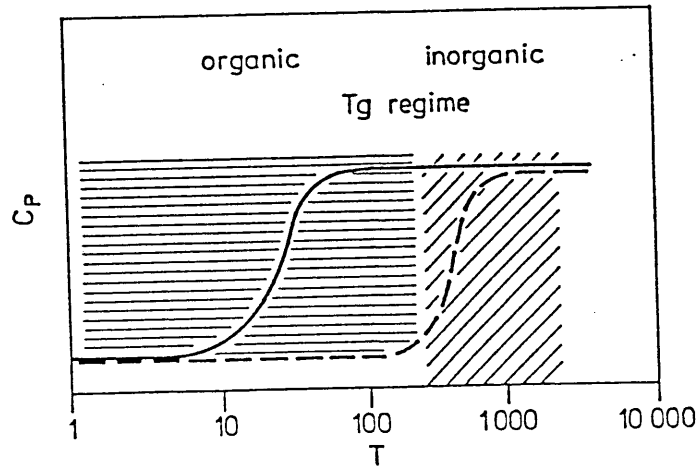
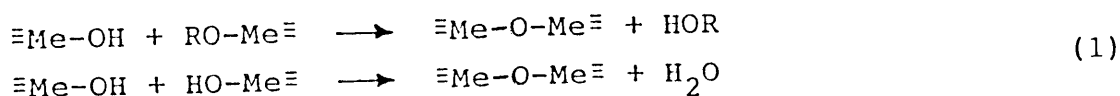


Figure 1. Main Tg regimes of inorganic and organic polymers.

The question arises how to synthesize composite materials with inorganic and organic components. In the living nature, the principle is used rather often. Bones are an excellent example for the combination of strength and elasticity based on a collagen/calcium phosphate composite. Other examples are plants which can precipitate silicates or oxalates as reinforcing components. In these cases, low temperature processes are the basis for the synthesis. These composites are characterized by the fact, that the unit size is quite small but still not in the molecular or nanometer size, but a perfect arrangement or microstructure is built up for an optimal strenghtening effect. It is difficult to define a lower limit for the unit size for the different composite components in order to consider the material still as a real composite. In this consideration, inorganic ions (like in ionomers) or inorganic atoms are defined to be not sufficient for an inorganic-organic composite. That means, for example, that silicones with the  $\equiv\text{Si-O}$ -bond as the polymeric chain forming element are excluded. The smallest units accepted in this consideration are inorganic network forming units like the  $[\text{SiO}_4]^{4-}$  tetrahedron or analogous structures (e.g. Ti, Zr, Al). As upper limit, the range  $\leq 1 \mu\text{m}$  is considered.

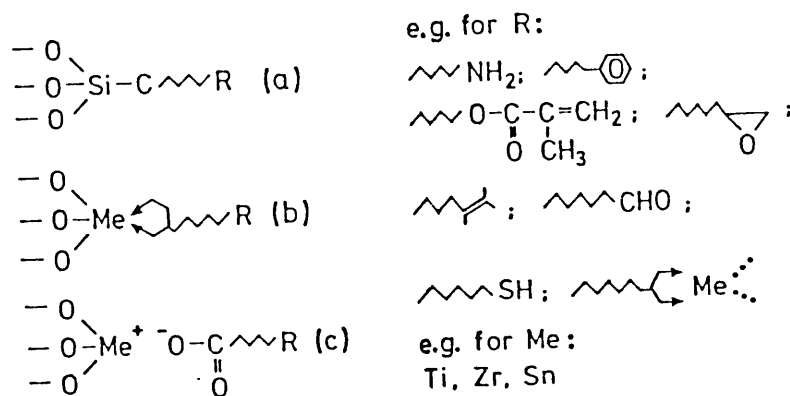
For the organic modification of ceramics, various possibilities exist. They all have to have in common, that a combination of the inorganic with the organic part takes place via a soft chemistry route, which has to be demanded for inorganic network forming steps during the synthesis, too. Therefore, the sol-gel process is a suitable mean where the network forming step can take place by a condensation reaction at low temperatures (1) [1-12].



R = alkyl; Me = metal atom

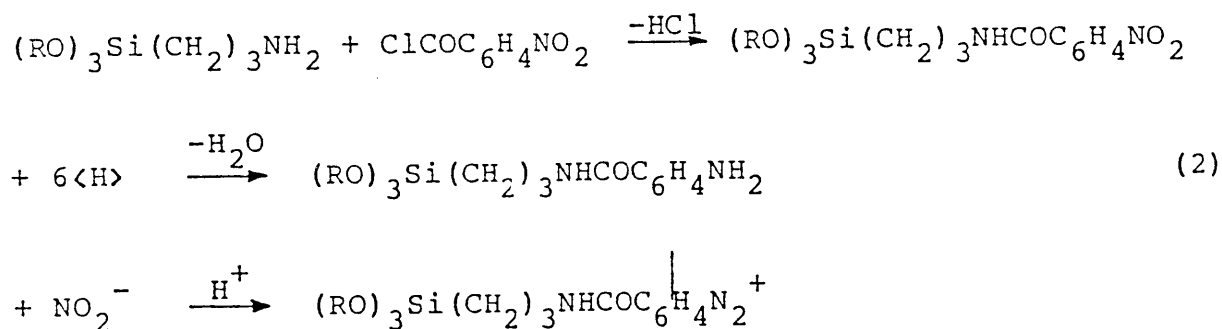
Some important examples to introduce organics into inorganic components are:

- penetrating porous glass or porous gels by organic monomers and polymerize them [13]
- penetrating inorganic polymer precursors into silicones [14]
- synthesizing independent inorganic-organic interpenetrating networks [15]
- linking organic groupings to an inorganic backbone via chemical bonds as shown in scheme 1.



Scheme 1. Models for linking organic groupings to inorganic backbones. (a): covalent bond to Si; (b): complex formation to a metal atom, e.g. Zr/acetylacetonates; (c): ionic bond to an organic acid (salt formation).

In this paper, the various possibilities resulting from the model (a) and (b) will be emphasized. Since (a) type molecules can be synthesized easily via the hydrosilylation reaction [16] in form of hydrolysable compounds  $[(RO)_3SiR']$  and a variety of them is already commercially available, they provide an easy way to bind organics to an inorganic network. In addition to this, chemical reactions can be carried out in order to modify or polymerize organic groupings to new structures. One example, therefore, is the modification of an amino group into nitro-anilino or diazo group according to [17] (2).



The incorporation of the silanes is based on the "sol-gel" reactivity of the  $(RO)_3Si$ - grouping. A variety of different structures is possible as shown in figure 2.

Organics can basically act as inorganic network modifiers and they can do that in two different ways. They can be crosslinked directly to the inorganic network via a chemical bond or they can be entrapped as molecules into an inorganic network, thus modifying it by creating a chemically or physically different site (a). Or they can act as network formers, e. g. if polymerizable ligands are used (b), which can be polymerized by themselves or with organic monomers. The structure model (c) can be considered as a variation of (b), and, of course, all three principles can be used in one and the same material.

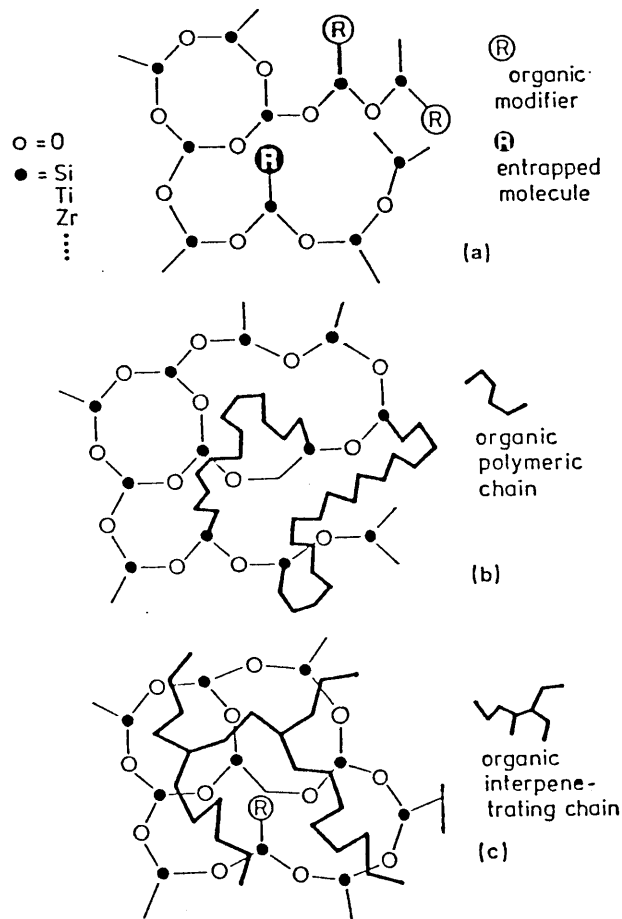
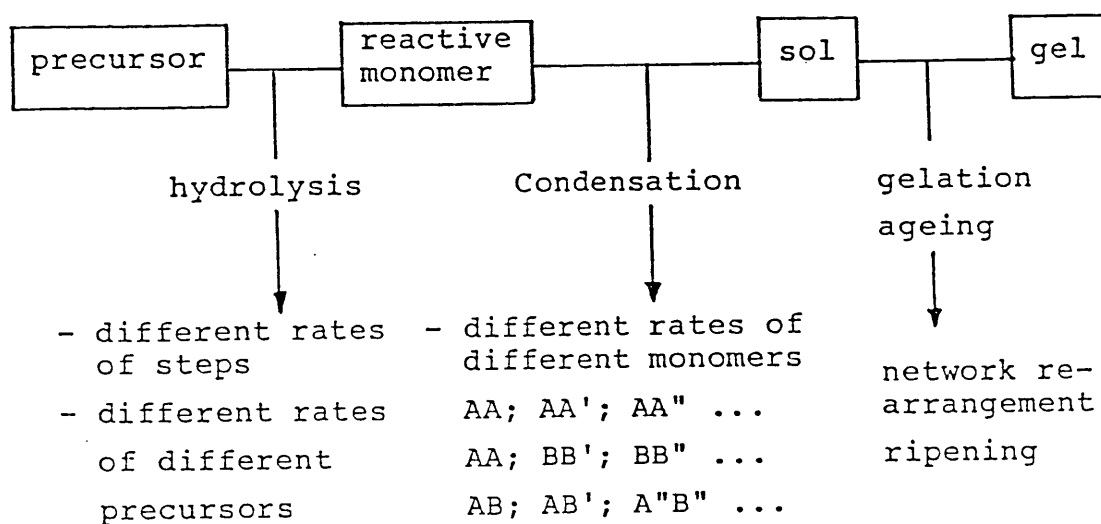


Figure 2. Structure models of organically modified ceramics:  
a) organics as network modifiers  
b) organics as network formers  
c) organics as independent networks.

## 2. Reactions

If sol-gel reactions are carried out, some basic questions have to be taken into account. If one starts from alkoxides, hydrolysis rates, especially in multicomponent systems, become important. The hydrolysis reaction is the step which provides active monomers, and their concentrations as a function of time define the distribution of different components in a condensate, produced by the second important step, the condensation reaction. Thus, homogeneity or inhomogeneity of gels can be influenced strongly. This is demonstrated in scheme 2 (after [18])



AA': monomer A with different states of hydrolysis  
(e.g.  $A \equiv \text{SiOH}(\text{OR})_3$  .....  $A'' \equiv \text{Si}(\text{OH})_4$ )

B: monomer B

Scheme 2.

In systems, which can react to pure inorganic materials it is possible to add a second structure forming step by a high temperature treatment e.g. crystallization to ceramics or densification to glasses. In this step, it is possible to overcome to a limited extent structure preformation as a result of hydrolysis and condensation. If organics are present, this possibility has to be abandoned in most cases, since the temperatures to be applied for the inorganic network softening (which would represent a fictive "inorganic"  $T_g$  in the composite) generally are too high with respect to the thermal stability of organic groupings. As a consequence, one has to pay all attention to the chemical synthesis up to gelation as the structure (or microstructure forming) step.

Numerous investigations have been carried out for the determination of hydrolysis rates [19-27] of silicic acid orthoesters, which show that protons and hydroxylions increase the rate, and

increasing chain length of the hydrolysable OR slows down the rate. But only a few data are available on the influence of non-hydrolysable groupings on hydrolysis and condensation. In figure 3, after [28], the hydrolysis reaction of different esters are shown. The rate is followed by the IR detection of the water consumption of the system. The acid catalyzed systems (figure 3a) show a rate increase with increasing number of Si-R

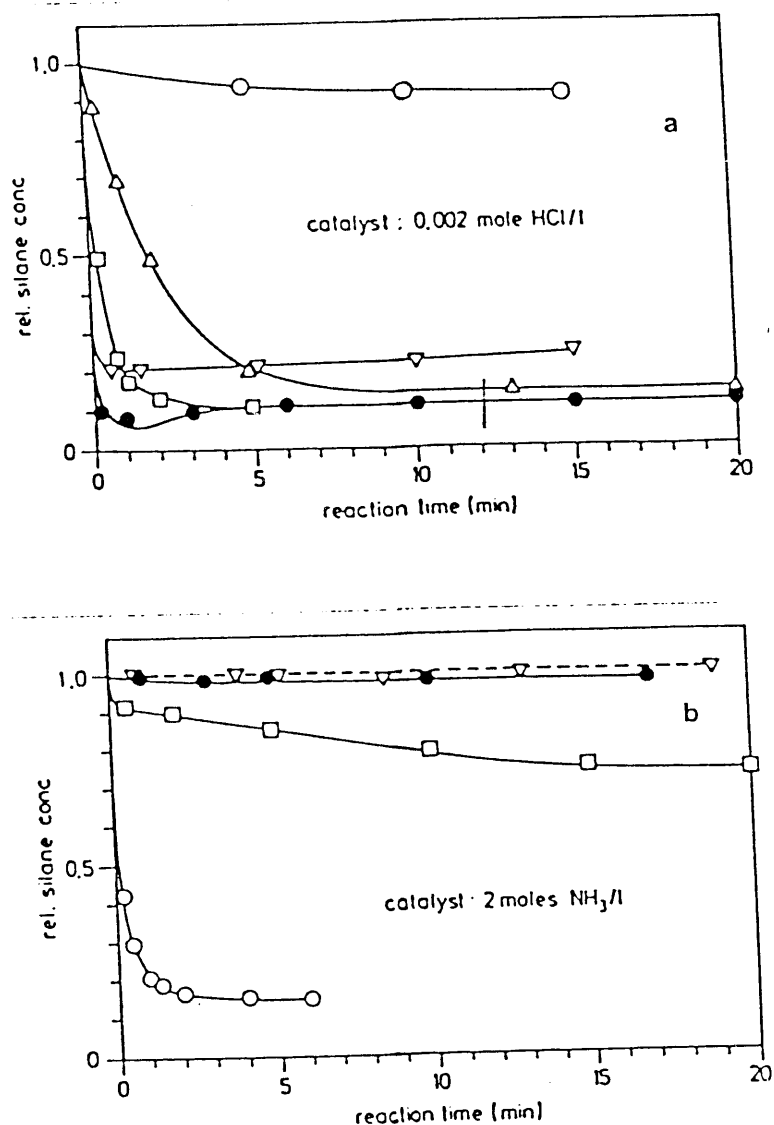
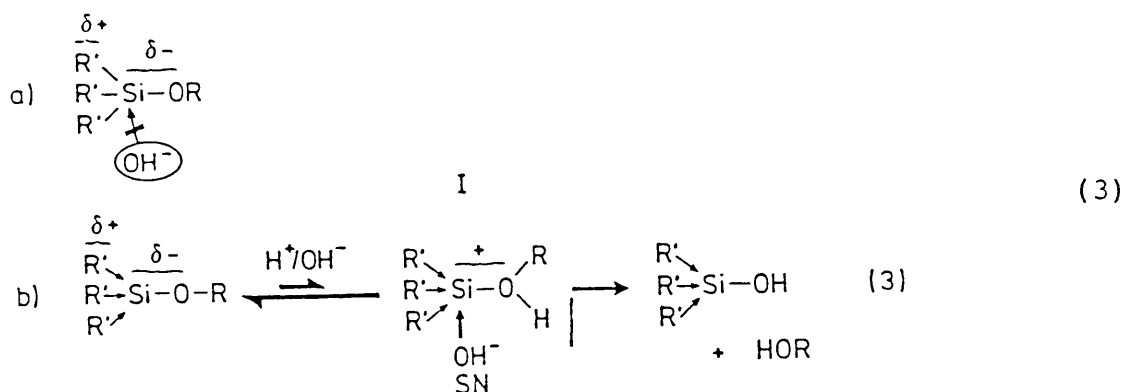


Figure 3. Hydrolysis of different silanes in ethanol as solvent (volume ratio 1:1); ●:  $(\text{CH}_3)_3\text{SiOC}_2\text{H}_5$ ; ▼:  $(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2$ ; □:  $\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$ ; ○:  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ; Δ:  $\text{Si}(\text{OCH}_3)_4$ .



substituents. In the base catalyzed process increasing numbers of unhydrolysable groupings seem to inhibit the hydrolysis reaction. This surprising effect can be explained by the electron donating (+I) effect of alkyl groups. Due to the increasing electron density on the silicon atom with increasing numbers of R' per silicon atom, a direct nucleophilic attack of an OH<sup>-</sup> to the Si within a nucleophilic substitution becomes more and more difficult. In this case, the acid mechanism including a protonisation of the =Si-O-R bond remains as the rate limiting step (3):



Due to the the concentrations of H<sup>+</sup> in an alkaline media, the concentration of the transition complex becomes extremely low and, according to the model of Eyring and Polyiani the overall rate decreases. Measurements with R' as alkyls and epoxy show the same tendency. Other alkoxides like Ti(OR)<sub>4</sub> or Al(OR)<sub>3</sub> exhibit higher hydrolysatation and condensation rates, too, compared to silicic acid esters. In order to control homogeneity it is necessary to develop reaction processes which can overcome these rate differences. Addition of water to a mixture of Si(OR)<sub>4</sub>/Ti(OR)<sub>4</sub> leads to a precipitation of TiO<sub>2</sub>·aq. and a maximum inhomogeneity of the system. There is a limited chance to equalize rate differences by the variation of the OR chain length. But increasing the chain length requires the development of new synthesis methods, the introduction of high amounts of organics into the system, and a remarkable cost increase. Another way described by Dislich [10] is the complex formation with acetyl acetate (acac) which seems to equalize condensation rates in multicomponent systems. Livage [29] could show

that the hydrolysis rate of  $Ti(OR)_4$  decreases with acetate complexation. For  $Al(OR)_3$   $\beta$ -diketone complexation was proved to decrease condensation rate only [30]. The hydrolysis rate was not affected. Figure 4 shows the NIR spectra of a hydrolyzed and non-hydrolyzed  $Al(OR)_3$ /ethylacetoacetate complex. In the "hydrolysed" spectra, no water can be found (which can be clearly detected in the alkoxide-free mixture with water). This proves the consumption of water by the reacting system ( 30 sec after addition). But in contrast to the uncomplexed alkoxide, no precipitation takes place, indicating that the condensation rate in this case is slowed down remarkably.

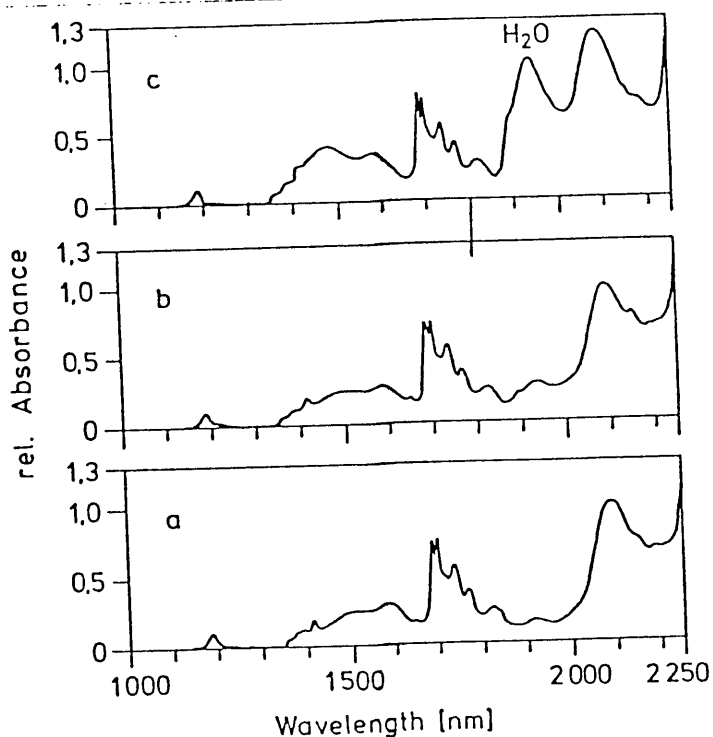
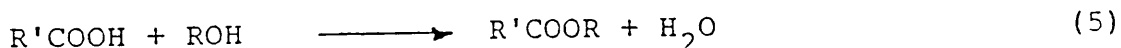
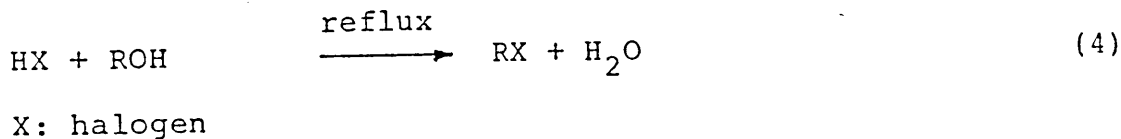


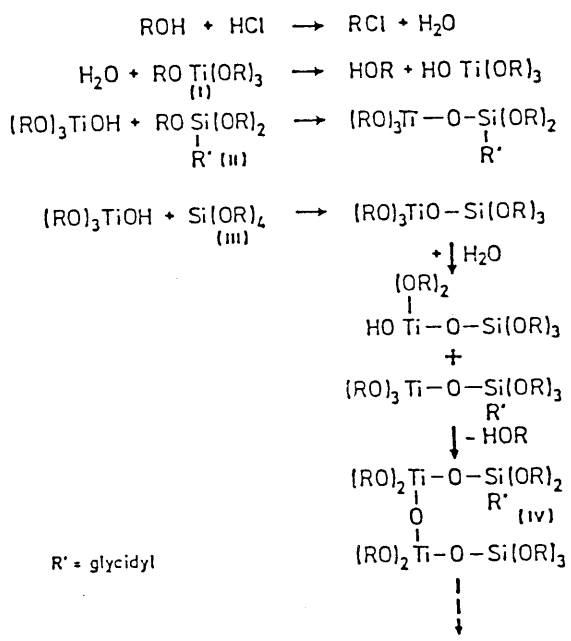
Figure 4. NIR-spectra of the  $Al(OR)_3$  complex and the  $H_2O/Pr^iOH$  solution  
a)  $H_2O/Pr^iOH$  solution  
b) sample after hydrolysis (reaction time 1 minute)  
c) unhydrolyzed sample.

Similar results are obtained with zirconia [31]. This means, that complex formation can be successfully used to eliminate undesired reactions from fast reacting alkoxides. Another process had been developed, which was called the CCC (chemically

controlled condensation) method [32]. In this case, water is generated within the reacting system chemically. The advantage of this method is to avoid concentration gradients and to control the water concentration (4, 5).



By proper choice of reaction conditions, the H<sub>2</sub>O generation rate can be adapted to the system. With this method, for example, in mixtures of I:II:III = 30:50:20 (scheme 3) it is possible to fix the titanium into a prepolymeric network (IV) by only generating about 1/16 of the amount of water necessary for total hydrolysis by ester formation. Direct addition of excess water to this prepolymer does not lead to any precipitates of TiO<sub>2</sub>·aq; no complex former is required. The effectiveness of this method has been proved for a variety of reactions.



Scheme 3.

As an explanation for this surprising finding, it has to be concluded that the water at first leads to partially hydrolysed fast reacting species, in this case to  $(RO)_3TiOH$ . The  $\equiv TiOH$  then reacts statistically with all type of  $\equiv MeOR$  groups and thus is linked to heteroatoms. Once mixed polymers are formed, additional water no longer can lead to  $TiO_2$  precipitates. The method works fine with other alkoxides like Al and Zr, too. By the CCC method, perfect homogeneities (e.g. extremely low light scattering, no phase separation detectable in the high resolution TEM) can be achieved and optical applications are possible. But phase separation can be introduced, if desired by chemical reaction, too. For example, in a glass made from Si-epoxy silane, Si-methacroyl silane and hexamethylen-diamin (HMD) as crosslinking agent phase separation takes place at Si-epoxy:HMD = 1:1 (Si-epoxy:Si-methacroyl = 1:1) indicating a lower degree of crosslinking due to the HMD excess. The two phases have about the same Si content (high resolution EDAX). One can conclude that in this system, the immobilization of the different phases can be carried out by organic crosslinking, if proper conditions are applied, but also that phase separation can be introduced. The samples are prepared by hydrolysing Si-epoxy silane to a slightly viscous liquid in ethanol/ $H_2O$ /HCl, adding the Si-methacroyl silane, continuing hydrolysis and condensation, removing the solvent and HCl, then adding the amine. Figure 5a shows the homogeneous and Figure 5b the phase separated case.

In the sol-gel process with precursors leading to purely inorganic materials, generally gels are produced which are brittle and porous. This is due to the three-dimensional network formed by condensation, by which a porous microstructure is formed. For further densification, temperatures around the network softening point or temperatures for crystal formation by diffusion processes are required. Figure 6 gives a schematical description.

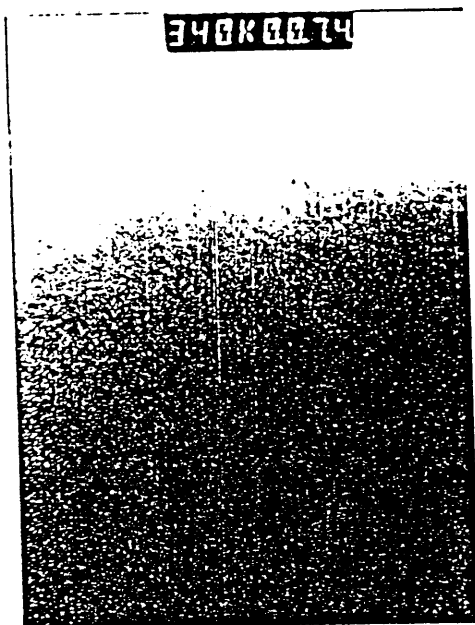


Figure 5a. STEM micrograph of a modified glass according to scheme 3; bar = 200 nm.



Figure 5b. STEM micrograph of a modified glass (composition see text) with phase separation; bar = 50 nm.

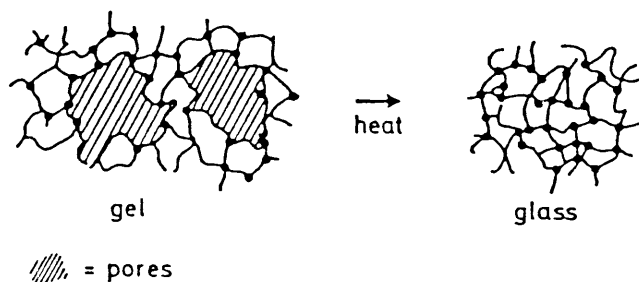


Figure 6. Gel to glass transformation: shrinking and decrease of porosity.

In case of organics included in the gel, the inorganic network has either to be widened or the pores have to be smaller or they are lacking completely (figure 7). In the latter case, shrinkage should decrease substantially or, in other words, the materials should reach their final density at comparingly lower temperatures compared to the "inorganic"  $T_g$ .

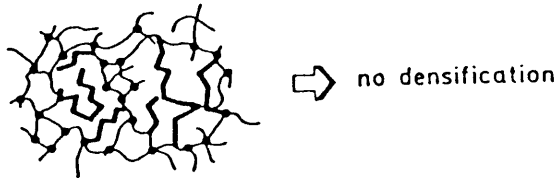
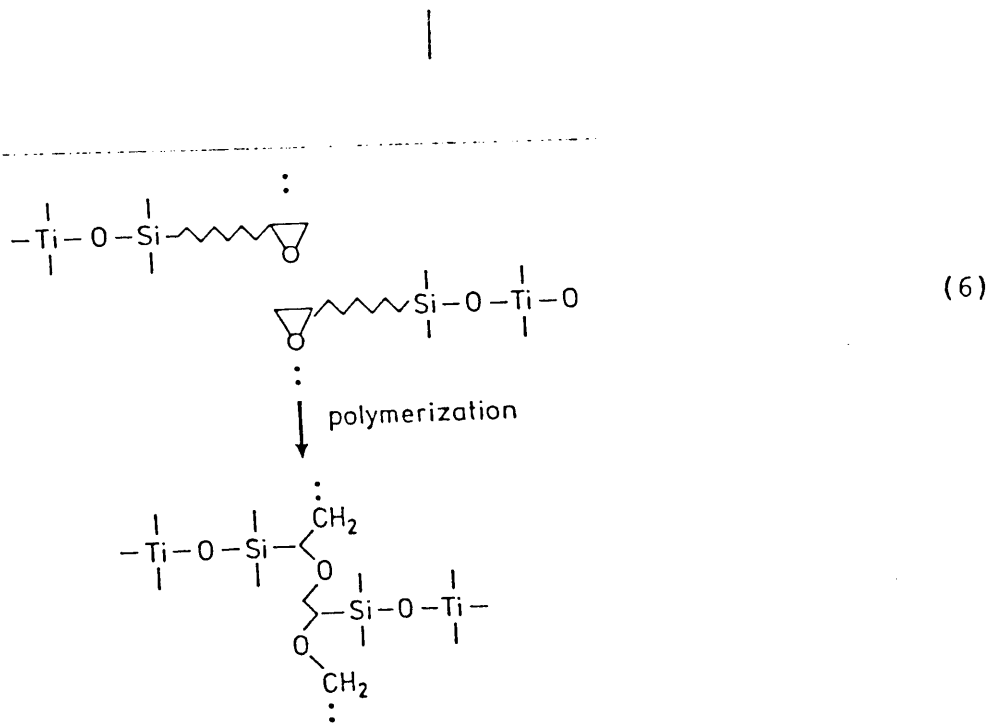
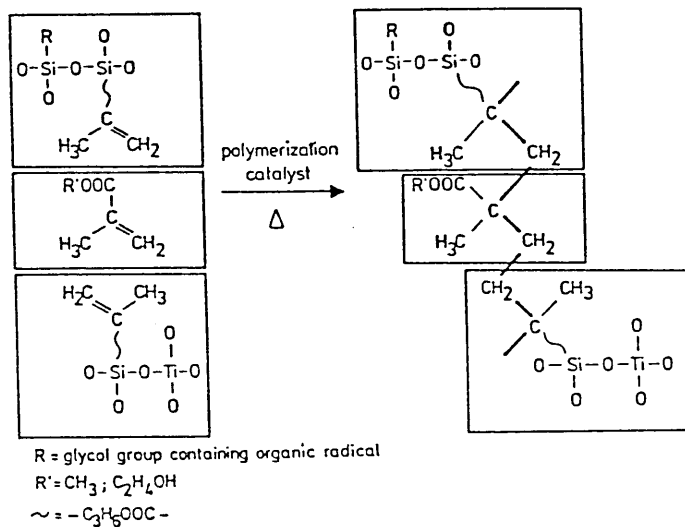


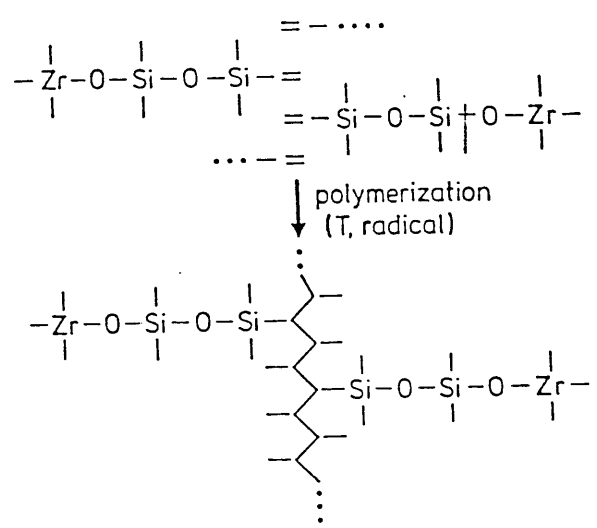
Figure 7. Lack of substantial densification in organically modified glass structures if pores are filled by organics.

Short organic groupings, e.g. covalently linked to the inorganic network are restricted in their "distribution" to the host Si atom. Longer chains can be "distributed" within the inorganic network or can be crosslinked one to another, if reactive ligands are present. Polymerizable groupings can be used for being crosslinked with organic monomers. Some examples for crosslinking are given in equations (6) to (8).





(7)



(8)

Of course, proper reaction conditions have to be chosen. The processing steps for sol-gel synthesis and organic reaction can be separated from each other and mouldable intermediates can be synthesized. The curing of solids can be achieved either by inorganic condensation, polymerisation, polyaddition, or by organic polycondensation. Multifunctional structures can be obtained, as shown in figure 8.

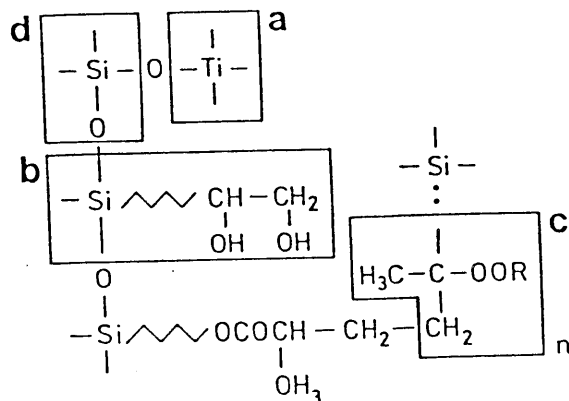
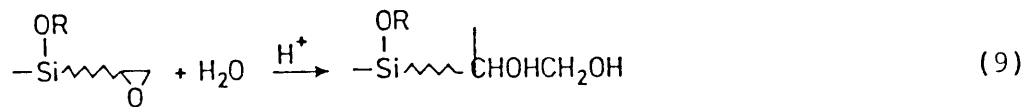


Figure 8. a, d: network formers; b: hydrophilic component; c: strengthening component.

The glycol function in this case has to be synthesized from an epoxy compound (equation (9)), since aliphatic alcoholic groups



react in transesterification reaction to new silicic acid esters according to equation (10).



The reaction has to be carried out under CCC conditions since ring opening takes place with water and catalyst addition to the reacting system. These examples show, that various chemical reactions can be carried out but they cover only a tiny aspect of the almost unlimited spectrum of possibilities.



### 3. Materials

#### 3.1. General considerations

In the following chapters, material developments will be presented. These developments are all system orientated, that means they have been developed for special application purposes. Therefore, it is somewhat difficult to draw general conclusions for the potential for other fields. In the conclusions, the attempt is made to summarize the application of this type of materials, which can be considered as organically modified ceramics (ORMOCERS).

#### 3.2. Porous materials

The incorporation of organics into the sol-gel process and the inorganic network can lead to various changes of properties. If hydrophobic groups are used, they can cover the inner wall of the pores and thus create hydrophobicity (figure 9). As a consequence, macroscopic properties of the porous materials can change, too.

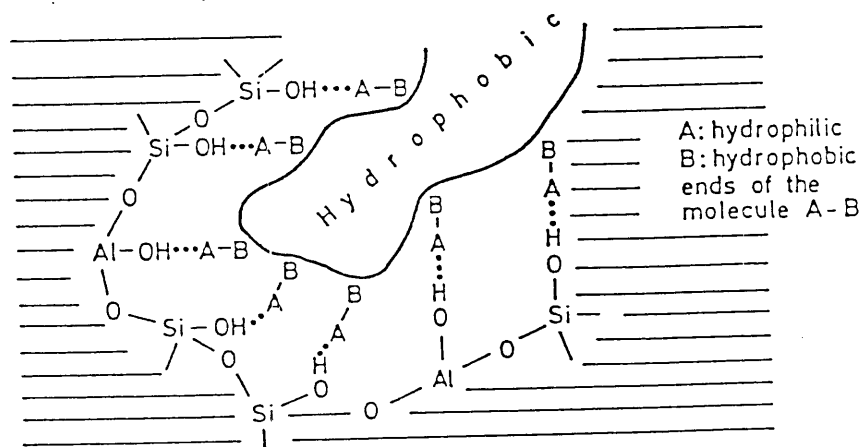


Figure 9. Effect of bipolar molecules on pore wall properties.

The effect of methyl groups on surface area and density is shown in figure 10.

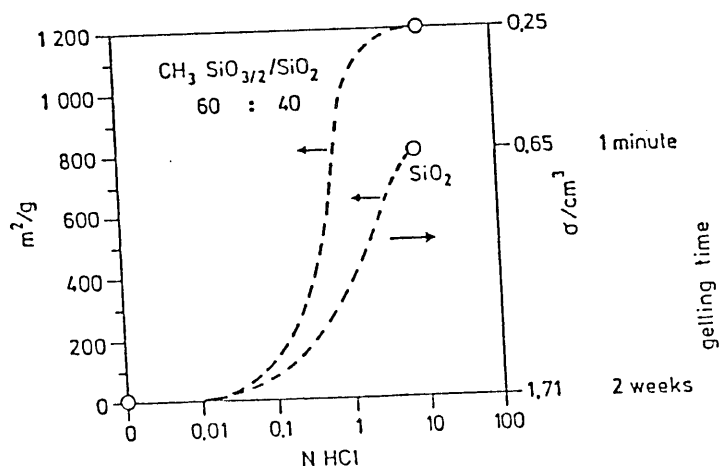


Figure 10. Gelation, BET surface and densities of different gels depending on HCl concentration during hydrolysis and condensation.

Thereby, despite high content of a network modifier which should lead to lower specific surface areas, the specific surface area increases, caused by increasing hydrophobicity. This increase can be interpreted by the decreasing interaction between the residual water in the pores and the pore walls, thus increasing the contact angle and decreasing interface tensions.

The influence of the catalyst concentration (HCl) on surface and density shows the same tendency for  $(\text{CH}_3)\text{SiO}_{3/2}/\text{SiO}_2$  and  $\text{SiO}_2$ . The hydrophobicity causes an additional effect: The water vapour adsorption is reduced drastically, as shown in figure 11. That might be very important for various applications of porous materials.

As indicated, amino groups reduce hydrophobicity and they can be used for additional adsorption effects, too. As shown in figure 12, the  $\text{CO}_2$  adsorption can be influenced remarkably.

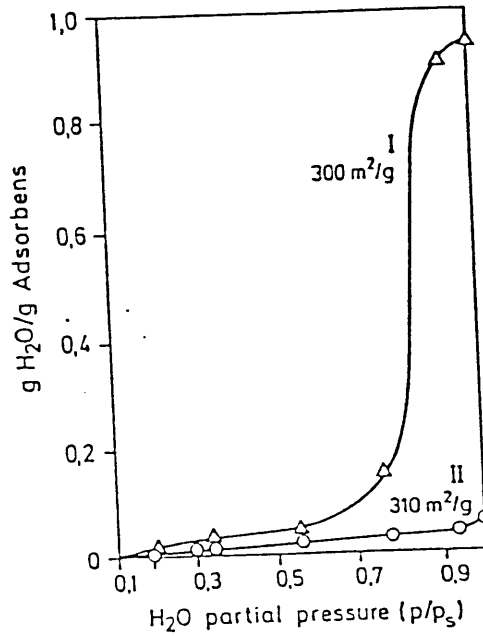


Figure 11. Water vapor room temperature absorption isotherms on two different gels; I = amino group containing gel (hydrophilic); II = methyl group containing gel (hydrophobic).

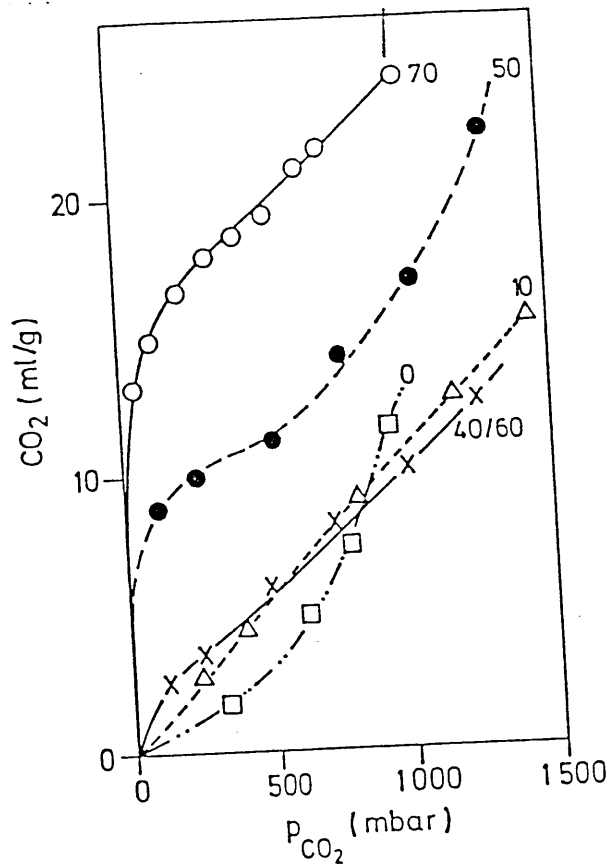


Figure 12. Adsorption isotherms of CO<sub>2</sub> on different network modified adsorbents: 70, network former SiO<sub>2</sub>, to network modified (am) ratio (molar): 30:70; 50, 50:50; 10, 90:10; 0, 100 % SiO<sub>2</sub>; 40/60, 40 SiO<sub>2</sub> and 60 CH<sub>3</sub>SiO<sub>3/2</sub> (molar); specific surface areas all between 200 and 300 m<sup>2</sup>/g.

In our investigations the adsorption behaviour of  $\text{CO}_2$  as a function of organic modification in porous  $\text{SiO}_2$  systems was measured. Figure 12 shows the comparison of three adsorbents, synthesized under equal reaction conditions (hydrolysis and condensation of  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ,  $\text{CH}_3\text{-Si}(\text{OC}_2\text{H}_5)_3$  and  $\text{NH}_2(\text{CH}_2)_3\text{-Si}(\text{OC}_2\text{H}_5)_3$  (am) in 50 vol.%  $\text{CH}_3\text{OH}$  with 0.1 N HCl and stoichiometric amount of water). The influence of the modification on adsorption behavior is obvious. The extreme high load at low  $\text{CO}_2$  values can be attributed to a weak dipole-dipole interaction between the aminogroup and  $\text{CO}_2$ , the relatively high load of  $\text{CH}_3$  group containing adsorbents to a hydrophobic interaction. The example demonstrates the influence of structural changes of inorganic polymers by organic modification on selected properties. A chemical heat pump was developed by use of two different types of adsorbents with  $\text{CO}_2$  [33]. Figure 13 shows a granular  $\text{CO}_2$  adsorbent.

In addition to this, amino group containing materials are useful for reversible acid adsorption from aqueous media and for enzyme immobilization [34].

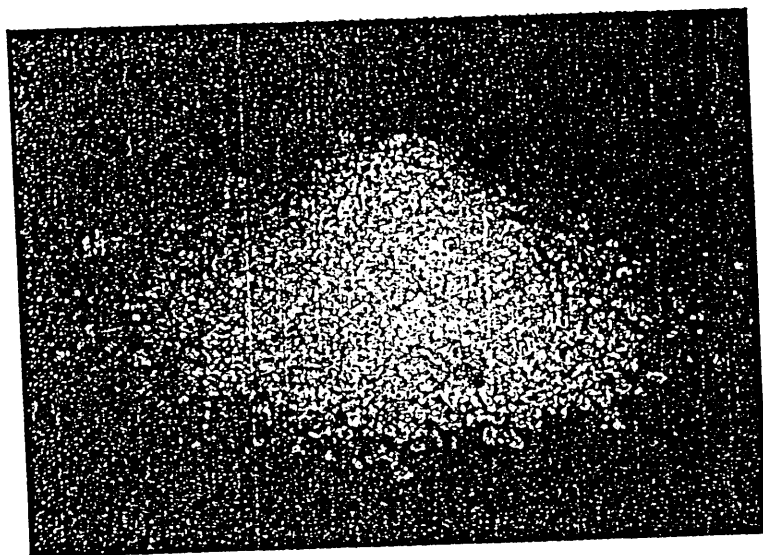


Figure 13.  $\text{CO}_2$  adsorbent.

Another possibility for application of porous materials is the field of abrasives. For special applications like cosmetic treatment or therapies of the human skin it is necessary to use softer abrasives or abrasives with limited effectiveness in order to avoid hurt. Moreover, these materials have to be absolutely free from toxic or irritating components. For the latter reason, silica or silicones are very suitable, but silicones as abrasives are too soft, while silicas for skin therapy in general are too hard. The development of mixed polymers based on  $[\text{SiO}_4]^{4-}$  and  $[(\text{CH}_3)_2\text{SiO}_2]^{2-}$ , however, should lead to materials, with suitable properties. Figure 14 shows the influence of composition on the abrasive properties on the material (abrasive number corresponds to the number of uncrashed grains after an abrasive test described in [35]).

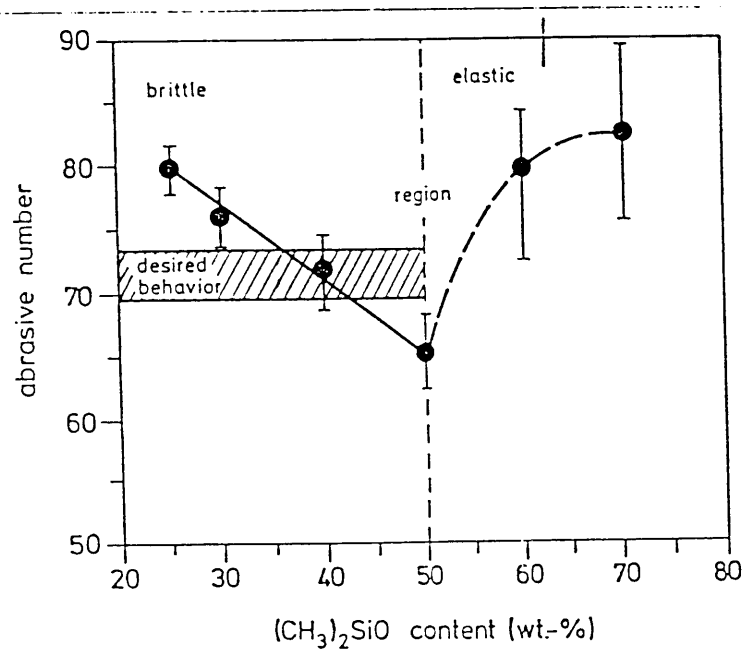


Figure 14. Abrasion behavior of a  $(\text{CH}_3)_2\text{SiO}/\text{SO}_2$  condensate depending on composition.

The material is used in an acne ointment as shown in figure 15.



Figure 15. Commercially available acne ointment.

These few examples demonstrate the variation of possibilities of inorganic-organic porous microcomposite materials. An interesting potential for further developments is

- carriers for enzymes and cells
- tailored adsorbents for solvent stripping
- gas sensors
- porous coatings
- membranes [36,37].

Membranes can be synthesized in a biphasic system [35] and used for improving filtration processes.

### 3.2. Thermoplastic materials

Inorganic polymers with "thermoplastic" properties in a common sense do not exist. Glass shows a high temperature "thermoplasticity", which is based on bond cleavage by temperature and thus leading to a softening. Thermoplasticity of organic polymers is based on mechanisms not including bond cleavage. The question arises, whether thermoplastic ORMOCERs can be synthesized. A prerequisite, therefore, in analogy to organic polymers is to keep the three-dimensional crosslinking limited and in addition to this, to keep the molecular size relatively low. For controlling the crosslinking, "linearizing" components, e. g. the  $R_2Si=$  or  $R'R''Si=$  with  $R = C_6H_5$ ,  $R' = \text{alkyl}$ ,  $R'' = \text{vinyl}$  are necessary.  $R'R''Si=$  is used in silicone chemistry for reactive crosslinking, too.

In figure 16, the influence of composition on properties is shown in a diagram.

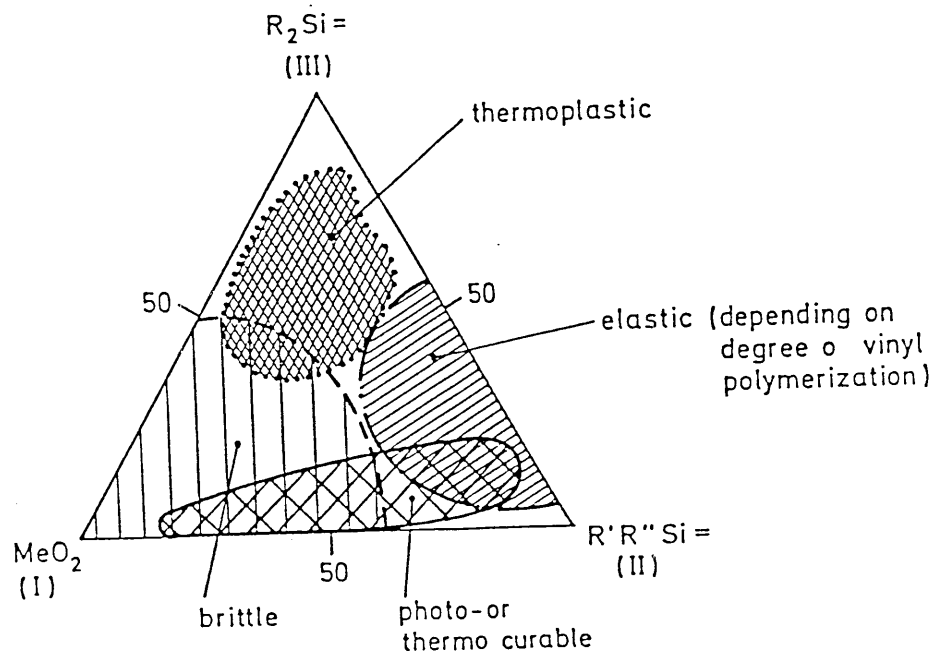
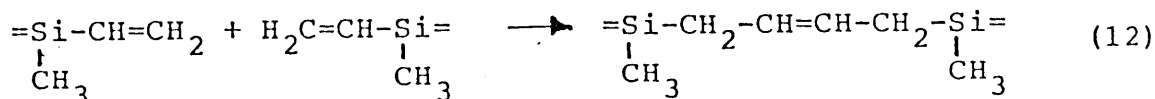
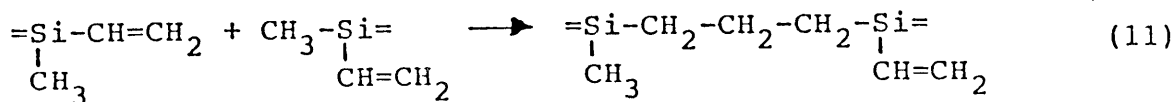


Figure 16. Property regimes in the system  $Me_2O/R'R''Si=R_2Si=$  (Me = Si, ti, Zr).

This diagram can only show tendencies. The exact properties depend on the special reaction conditions, especially on the degree of the vinyl reaction (equations (11) and (12)).



Compositions in the thermo- or photocurable regime can be prepared with thermoplastic or high temperature (up to 300 °C) melting properties and cured to non-thermoplastic solids by heat treatment, based on a thermoinduced radical reaction according to equation (11) or (12) or, at lower temperatures by use of a proper photoinitiator. Based on this composition, various types of materials had been developed.

### Adhesives

Adhesive groups with high reactivity to hydroxylated surfaces can be synthesized from  $(\text{C}_6\text{H}_5)_2\text{SiCl}_2$ , methylvinyl-SiCl<sub>2</sub> and Si(OR)<sub>4</sub> (or Ti(OR)<sub>4</sub>) [13,38].

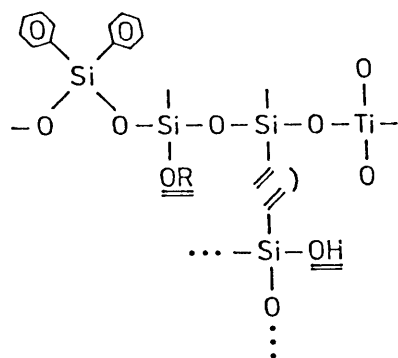


Figure 17. Reactive adhesive.



The reactivity is based on the residual OR and OH groups in the composite, which can be controlled by catalyst ( $H^+$ ) concentration during synthesis and monitored by IR spectroscopy. The adhesive can be used as a hot melt for glass container sealing or, after addition of an photoinitiator, as a seal to glass, where the UV curing process occurs by radiation through the glass. The seal shows a unique moisture resistance [39] compared with organic polymers based hot melts.

### Protective coatings

Based on these findings, a protective coating system for medieval stained glasses has been developed. This system is described in [14]. It adheres to glasses and corroded glasses and, in order to stop  $H_2O$  diffusion, a mechanical barrier system is included into the coating (mica or glass flakes, figure 18).

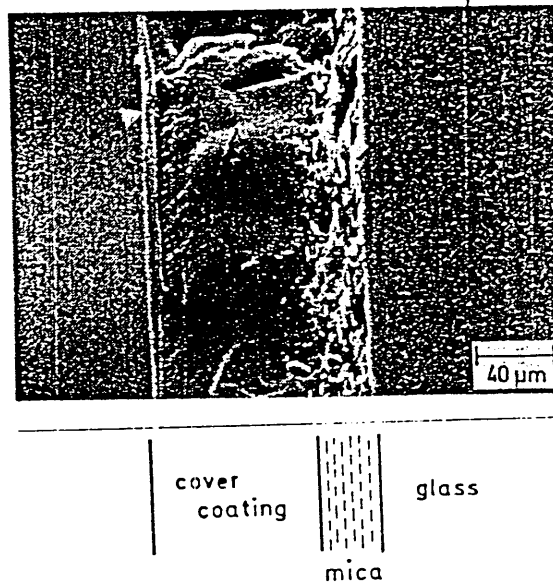


Figure 18. Compact protective system (two layers).

The diffusion barrier can be made "invisible" by adaption of the refractive index to mica or glass.

## Electronic materials

Dielectric coatings for electronic applications are another example for an application of this system [40]. Due to the unique electric properties [ $\epsilon \approx 2.3$ , surface resistivity  $10^{16} \Omega$ ] the material can be used for metal substrate coating in metal core circuit boards. Other applications are:

- protective coatings for corrosion sensitive substrates
- diffusion barrier in microelectronics
- hot melt for various purposes.

### 3.3. Hard coatings

Si, Ti, Zr, or Al oxide networks show interesting surface properties if crosslinked with proper organic components [32,41,42]. Useful basic compositions are  $[\text{MeO}_2]_x / [\text{SiO}_2]_y / [\text{SiO}_{3/2}\text{R}]_z$  ( $x = 0.05 - 0.3$ ;  $y = 0.05 - 0.1$ ;  $z = 0.4 - 0.7$ ), with Me = Ti, Zr, Al, B, Sn, and R = epoxy, methacryl, propyl or vinyl, as examples. These coatings have to be prepared by the CCC process for achieving high optical qualities. They show unique surface hardnesses. The modulus of elasticity can be adapted to the substrate by curing temperatures (50 to 150 °C; low temperature curing with methacryl groupings by use of photoinitiators is possible). The hardness depends on the  $\text{MeO}_2$  and increases with  $\text{Si} < \text{Zr} < \text{Ti}$   $\text{Sn} < \text{Al}$ . Due to the flexibility and the low temperature curing, plastics can be coated and their surfaces can be improved remarkably. Depending on composition, the coatings show hardness combined with corrosion protection, flaw healing effects on glass (strengthening) and good adhesion to various substrates. They are or can be used for

- hard coatings for all types of plastics like PC, PMMA, PVC, PET, PVB, PE, PP, and others

- corrosion protective and hard coatings on metals like brass, Al, Cu, Ag, Au (protection of metallized glass, plastics; mechanical protection of high performance metal surfaces)
- mechanical protection of paper, wood, wax
- mechanical protection of electronic circuit board master copies or other electronic parts
- outdoor applications for glasses or plastics
- matrices for host molecules (transition metals)
- decorative coatings with dyes included
- highly antiabrasive coatings with fillers included.

The multicomponent system allows to incorporate additional "functions" like hydrophilicity (antifogging effect) and various others.

This comprehensive survey shows the advantage of these types of microcomposites: "Inorganic" and "organic" function can be used to create new or tailored material properties.

Due to the high relaxation ability and the low shrinkage (5 - 10 vol.-%), bulk materials can be prepared as shown by the development of contact lens materials with intrinsic hydrophilicity, good mechanical strength and O<sub>2</sub> permeability (see figure 8) [43]. Figures 19 (page 28) to 20 (page 29) show examples for hard coating applications.

Table 1 shows the properties of materials developed for eye glass lenses.

Table 1. Scratch and abrading tests of different coatings composition (mole-%): MeO<sub>2</sub>: 20; epoxysilane: 50; SiO<sub>2</sub>: 30

Coatings and polymers					
Test	CR 39 (uncoated)	PMMA (uncoated)	Coating 1	2	3
A (load in g)	1 - 2	< 1	10	20 - 30	50
B (haze in %) (200 rev.)	12 - 13	> 20	-	1.5	-
C (haze in %)	4* 15**	- -	- -	1.2* 6**	- -

1 Zr-containing )  
 2 Ti-containing ) coatings | \* diamond powder and  
 3 Al-containing ) \*\* boron carbide powder  
 as abrasives

A vickers diamond scratch test: diamond load of the first visible scratch (by microscope)  
 B taber abrader: haze after abrasing  
 C special abrasion test with abrasive powders: haze after abrading.

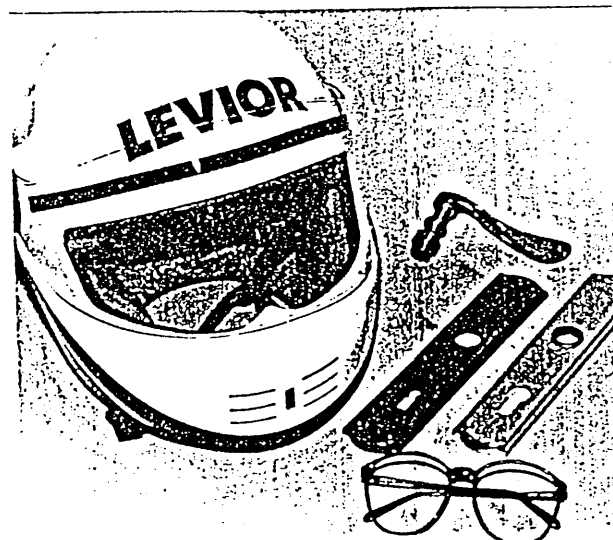


Figure 19. Scratch resistant coated articles.



Figure 20. Coated eye glass lens.

For the eye glass coating, a fully automated process has been developed (spin-on technique, figure 21).

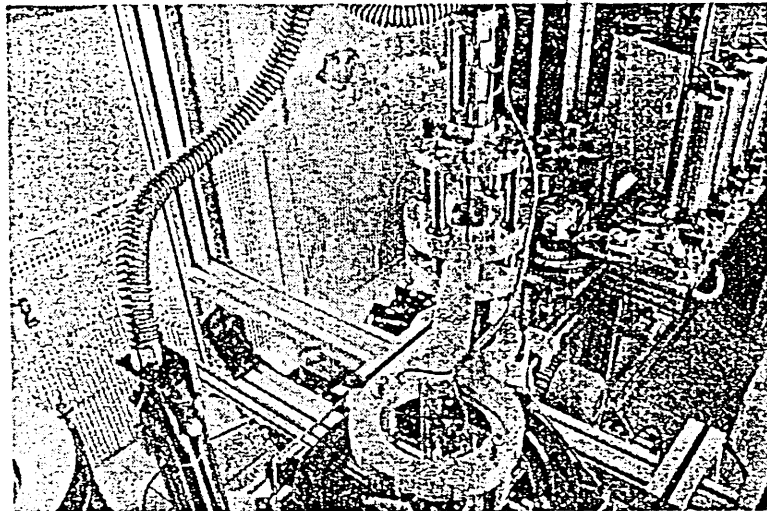


Figure 21. Automated eye glass lens production line.

#### 3.4. Functional materials

In this group, materials with very special functions are described. As mentioned above, by incorporation of special organic (or inorganic functions) special properties can be achieved.

## Sensors

Composite materials on the basis of  $\text{SiO}_2/\text{SiO}_{3/2}(\text{CH}_2)_3\text{NR}_2/\text{SiO}_{3/2}$  propyl can be synthesized by CCC sol-gel techniques [44]. These materials are able to incorporate reversibly up to 40 wt.%  $\text{SO}_2$  by complex formation, as proved by IR. Applied as coatings on an interdigitated capacitance device, the system can be used as a  $\text{SO}_2$  sensor with high sensitivity and selectivity. The mechanism is the change of the permittivity constant by the  $\text{SO}_2$  complex formation. Other developments show that analogously materials for sensing  $\text{CO}$ ,  $\text{NH}_3$ ,  $\text{NO}_x$  can be synthesized. Figure 22 shows the structure of a  $\text{SO}_2$  chip.

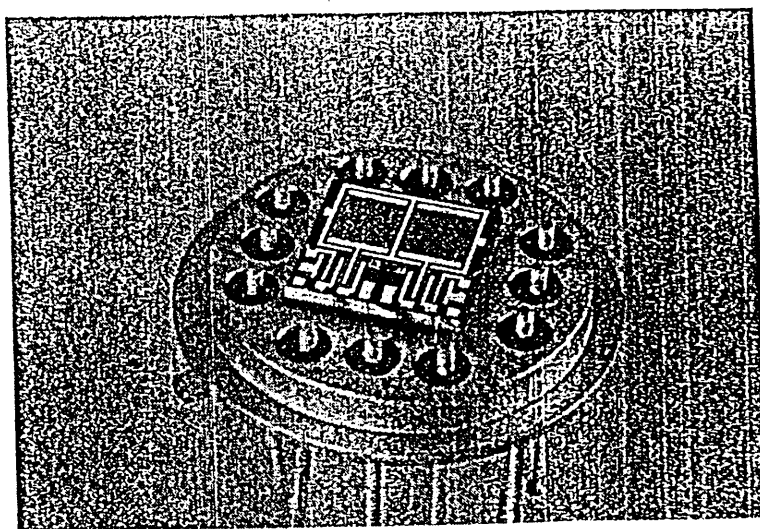


Figure 22.  $\text{SO}_2$  chip with an interdigitated structure.

## Catalysts

The incorporation of Rh-complexes into a sol-gel derived  $\text{SiO}_2$  porous matrix leads to new materials [45] with a high potential for new catalytic application.

## Biochemical compound immobilizing coatings

The incorporation of organofunctional groups like amino, amino, or aldehyde leads to materials with reactive surfaces. They can be used for immobilization of enzymes or antibodies,

e. g. for immunological assays. A T3-RIA based on a coated tube system has been developed [17] with good performances. The active coating contained aldehyde groups for direct coupling of T3 antibodies by a Schiff base reaction.

### Ion conductive solid state electrolytes

The advantage of these types of material is the structural stabilisation effect of the inorganic backbone in combination with properties of polymeric solid state electrolytes (flexible, thick film techniques) and the possibility for using sol-gel techniques for thin film coatings. First results [46] show that good conductivities can be achieved.

### 3.5. Reinforcement of polymers

Sol-gel techniques may be used for building up interpenetrating networks by simultaneous or consecutive synthesis of both types of networks. As an example, an amorphous -O-Ti-O-Ti-O- containing interpenetrating network was synthesized by use of an ethyl vinyl acetate copolymer dissolved in toluene as liquid phase.  $Ti(OR)_4$  was added slowly, hydrolysis and condensation were carried out through a  $H_2O$  vapor pressure controlled atmosphere. The resulting insoluble polymer exhibits a high scratch resistance in the diamond scratch test. Diamond loads of up to 20 g (Vickers diamond) do not result in visible scratches (microscope observation).

The unit size in this case is in the nanometer range. This example shows the potential for the generation of new types of polymers.

### 3.6. Inorganic-organic processing

Sol-gel technologies sometimes, as already discussed in the introduction, suffer from a lack of adequate reaction control. Complex formation can be a helpful mean to overcome these problems. Complex formation of aluminum alkoxides with excess of ethylacetate leads to polymeric complexes with low molecular weights (figure 23) [30].

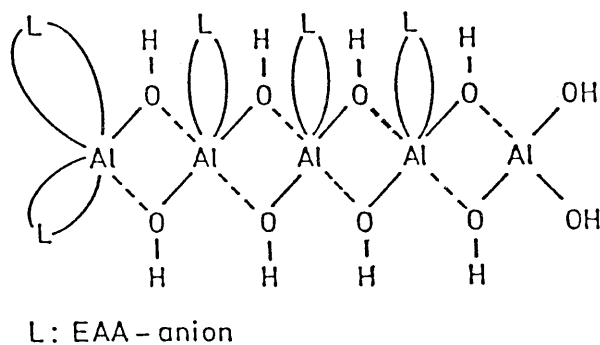


Figure 23. Model for the structure of  $[\text{Al}(\text{OH})_2\text{EAA}]_5$ .

The structure model is based on various methods (FTIR, NMR, TGA). Depending on reaction conditions, these complexes can be used for coatings (perfect coatings of  $\text{Al}_2\text{O}_3$  up to 1  $\mu\text{m}$  thickness), and they have a potential for nano particle preparation [47], or for fiber drawing. These methods can be used for Zr, too [31].

### 4. Conclusions

As discussed within the general considerations and shown on several examples, inorganic-organic microcomposites offer a wide spectrum of possibilities for material developments. The main route for the synthesis of the inorganic unit is the sol-gel process. This technique allows to tailor the properties in a wide range. One has to take into consideration, that the



sol-gel chemistry is influenced remarkably by the introduction of organic groupings, and processing and moulding is influenced, too. This means, that for new compositions new chemical processes have to be developed. Due to the numerous variations additionally provided by the organic chemistry, the number of possibilities increases almost infinitely. The few examples developed up to now prove the high potential of these new materials for very special applications including high technologies. To exploit this potential, a lot of effort is required from chemists and material scientists, and as one can see now, this is at its very beginning.

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