THE SOL-GEL PROCESS FOR ORGANIC-INORGANIC HYBRID MATERIALS

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1. Introduction

Tayloring of specific material properties has become a very important task for new material developments. Especially in the field of ceramics where the final properties are obtained by high temperature processes, structural and microstructural control are a desirable means for proper tailoring. In this connection, it is of interest how far structures of ceramics can be "prefabricated" during low temperature processing steps e. g. by use of nanosized precursors [1] or molecular design of structural units. As shown by Hirano [2] and Payne [3], structures built up by wet chemistry can affect processing and final material properties substantially, even if the basic structure cannot be maintained from the precursors (molecular building blocks, double or multiple alkoxides) into the final crystalline state. Conventional wet sol-gel processing does not lead to completely densified polycrystalline materials usable for ceramic parts, and high temperature densification steps have to employed. As a rule, during the high temperature treatment, organic components still present in the gel are decomposed or oxidized.

In [3], organics play the role of a structure controlling element, enabling the precursor to build up a very special structure. But they do not play any role in the final product. If they are used, however, for the reduction of the network connectivity, the gels can be densified at low temperatures as shown in [4 - 6]. The organics can play a manifold role if they remain within the structure. They can provide special functions, e. g. acids and bases, reactive groups for polymerization, polycondensation or polyaddition or act as ligands for complex formers. Moreover, they can vary the matrix properties in many directions, e. g. hydrophilic or hydrophobic, and thus influence the permeation and diffusion properties of small molecules. Meanwhile, a lot of inorganic-

organic sol-gel materials have been developed, and it has been shown that the ORMOCER system (organically modified ceramics) has an interesting potential for applications, too [7 - 9]. Due to the low temperature processing which is necessary not to destroy the organics, structures are built up during the sol to gel transition which, with a few exceptions, can be maintained completely in the final material. That means, the potential of molecular chemistry to tailor structures can be used advantageously for ORMOCER processing.

2. Structural Principles

The schematics for ORMOCER synthesis are given in fig. 1:

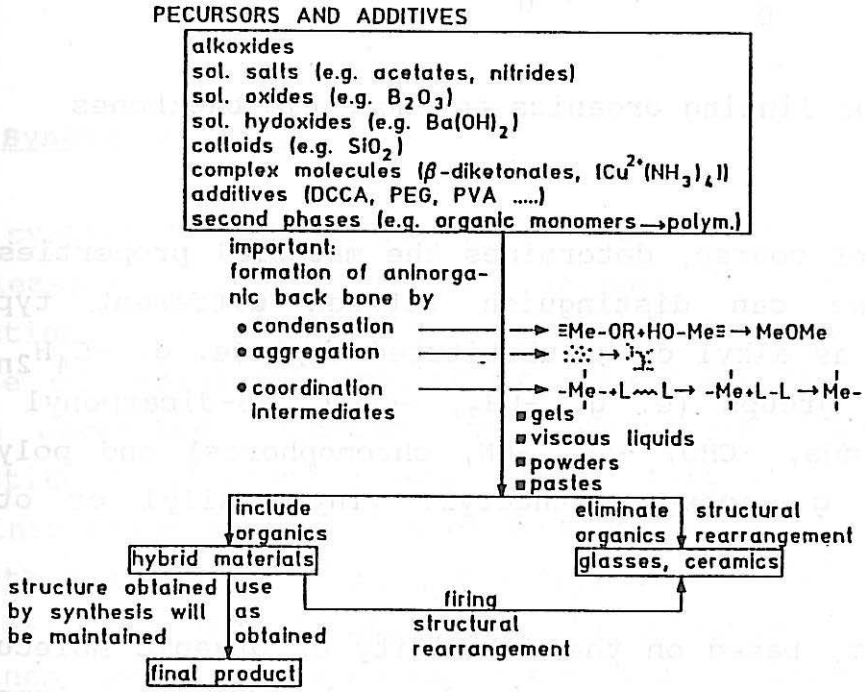


Fig. 1: Principles of ORMOCER sol-gel synthesis

Generally, the inorganic backbone is synthesized by the sol-gel process. The link between organic grouping and the inorganic backbone is very important. Covalent bonds, ionic bonds and coordinative bonds can be used, as shown in fig. 2:

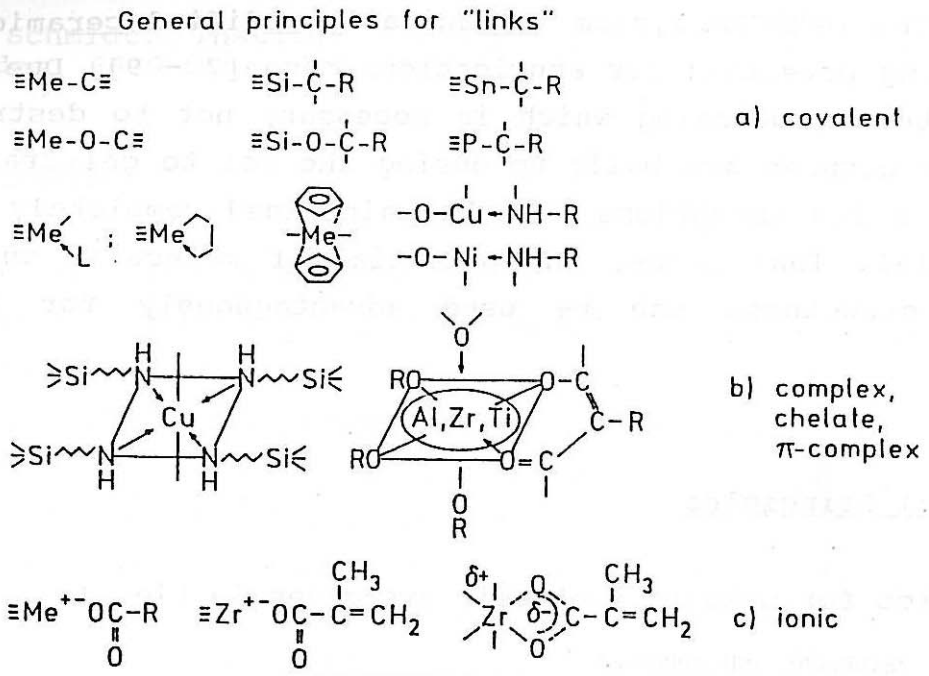


Fig. 2: Examples for linking organics to inorganic backbones

The type of "-R", of course, determines the material properties to a great deal. One can distinguish between different types: Indifferent groups as alkyl or unsubstituted aryl (e. g. $-C_4H_{2n+1}$, $-C_6H_5$), functional groups (e. g. $-NH_2$, -COOH, -ß-dicarbonyl and other chelate ligands, -CHO, -SH, -CN, chromophores) and polymerizing groups (e. g. epoxy, methacryl, vinyl, allyl or other olefines).

In addition to that, based on the solubility of organic molecules non-crosslinked components as organic dye molecules or polymeric chains can be entrapped within the inorganic backbone. In fig. 3, the variation possibilites of the structure are shown schematically:

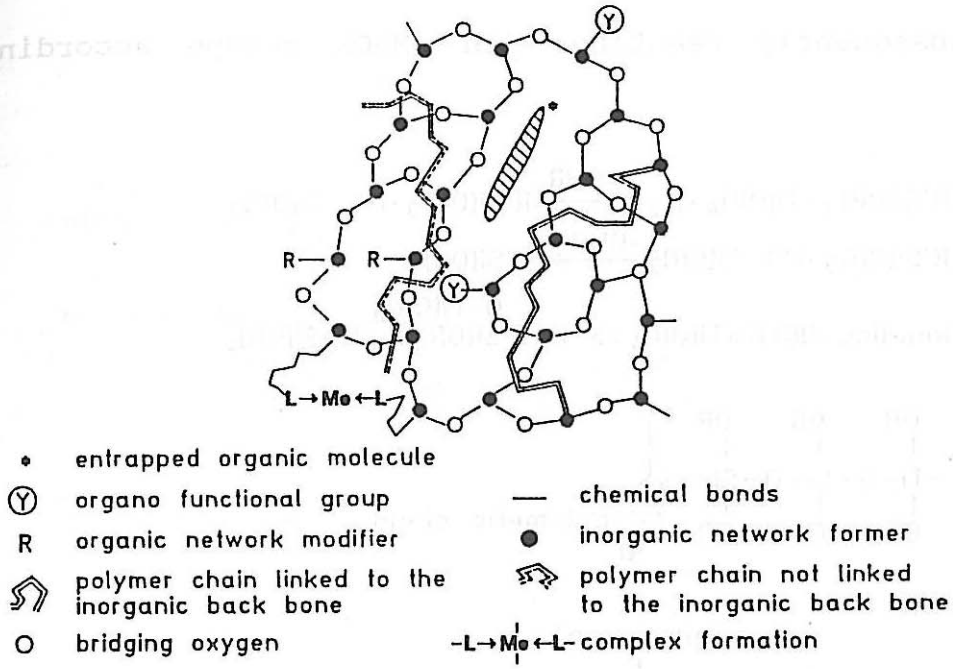


Fig. 3: Schematics of the variability of ORMOCER networks.

3. Synthesis Principles

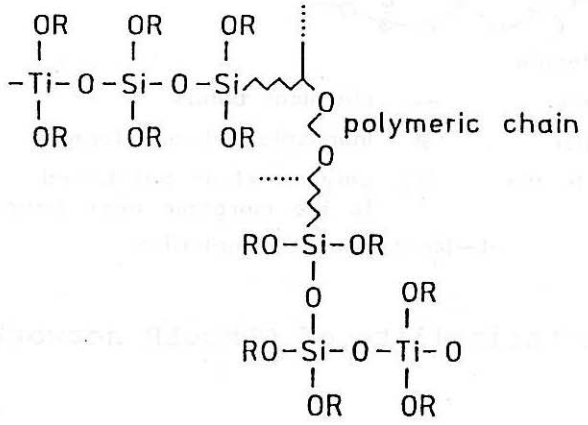
The synthesis of ORMOCERs follows the rules of sol-gel synthesis, at least with respect to the inorganic backbone. The problems of reaction rate control in multicomponent systems are similar to those of precursors leading to pure inorganic materials. It has been described elsewhere that hydrolysis rates of organically substituted silanes increase in the case of acid hydrolysis with an increasing number of substituting ligands and increasing chain length [10], e. g. $Si(OR)_4$ < $(RO)_3SiR'$ < $(RO)_2'SiR_2'$ < $ROSiR_3'$ and $(RO)_3SiCH_3$ < $(RO)_3SiC_2H_5$. Thus, in mixtures of TEOS, substituted silanes and other alkoxides, one has to take care of avoiding negative effects of the rate differences on homogeneity. Molecular tailoring only works well if the crosslinking of the different components is controlled. One example, as described in [11] and [4], shows an effective route for chemical tailoring. As shown by the theory of Livage [12], the condensation of ≡MeOR + HOMe≡ is preferred to the reaction ≡MeOH + HOMe≡ and increases with increasing positive charge of the metal in the ≡MeOH grouping. In [4], the three component system from $Ti(OR)_4$, $(RO)_3Si(CH_2)_3OCH_2$-CH-CH_2 and SiO_2, it is favorable to generate reactive $(RO)_3TiOH$

groupings subsequently reacting with ≡MeOR groups according to (1).

$$R'Si(OR)_3 + Ti(OR)_4 + H_2O \xrightarrow{-OHR} R'Si(OR)_3 + HO\ Ti(OR)_3$$

$$R'Si(OR)_3 + HO\ Ti(OR)_3 \xrightarrow{-OHR} R'Si(OR)_2(O\text{-}Ti(OR)_3)$$

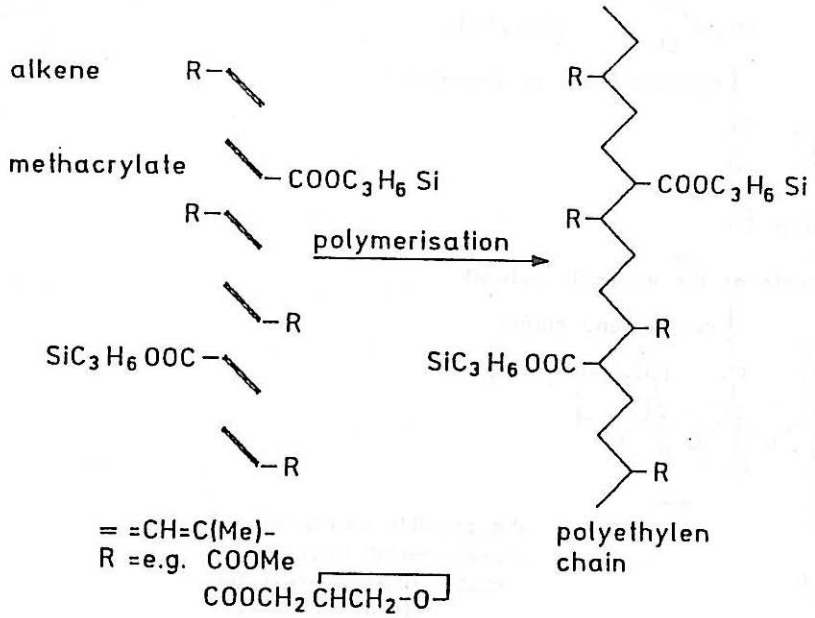
kinetics (IR): $K_H Ti(OR)_4 >> K_H R'Si(OR)_3 > K_H Si(OR)_4$



(1)

The only prerequirement is to generate the water necessary for hydrolysis very homogeneously within the reaction mixture in order to avoid precipitation of TiO_2. Thus, it is possible only by hydrolysing one OR group per $Ti(OR)_4$ to fix the fast reacting $Ti(OR)_4$ completely to the silanes. After this reaction is finished, exess water can be added to the system without causing any precipitation. It is possible to produce coatings with homogeneitiex suitable for optical applications, e. g. coating of eye glass lenses.

In addition to the sol-gel reaction, the chemical reactivity of organic groupings can be used in a variety of reactions. Some examples are shown in fig. 4a-d.



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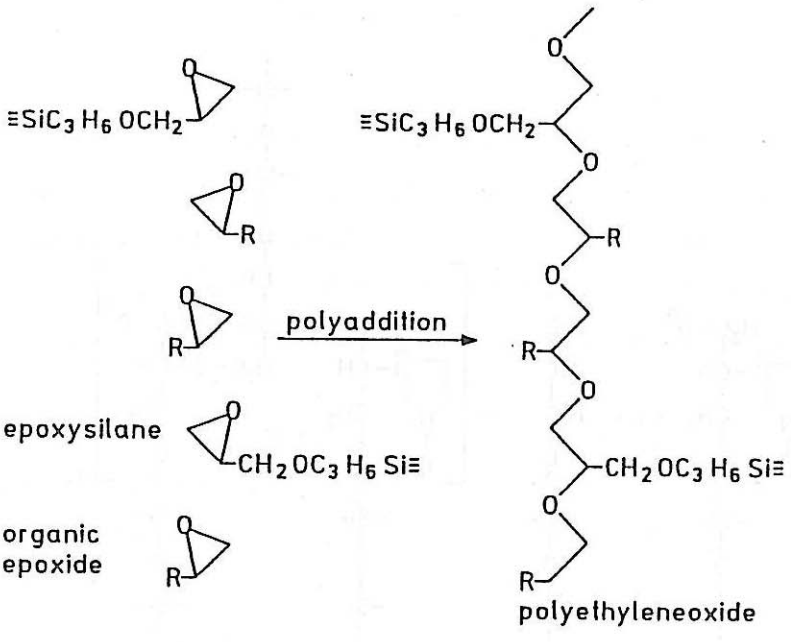
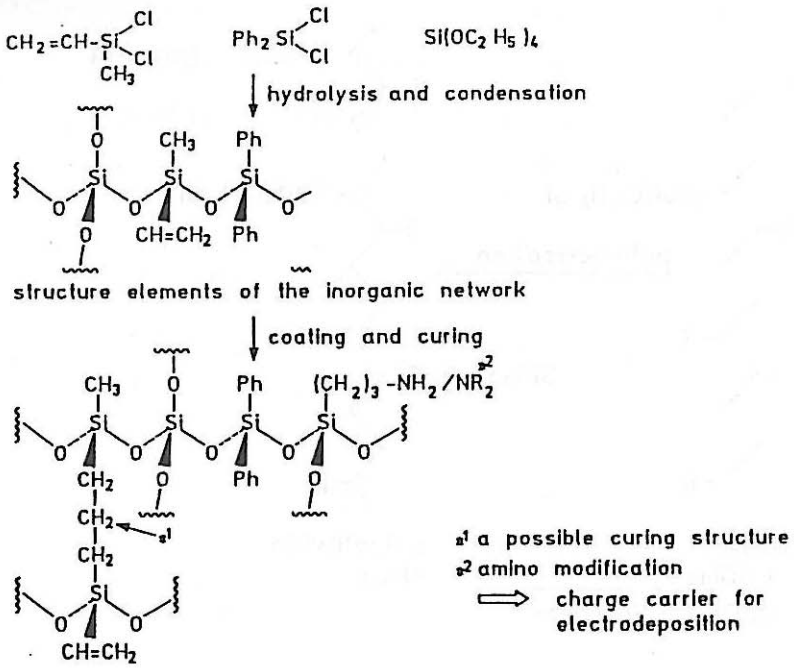


b

Fig. 4a - b: Examples for reactions of organic groupings in ORMOCERs.



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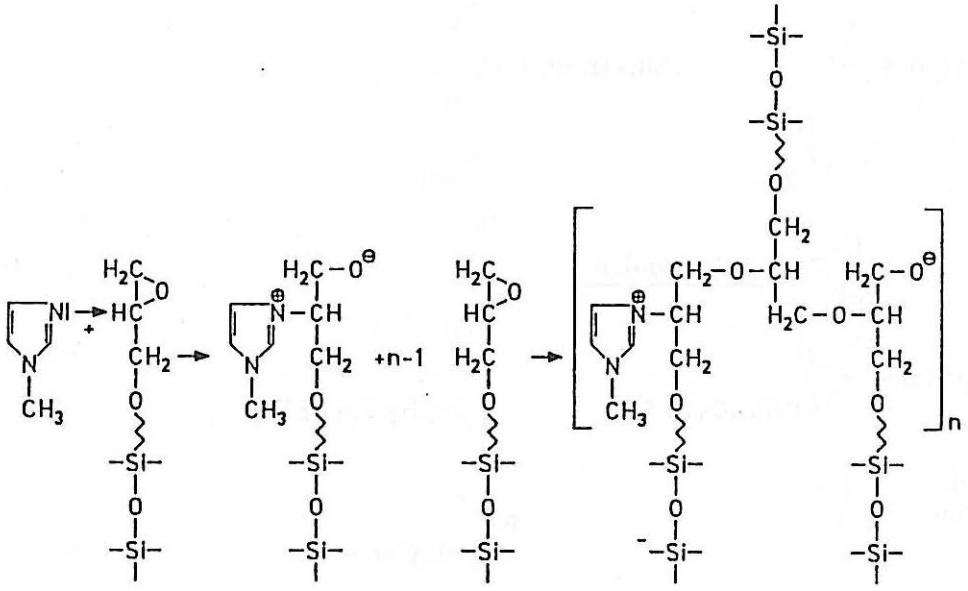

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Fig. 4c - d: Examples for reactions of organic groupings in ORMOCERs.

since a large variation of organic groups is possible, an almost unlimited number of organic reactions can be carried out. A general reaction scheme is given in fig. 5.

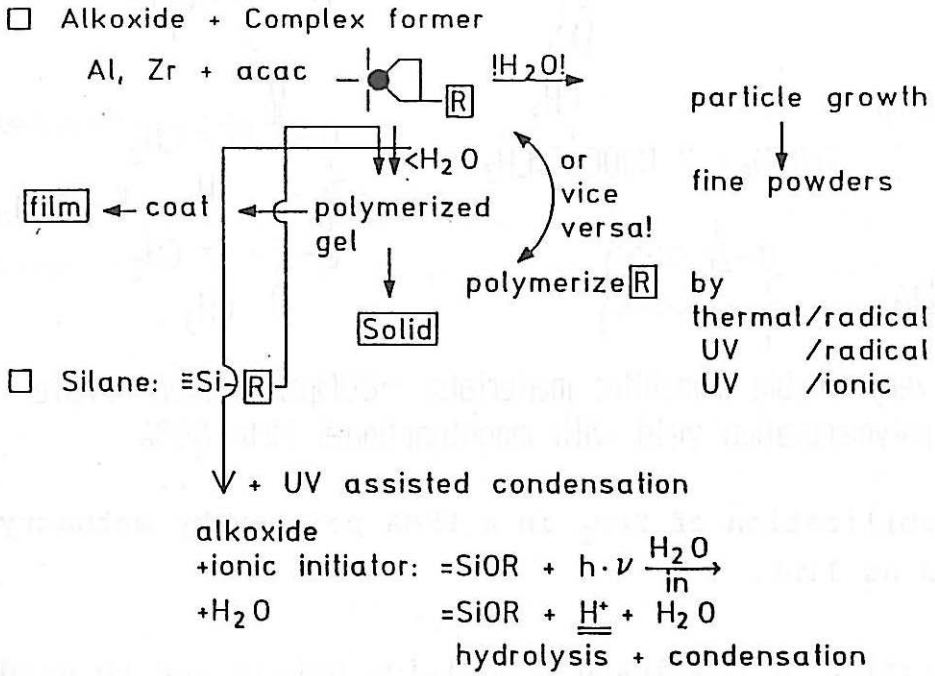


Fig. 5: General reaction scheme for the combined sol-gel and organic synthesis of ORMOCERs.

Fig. R is a polymerisable ligand, various polymerization mechanisms can be applied, e. g. ionic mechanisms or radical mechanisms (photo or thermal initiated). Moreover, the sol-gel process can be affected by ionic mechanisms if initiators are used which create protons in the system catalyzing hydrolysis or condensation [13].

Another example of molecular tailoring is shown in fig. 6, where the incorporation of ZrO_2 into a PMMA polymer is shown. The tendency of aggregation of ZrO_2 particles (sol) can be stopped by fixing them to methacrylic acid and form polymeric chains from methacrylic acid and MMA.

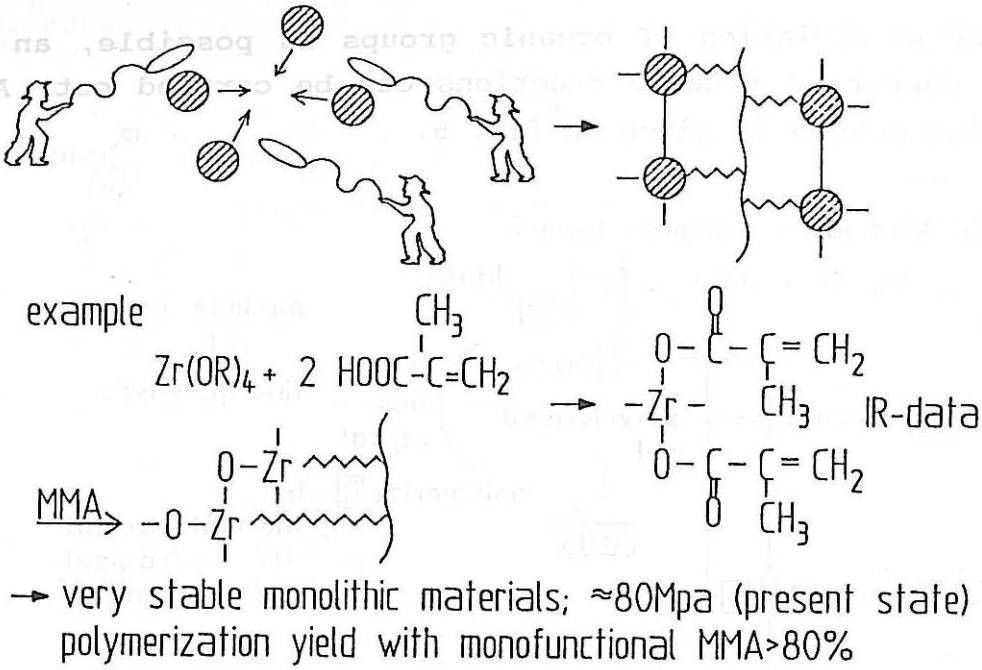


Fig. 6: Immobilization of ZrO_2 in a PMMA polymer by methacrylic acid as link.

The incorporation of complexed transition metals can be used as a structure forming element, as shown in fig. 7.

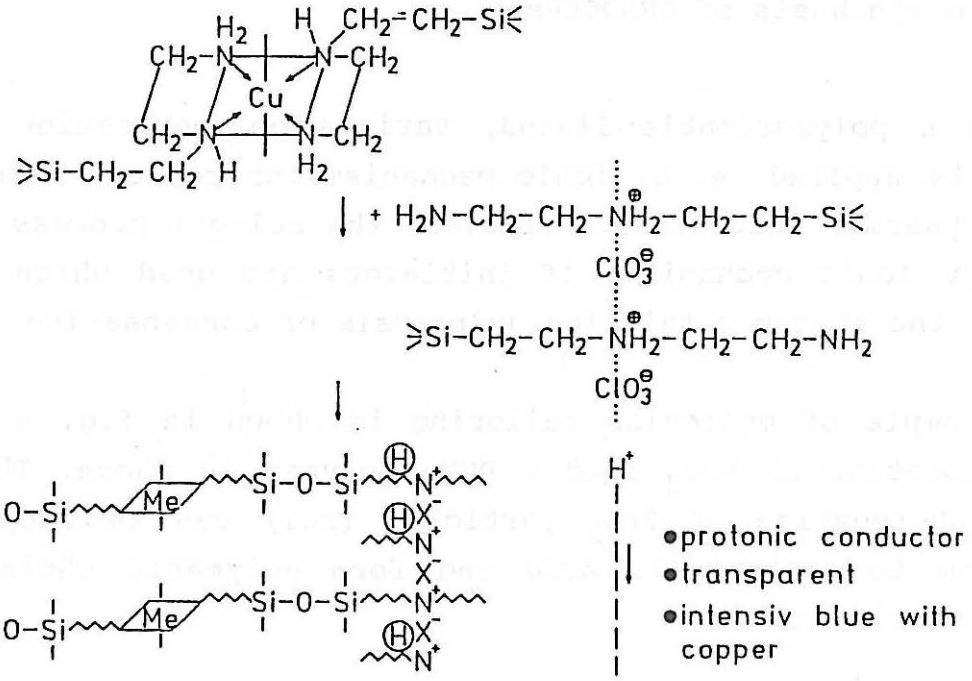


Fig. 7: Incorporation of a Cu tetrammine structure into a silicate network by NH_2 Si≡ as link.

In this case, the coordination of the Cu by aminosilane groups leads to blue flexible polymers which, in case of doping with protons, can act as protonic conductors. These few examples show the possibility of material tailoring by molecular design of structures by chemistry.

4. Material Developments

The synthesis principles shown above allow a wide range of material developments. In fig. 8, a survey over the basic features is given.

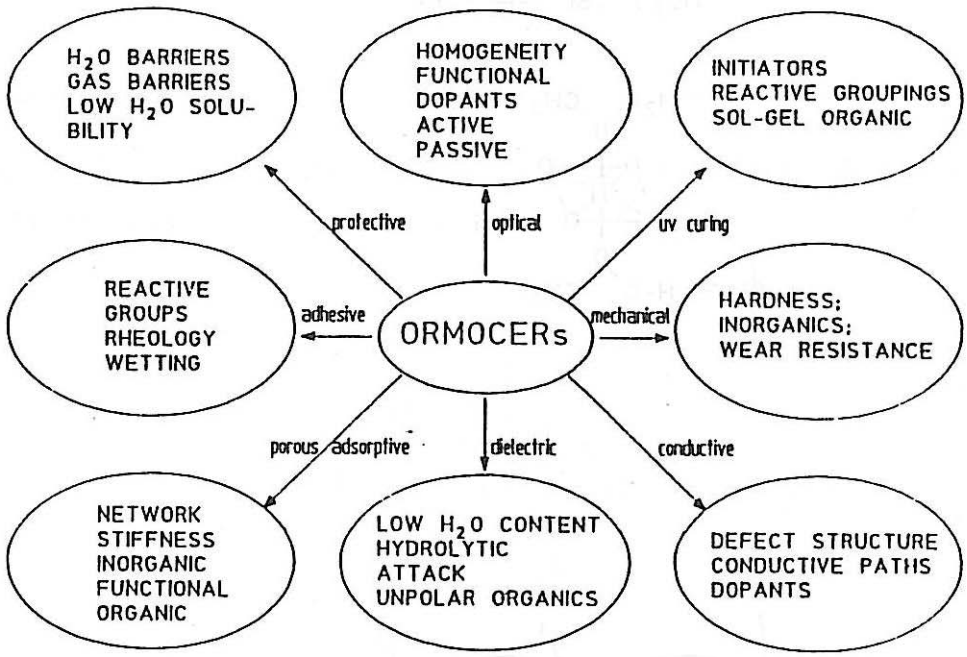


Fig. 8: Survey over the material development possibilities

4.1 Hard and Scratch Resistant Coatings

Mechanical protection is provided mainly by systems containing Ti, Zr, Al and polymerizable silanes with epoxy or methylmethacrylate groups [4, 14]. The low temperature required for the curing of the materials can be used for conventional coating processes and coatings on CR 39 (commercialized), brass (commercialized), PC, PET, Al and others.

4.2 Conductive Materials

Ti-containing materials within special polymeric ORMOCER matrices (e. g. PEO) show electronic conductive properties ($\approx 10^{-4} - 10^{-5}$) [15]. Proposed mechanisms (defect structure transported by chain moving) is shown in fig. 9a and b.

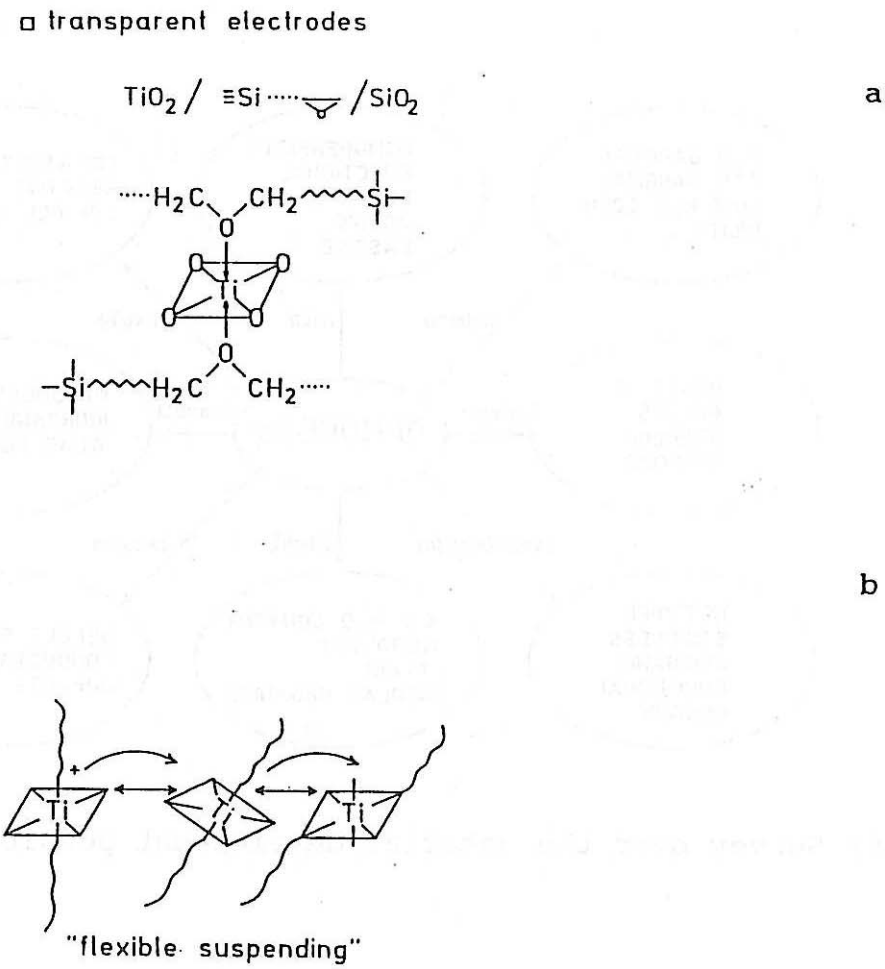


Fig. 9a and b: Suggested mechanisms for electronic conductivity in ORMOCERs with Ti.

Protonic conductivity can be obtained by doping condensates from $(RO)_3Si(CH_2)_3NH_2$ with strong acids [16] or by forming coordination polymers as shown in fig. 7.

4.3 Dielectric Materials

Low H_2O take up low ε materials with heat resistances up to 300 °C can be obtained by the basic reaction shown in fig. 4b [17]. They have been developed for photo lithography and direct laser writing [18].

4.4 Porous Materials

High contents of inorganic backbones can lead to porous materials with special mechanical properties [19], e. g. for abrasive uses in mechanical applications or as selective adsorption materials in gas adsorption or adsorption from liquids [20, 21].

4.5 Adhesive Materials

They are mainly based on materials containing short chains of phenyl/silane based units (fig. 10)

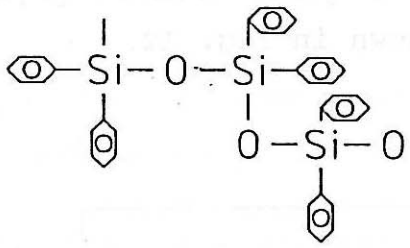


Fig. 10: Structural unit for hot melt adhesives

units with controlled ≡SiOH contents and can be used for a variety of sealing processes [22]. They can be combined with other groups, e. g. photo curable ≡Si vinyl or ≡Si methacryl groups, and be used for sealings with glass [23].

4.6 Barrier Coatings

Based on the inorganic backbone, low permeation for hydrocarbons were found. In fig. 11, the permeation behaviour of coated and uncoated HDPE (high density polyethylene) is shown.

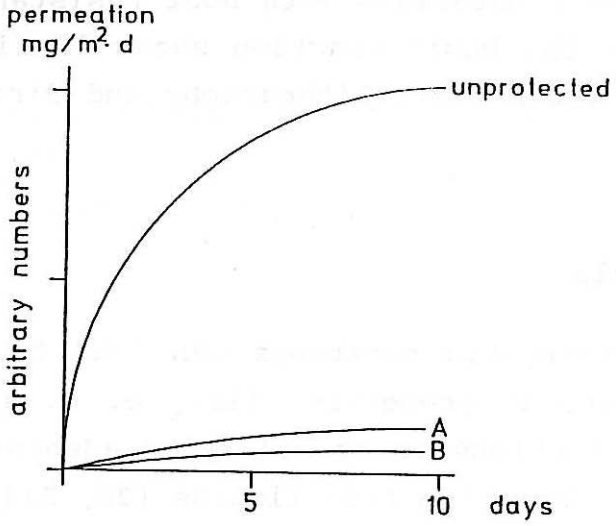


Fig. 11: 5 µm ORMOCER coatings on HDPE, A: UV cured, B: thermally cured, compared with the uncoated sample.

The incorporation of pigments (e. g. mica) can be used for low permeation coatings, e. g. for passivation in electronics or protection of medieval stained glass windows [6]. The reduction of H_2O permeation by mica is shown in fig. 12.

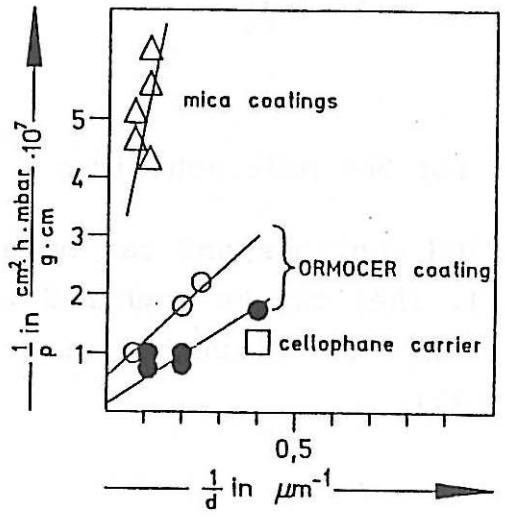


Fig. 12: Comparison of filled and unfilled mica coatings. The coatings were used on cellophane as substrates.

4.7 Functional materials

Addition of fluorescent dyes to ORMOCERs leads to fluorescent coatings [24]. It depends strongly on the dye molecule which function will be obtained (e. g. photochromic effects) (fig. 13). Other molecules of interest are lasing dyes or χ^2-molecules.

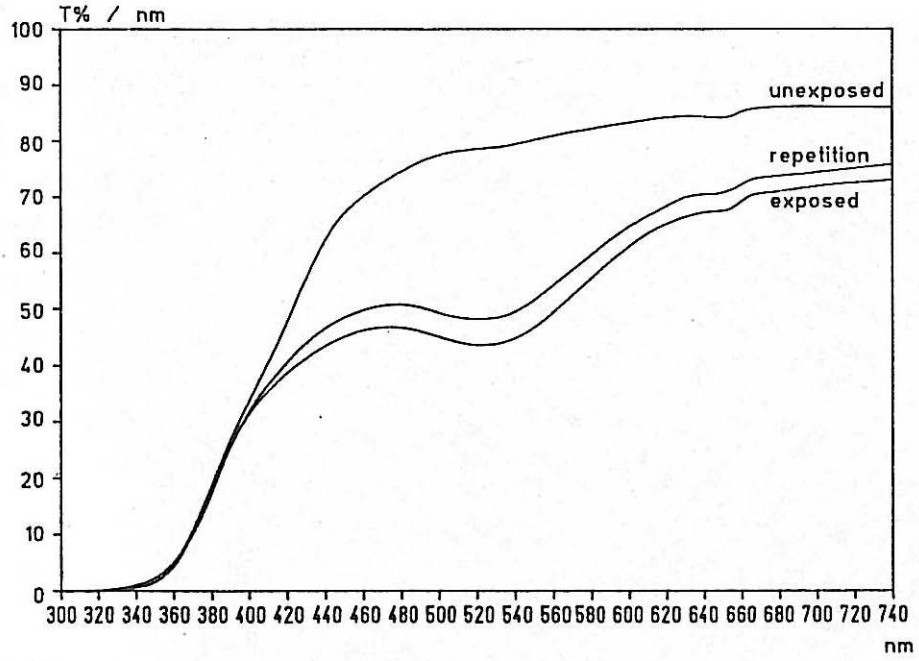


Fig. 13: Effect of photochrome dyes in ORMOCER coatings:
upper curve not irradiated; lower curves: UV radiated.

In fig. 14, some examples for other functional coatings are given. The SO_2 sensor is based on the complex formation of SO_2 with amines and the change of capacity within the ORMOCER [25].

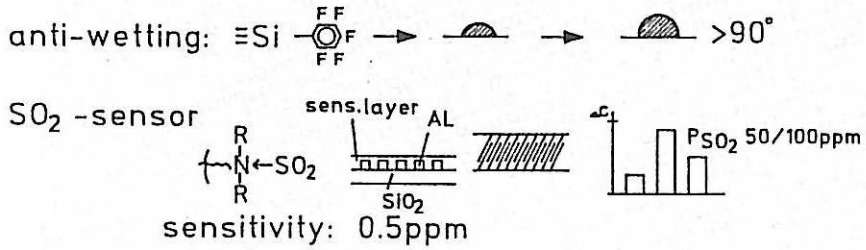
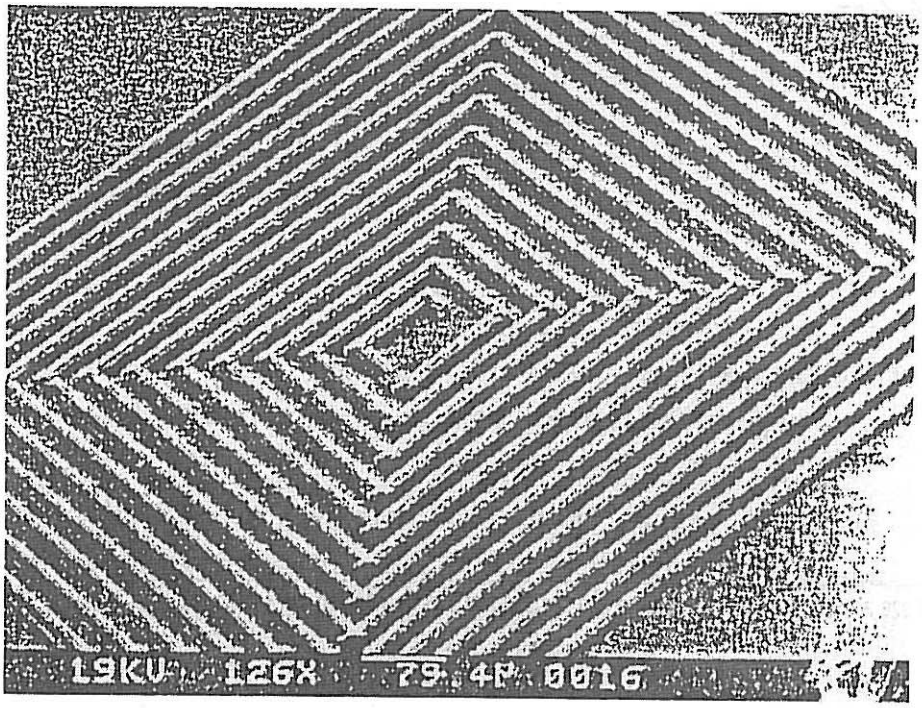


Fig. 14: Antiwetting and sensor applications of ORMOCERs.

4.8 Photocuring Materials

This type is characterized by groupings which can react with themselves or with monomers in order to perform a curing process based on the well known mechanisms known from organic polymerization chemistry. The application of these methods allows to develop fast curing processes for films, photolithography, laser writing and embossing processes for micropatterning (fig. 15 a - b).



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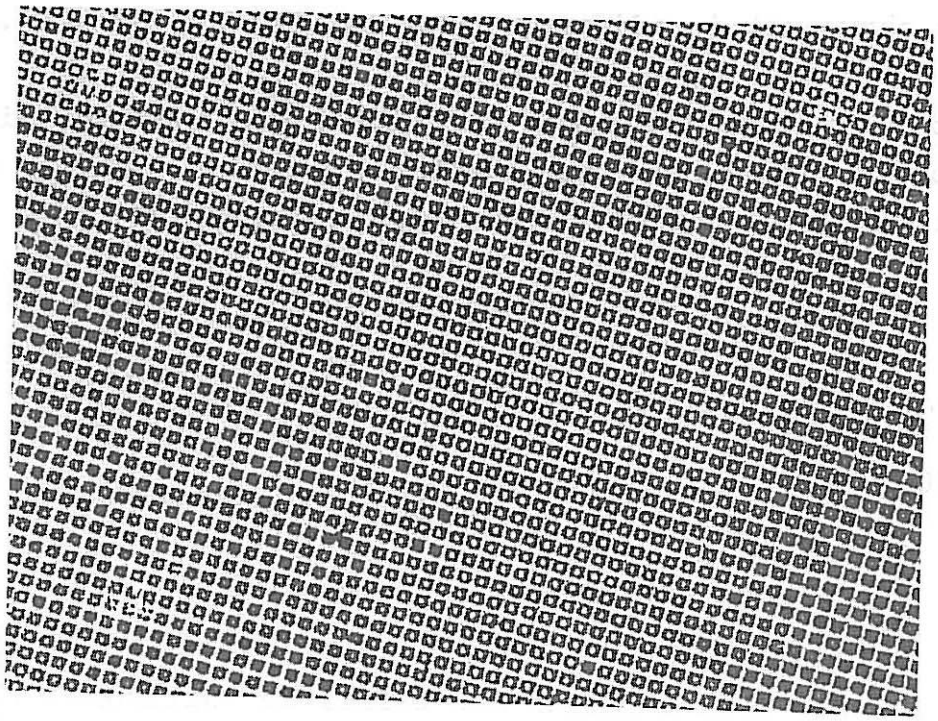

b

Fig. 15 a - b: Examples for laserwriting (a) and embossing of ORMOCERs (b).

combined with functional properties and molecular design of the materials, these techniques offer interesting opportunities for new and interesting applications.

5. Summary

The sol-gel process offers the possibility of incorporating organic functions into basically inorganic materials. This leads to a variety of different types of materials and, in addition to this, to a variety of processing techniques, too. Since the structure of complex precursor units can be maintained during the processing, it is possible to apply molecular tailoring processes. The incorporation of new functions allows the synthesis of smart materials, too.

6. References

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