

CHEMISTRY AND APPLICATIONS OF INORGANIC-ORGANIC POLYMERS
(ORGANICALLY MODIFIED SILICATES)

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ABSTRACT

The combination of inorganic polymeric networks with organic components leads to inorganic-organic polymers. A convenient method for the introduction of organic radicals into an inorganic backbone is the use of organo-substituted silico esters in a polycondensation process. This leads to $\equiv\text{Si-O-Si}\equiv$ network containing materials, so-called organically modified silicates (ORMOSILs). For the synthesis of the inorganic backbone, in opposition to the high temperature preparation of non-metallic inorganic materials like ceramics, "soft chemistry" methods have to be applied in order to preserve organic groupings to be incorporated. Therefore, the sol-gel process is a suitable technique [1-5]. A review over basic synthesis principles and chemical methods, their effect on special material properties and the application potential will be given.

1. INTRODUCTION AND GENERAL CONSIDERATIONS

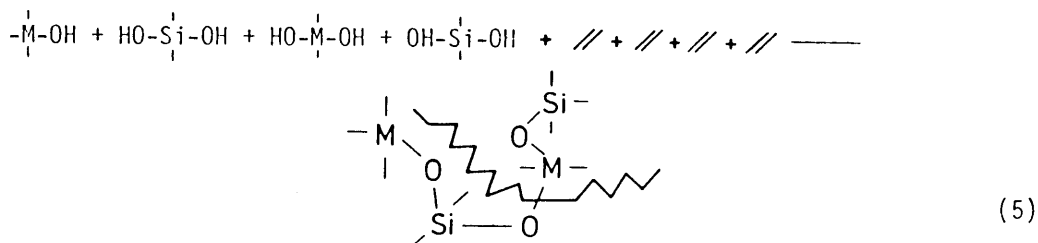
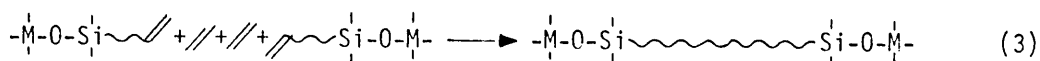
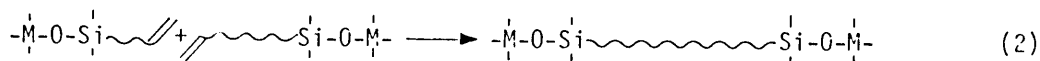
The desire to combine properties of very different materials in one and the same product has led to composite materials on a macroscopic scale. Examples therefore may be filled polymers, laminates like automotive screens, fibre reinforced epoxides or even coating all type of materials with paints. Another possibility is opened by the idea to combine properties of different components on a molecular scale, as it is shown on large scale with organic copolymers. The idea to combine inorganic with organic components on a microscopic scale requires a formation process of an inorganic network which is compatible to the thermal stability of organic components. For example it is not possible to add organic monomers or polymers to a glass melt in order to get hybrid materials. A "soft" chemical synthesis of inorganic polymers can be provided by the sol-gel process. In most cases, sol-gel synthesis of inorganic polymers leads to porous gels as intermediates, which in general are more or less amorphous. For densification a heat treatment has to be applied. The temperature depends on the system, but with few exceptions the temperatures to be applied are above the level of thermal stability of organic groupings. That means that in the case of ORMOSILs high temperature moulding procedures will be restricted to very special systems. The question arises, whether it is possible to change the properties of the inorganic network by the incorporation of organic groupings in a way, that the described disadvantages can be avoided, e.g. by gaining network flexibility in order to receive dense products without high temperature treatments. The opposite problem may arise, if porous materials have to be prepared.

An introduction of an organic group into an inorganic network may act in two basically different ways [6, 7]. It may act as a network modifier or as a network former. Both functions can be realized in ORMOSILs. A suitable way to achieve this is the use of organosubstituted silicic acid esters of the general formula $\text{R}'\text{Si}(\text{OR})_{4-n}$, where R' can be any organofunctional grouping [8-10]. If R' is a non-reactive group, it will have a network modifying effect; if it can react with itself or additional components, it acts as network former. For the synthesis of the described hybrid materials, the chemistry plays the key role. Reaction condition have to be developed for

each system which take into consideration the sol-gel requirements as well as those defined by the organic groups.

2. REACTION PRINCIPLES

The reaction principles of the sol-gel process are well known and not described here. Examples for the introduction of organic components using sol-gel techniques are schematically given in eq. (1-5):



R = organofunctional group, e.g. amino, carboxy,
M = network forming metal, e.g. Ti, Al, Zr

Eq. (1) represents the introduction of network modifying units. Eqs. (2-4) show examples for building up an organic polymeric network in addition to the sol-gel derived inorganic one. In eq. (5) the formation of two independent interpenetrating networks is indicated.

3. CHEMISTRY OF SYNTHESIS AND TAILORING OF SPECIAL MATERIAL PROPERTIES

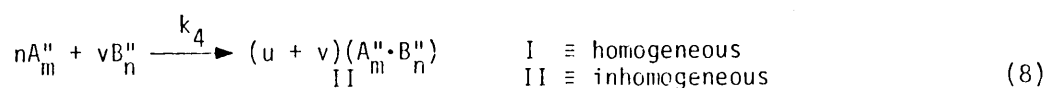
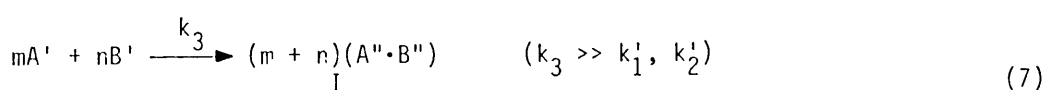
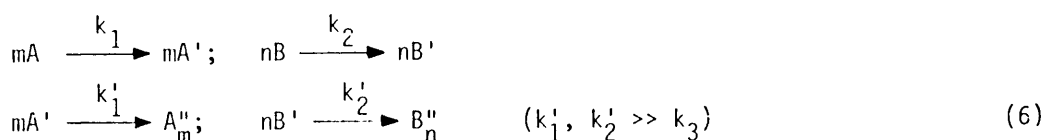
3.1. General considerations

Synthesizing inorganic polymers by the sol-gel route requires soluble reactive monomers. An easy way to do this, is to use soluble alkoxides and carry out a hydrolysis and condensation reaction. As known from investigations from different authors, the reactions and the polymeric structure formation processes are very sensitive to reaction condition, composition and starting monomers [11-14]. The knowledge of detailed mechanisms of hydrolysis and condensation is very poor, partially due to the complexity

of these processes, partially due to the lack of interest based on an underestimation of their importance. In spite of this, basic features for the reaction of simple systems, e.g. Si-, Al- and Ti-alkoxides, could be developed and the influence of reaction condition on the derived materials could be evaluated. The introduction of organic components into the sol-gel process in general means a drastic change of the system: Firstly substituted esters $R_nSi(OR)_{4-n}$ behave quite different than other esters and other alkoxides in hydrolysis and condensation as shown in [15] and secondly the organic groups or the addition of organic monomers can influence the structure of the inorganic backbone. That means, that one has to expect a complex set of influencing parameters caused by organics, which presumably will affect more than a "simple" additional behavior. In the following, examples will be given to illustrate how special properties can be achieved or manipulated in ORMOSILs.

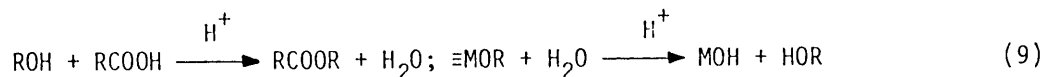
3.2. Influence of synthesis on material properties

As pointed out above the step of formation of polymeric structures plays a key role for the properties of the derived material. Two main different processes have to be distinguished. The first one can be described as a "monomer connection" step. With three dimensional crosslinking monomers a large variety of structures and, based on them, of properties is possible. Thus, even in one component systems very different materials can be prepared as shown by the variety of silicagels. In multicomponent systems a second step, which can be described as a "component distribution" process, in addition has to be considered. The latter one is related to different reactivities in hydrolysis and condensation. Eq. (6-8) illustrate the influence of the reaction kinetics on homogeneity of a two components system (A, B: starting alkoxides; A', B': hydrolysed monomers; A'', B'': condensates; k_i : rate constants)



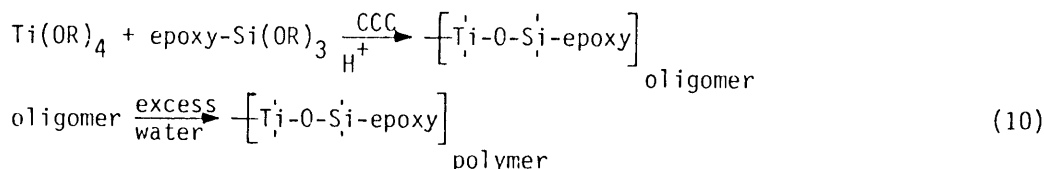
It is clear, that the component distribution influences properties drastically. If homogeneous materials are required, techniques have to be developed to overcome the effect of different reactivities.

Therefore the chemically controlled condensation ("CCC") method was developed which allows a precise control of hydrolysis and condensation rate, by chemical water generation within the system. The water producing reaction is an ester formation, which uses the solvent alcohol as one and the catalytic effective acid as the other reaction partner (eq. 9). By pro-

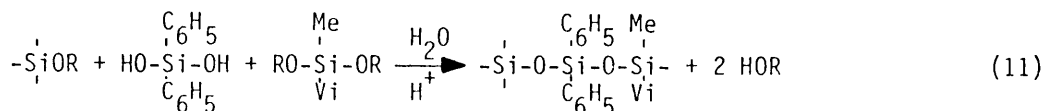


per choice of the type of alcohol, concentration of acid and temperature, very different water formation rates can be established. Another important advantage of the method is the homogeneous water formation within the reac-

tion mixture, avoiding concentration gradients which necessarily occur if pure water or water containing phases are mixed with water free ones. It is supposed that in a mixture of two alkoxides with very different hydrolysis rates, like $\text{Ti}(\text{OEt})_4$ and $\text{Si}(\text{OEt})_4$, the CCC-method leads preferably to the partial hydrolysis of $\text{Ti}(\text{OEt})_4$. After only one sixteenth to one tenth of the CCC-formation of water necessary for hydrolysis of the total amount of OR-groups, pure water can be added to the system without causing precipitation of TiO_2 . One has to conclude, that the $(\text{TiO}_4)^{4-}$ units are immobilized in an polymeric structure, probably including $(\text{SiO}_4)^{4-}$ units, since pure $(\text{TiO}_4)^{4-}$ -based oligo- or polymeric units should not be able to prevent completely TiO_2 precipitation with excess water. Thus, it is possible to prepare easily water based laquers from systems of the type $\text{R}'\text{Si}(\text{OR})_3/\text{M}(\text{OR})_n$ (with $n = 3, 4$, M e.g. = Al, Zr, Ti and R' e.g. = epoxy) by use of the CCC-method (10).



The polymer is a viscous liquid which reacts within some days to a monolithic transparent solid. The viscous liquid can be used in coating techniques and cured by heat within minutes to scratch resistant films. IR-spectroscopy shows, that the curing step from the viscous to the solid state is connected with loss of OH groups, which indicates a condensation based curing. After a heat treatment for several hours at 130 °C, there is still a remarkable amount of OH groups left. This phenomena was investigated more in detail in the system 65 MeViSiO/32.5 $(\text{C}_6\text{H}_5)_2\text{SiO}/2.5 \text{SiO}_2$ (Me = methyl, Vi = vinyl). The material is prepared by reacting diphenylsilandiol, $\text{Si}(\text{OEt})_4$ and $\text{MeViSi}(\text{OEt})_2$ in a mixture of toluene and ethanol and hydrolysing the whole mixture with excess water under H^+ catalysis by refluxing for several hours (11). After solvent removal a highly viscous product remains, which is



cured thermally. Fig. 1 shows the IR-spectra after different temperature treatments. It is shown, that at least two different types of OH groups appear, which can be assigned to bridged (lower frequency) and unbridged (higher frequency) species. The bridged species can condense more easily during the curing procedure than the unbridged ones. At $T > 100^\circ\text{C}$, the samples are liquid and remain lowly viscous during the whole heat treatment. In spite of this low viscosity, the condensation process is very slow. After cooling down, the products show a thermoplastic behavior. The presence of diphenyl silane seems to avoid a higher degree of three dimensional crosslinking by steric hindrance. If KOH or NaOH is added to the mixtures, even very low concentrations (0.01 mmole NaOH/l) affect a rapid condensation. In fig. 2, the spectra before and after the base addition demonstrate the effect. As known from other investigations, too, bases are more efficient condensation catalysts than acids. Similar tendencies are observed within the system epoxysilane/ TiO_2 from spectroscopic data too. Condensation experiments with different catalysts and IR analysis indicate a remarkable difference between HCl, NH_3 and KOH. The KOH catalysis shows the far lowest, HCl catalysis the highest OH-group content. All three type of reactions leads to viscous liquids

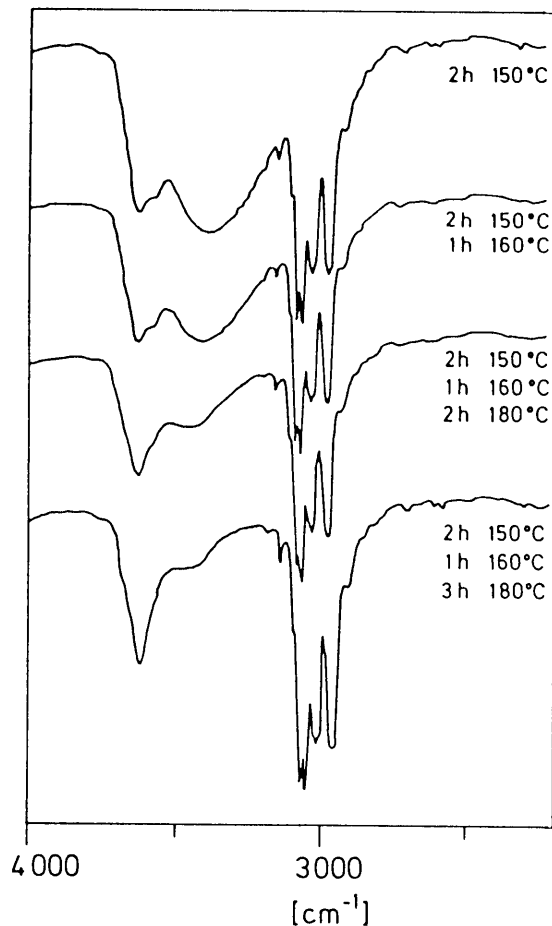


Fig. 1. Effect of thermal curing on ORMOSILs of the system $\text{MeViSiO}/\text{Ph}_2\text{SiO}/\text{SiO}_2$

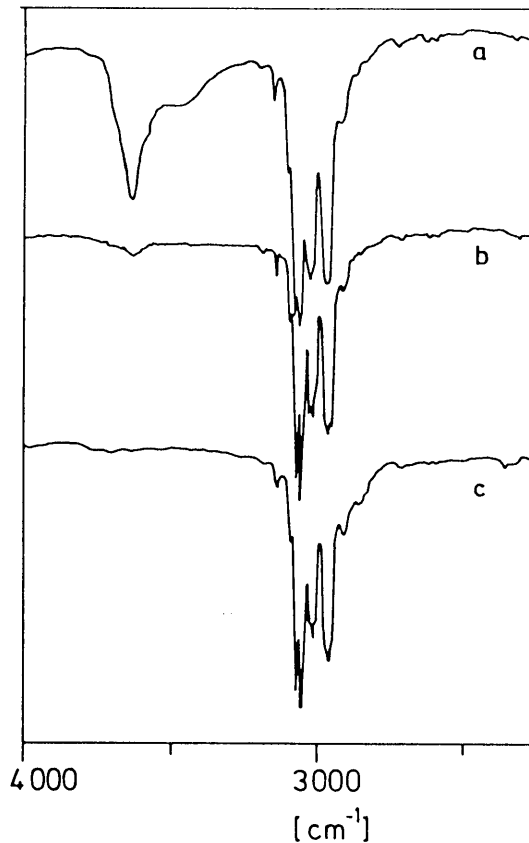


Fig. 2. Effect of catalyst on ORMOSILs of the system $\text{MeViSiO}/\text{Ph}_2\text{SiO}/\text{SiO}_2$
 a) thermally cured resin prepared with HCl catalysis
 b) resin heated up with 0.4% NaOH to 150°C for 30 min
 c) thermally cured resin prepared with KOH catalysis

which can be cured to monoliths. Underwater storage of the monoliths reveals quite different behavior depending on catalyst type, too: Whereas the HCl and NH_3 catalysed species show a swelling of about 5 to 10 % with crack formation after redrying, the KOH catalysed species show no detectable swelling and are extremely stable against any water treatment. The latter behavior is assigned to a low water take up due to low OH group content. This results turned out to be extremely important for all type of coatings to be used under wet conditions. Furthermore, in these experiments it could be proved that dense monoliths can be prepared at low temperatures due to the higher network flexibility caused by organic ligands.

For a sufficient understanding of inorganic-organic polymers, not only the inorganic process, but also the organic network forming should be known quite well. It has been shown elsewhere that epoxy groups are responsible for interesting mechanical properties like surface hardness [16]. The effect of different alkoxides on the epoxide polymerization has been described in [17]. It turned out that $\text{Zr}(\text{OR})_4$ was most effective in epoxide polymerization. Further investigations were carried out to optimize reaction

conditions. It could be shown, that even $Zr(OR)_4$ contents of about 1 mole-% affect rapid polymerization. Increasing $Zr(OR)_4$ contents increase the polymerization rate, whereas the HCl concentration does not affect the rate.

In this connection the question of the influence of acids with respect to the ring opening reaction (12) is of high interest and was investigated with different acids. Fig. 3 shows the results. $HClO_4$, H_2SO_4 and partially

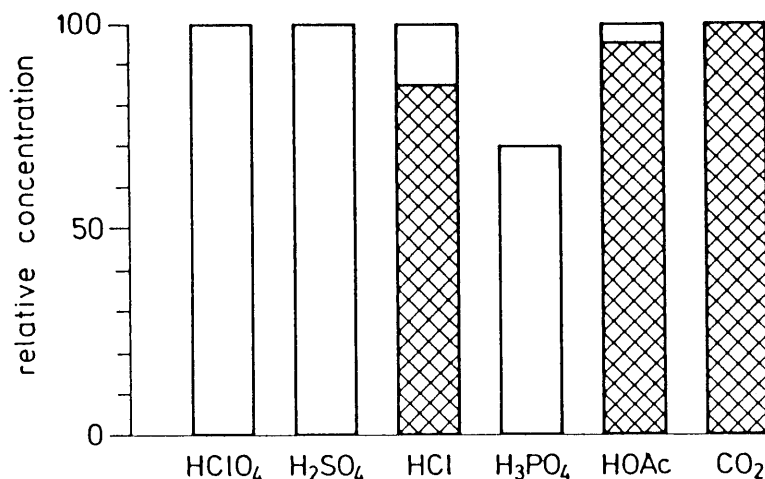
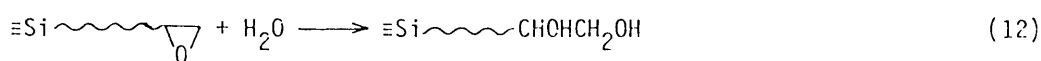
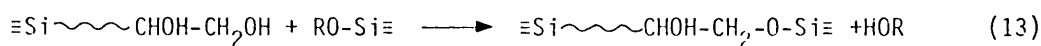
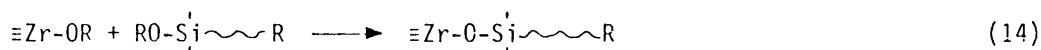


Fig. 3. Effect of catalysts on the relative concentration (based on starting material) of glycol and epoxy (hatched) groups in completely hydrolyzed epoxysilane

H_3PO_4 causes a complete ring opening under the applied experimental conditions (25°C for 17 hours, 1 mole H^+ /l) whereas acetic acid and CO_2 hardly attack the epoxy group. All the applied acids act as good catalysts in hydrolysis and condensation. Especially CO_2 is very convenient to promote the condensation process without ring opening. This process is important, if the epoxy ring has to be preserved during the inorganic backbone forming reaction for a subsequent epoxy polymerization or for preventing an internal reesterification reaction (13).



As mentioned above dense materials can be prepared within the system epoxysilane/ TiO_2 with the CCC-method up to at least 40 mole-% of TiO_2 . Substitution of TiO_2 by 25-30 mole-% SiO_2 leads to brittle and porous species. This may be attributed to the inorganic network densifying effect of TiO_2 , known from the silicon chemistry [18]. In analogy to TiO_2 , ZrO_2 can be incorporated into the network (14):



Thereby, in case of epoxy groups the polyethylene oxide formation is favored even at room temperature due to the excellent catalytic activity of $Zr(OR)_4$ [17]. Dense monoliths can be prepared easily with this system, too. The absolute densities of these products are surprisingly low, even at higher metal oxide contents, indicating "open" structures compared to the "inorganic" corresponding systems TiO_2/SiO_2 and ZrO_2/SiO_2 . In fig. 4 the

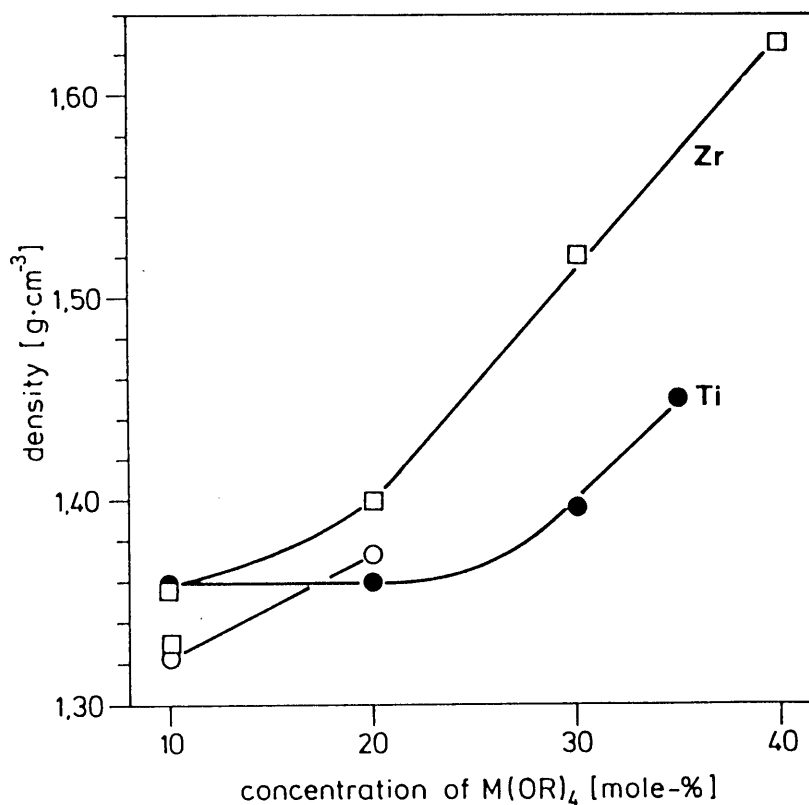


Fig. 4. Influence of $M(OR)_4$ concentration on the density of thermally cured ORMOSIL condensates (epoxysilane/ $M(OR)_4$); squares: Zr; circles: Ti; full symbols: one step hydrolysis of the whole mixture; open symbols: two step hydrolysis, reacting the epoxysilane before $M(OR)_4$

dependence of density on the metal oxide content is shown. One step reaction TiO_2 containing species with higher Ti contents exhibit low densities compared to ZrO_2 containing materials. At lower contents of M the opposite behavior is shown. Up to 20 mole-% there is almost no change in density in the TiO_2 case. Similar tendencies are shown by the ZrO_2 system. There is a big gap between the actual and the theoretical density, computed from the increments (polyethylenoxide: $\rho \approx 1.2$, SiO_2 glass: $\rho \approx 2.2$ and crystalline ZrO_2 : $\rho \approx 6$). The resulting density with 40 mole-% ZrO_2 would be about 3, the measured one is about 1.7. This demonstrates that the ORMOSIL structure does not follow an additional behavior based on the single components and that this is an influence of the reaction conditions. The more open structure of the ORMOSIL may result from the organic residue, but no plausible models could be developed up to now.

The refractive index shown in fig. 5 increases with increasing metal-oxide content, but seems to be surprisingly low with respect to the corresponding inorganic system. Considering the low densities, the measured values are in a good agreement with Lorentz-Lorenz calculations. Compared to this, phenyl group containing ORMOSILs show higher refractive indices, due to the contribution of the phenyl group (fig. 6). The addition of epoxy groups decreases the refractive index remarkably in this system.

Epoxy ORMOSILs have been developed as scratch resistant coating and contact lens materials. It could be shown, that the scratch resistance in the TiO_2 /epoxy system mainly depends on curing and preparation conditions [16, 17]. Since the TiO_2 systems shows some general disadvantages with

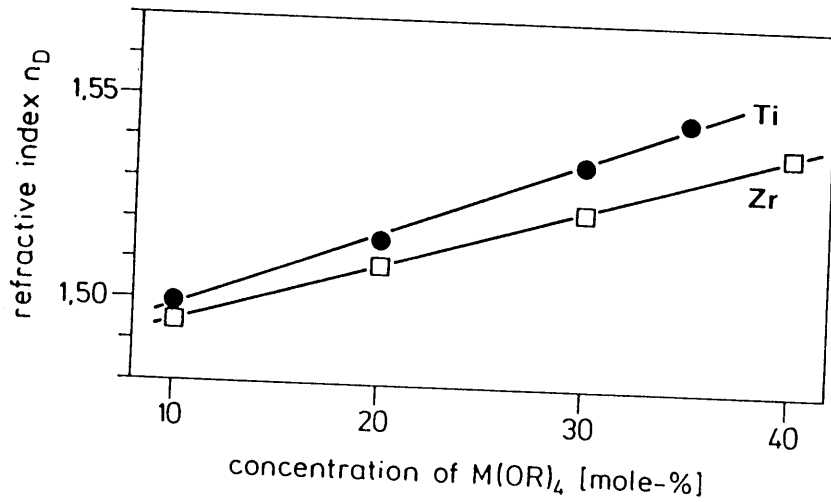


Fig. 5. Relation between refractive index n_D and concentration of $M(OR)_4$ in thermally cured ORMOSIL condensates (epoxysilane/ $M(OR)_4$)

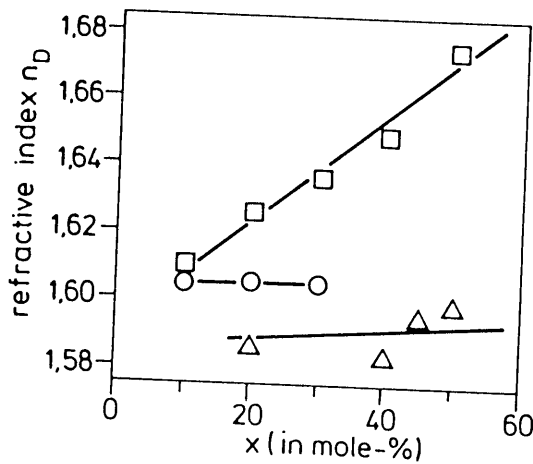


Fig. 6. The effect of concentration of $M(OR)_4$ ($M = Ti, Zr$) in different ORMOSIL systems
 □: $(100-x) Ph_2Si(OH)_2/x Ti(OEt)_4$
 ○: $(100-x) Ph_2Si(OH)_2/x Zr(OPr)_4$
 △: $(80-x) Ph_2Si(OH)_2/x Zr(OPr)_4/20$ epoxysilane

respect to UV stability (if not protected by UV absorbers), the effect of other metal oxides with respect to their scratch resistance was studied. The scratch resistance is measured by a modified Erichsen test, where a Vickers diamond is scratched over the surface and where the load causing the first microscopically visible scratch is determined. Table I shows the comparison of different compositions.

Table I. Scratch behavior of the compositions (mole-%) 50 epoxysilane/ $30 SiO_2/20 MO_x$ (curing temperature 90 °C)

M	diamond load
Si	< 1
Zr	5
Al	10-20
Ti	10

Standard UV tests with the unprotected systems show, that the Al_2O_3 and ZrO_2 systems are about 10 times more resistant than the TiO_2 system. The poor results from the TiO_2 system can be attributed to its photocatalytic activity [17]: UV light irradiation leads to Ti^{3+} formation which could be proved by spectroscopy.

With SiO_2 only instead of TiO_2 it is very difficult to receive compact materials. The samples are very brittle and are cracking during curing, that means they show a very poor mechanical stability. TiO_2 containing monoliths show a reasonable mechanical stability. The effect of composition was studied on this system. The results are shown in fig. 7. There seems to be a maximum at about 5 mole-% TiO_2 , due to the network densifying effect of TiO_2 . Higher contents lead to a higher modulus of elasticity with a corresponding increase of brittleness and decreasing tensile strength. The system approaches to a "glass like" behavior. The incorporation of a polymethylmethacrylate (PMMA) network improves tensile strength remarkable (15).

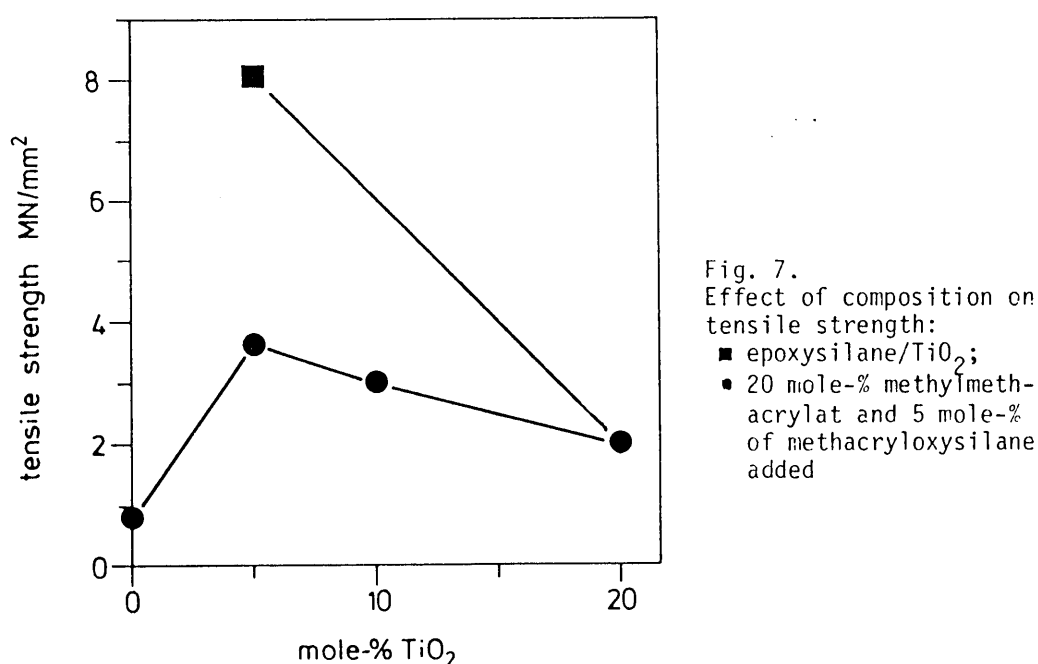
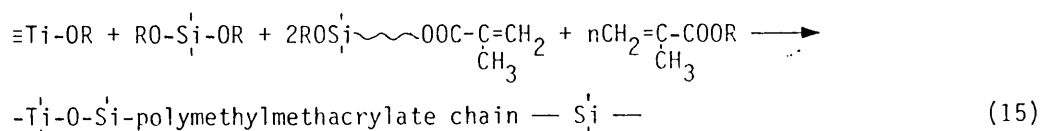


Fig. 7.
Effect of composition on tensile strength:
■ epoxy silane/ TiO_2 ;
● 20 mole-% methylmethacrylate and 5 mole-% of methacryloxysilane added

The results show that the polymeric network can be used to improve mechanical properties of ORMOSILs. It should be mentioned that due to the possibility of a radical polymerization mechanism, photo catalysis can be used and photo curing procedures can be applied.

Beside mechanical properties, chemical surface properties of coatings are of interest, if these properties can be used for special reactions, e.g. for sensor purposes: Systematic investigations have been carried out in order to synthesize chemical reactive coatings for the interaction with gaseous components. The idea was, to transduce the change in electronic state of a reacting surface molecule directly to a microelectronic device, e.g. a field effect transistor (FET). As model systems, the adsorption of CO_2 and SO_2 were chosen. Fig. 8 shows the CO_2 load of porous ORMOSILs ($\text{SiO}_2/\text{NH}_2(\text{CH}_2)_3\text{SiO}_3/2$) as a function of composition and BET surface. It is possible to receive remarkable loads. In spite of this no remarkable change of electric properties of the loaded coatings takes place, so that no detectable signals e.g. in capacitance tests can be monitored.

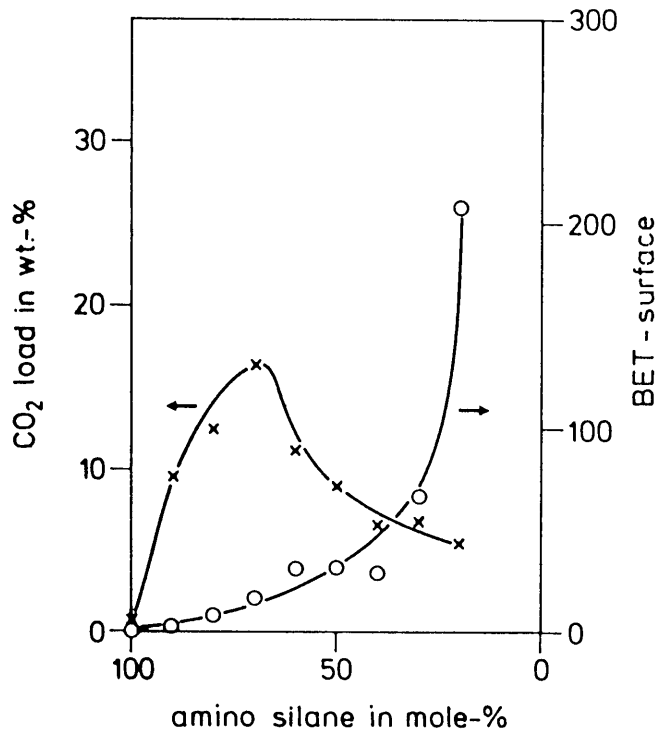


Fig. 8.
CO₂ adsorption at
40°C/10³ hPa CO₂
pressure and BET sur-
face depending on
composition of the
system SiC₂/amino-
silane

In opposition to this coatings from the system SiO₂/(C₂H₅)₂N(CH₂)₃SiO_{3/2} exhibit reversible change of capacitance with SO₂ [19]. First results on FETs confirm the capacitance experiments. In order to reduce influence of water vapor, hydrophobic components can be incorporated. Fig. 9 shows the

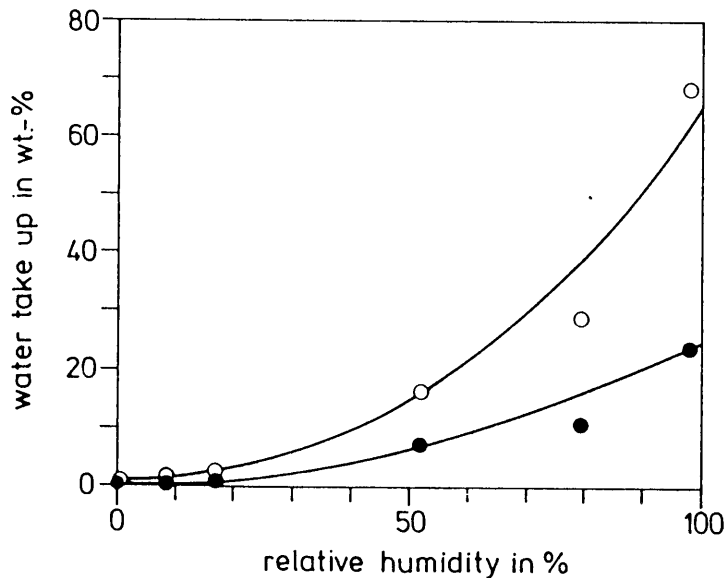


Fig. 9.
Water take up from
the atmosphere.
o pure aminosilane
condensate
● propylsilane/
aminosilane con-
densate (1:1
molar)

effect of H₂O adsorption on two different systems. It clearly points out the reduction in H₂O adsorption by the introduction of the propyl group. These results open the possibility of synthesizing a large variety of sensitive coatings for very different purposes.

Phenyl group containing adsorbents can play an important role for solvent stripping from air. From capacity reasons high specific surface areas are required. In former experiments systems from SiO_2 and $(\text{C}_6\text{H}_5)_2\text{SiO}$ have been synthesized. It was found, that even small contents of the diphenylsilane reduce the surface area drastically, if "normal" liquid reaction conditions (refluxing, ethanol as solvent, aqueous HCl addition) are applied. Bubbling HCl gas through the reaction mixture improves the specific surface area even of diphenylsilane contents up to 20 mole-% (fig. 10). Up to now it is not quite clear, why a minimum at pH 4 appears, but here the maximum gelation time is observed. Since short condensation times shorten the relaxation period for the system, "open" structures should be more preferably obtained in this case.

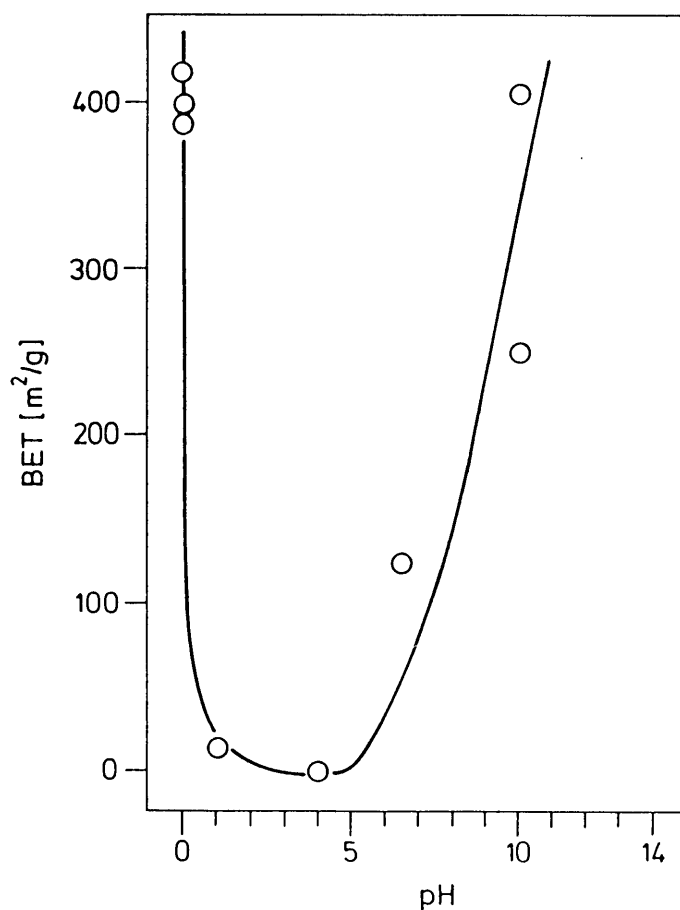


Fig. 10.
BET surface of a
 $\text{SiO}_2 : (\text{C}_6\text{H}_5)_2\text{SiO} =$
80:20 (molar ratio)
condensate depending
on pH during hydro-
lysis

4. CONCLUSIONS

The investigations on ORMOSILs have shown, that the sol-gel process can be advantageously used for the preparation of inorganic-organic polymers. Furthermore one can see, that the use of the rules of chemistry allow the tailoring of special material properties. Up to now, different groups of materials with common properties have been developed. There is the scratch resistant group which is mainly based on the epoxysilane with inorganic network formers. This group can be used for the preparation of coatings and bulk materials as well. The thermoplastic group is based on di-

phenylsilane contents of more than 40 mole-%. The photocurable group is based on photocurable ligands like methacryl, vinyl or allyl groups and can easily be combined with a big variety of polymerizable monomers. The thermoplastic and photocurable group can be used as coatings, adhesive films and bulk materials. The porous group is characterized by a high content of inorganic network formers and mainly monofunctional organosilanes and can be used as porous coatings, carriers for catalysts and membranes. A variation of this type are functional coatings with different surface groups to be used in the sensor field. Based on the wide modification, applications seem to be possible in very different branches, which opens a high innovative potential of these materials.

5. ACKNOWLEDGEMENTS

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