

ASPECTS OF CHEMISTRY AND CHEMICAL PROCESSING OF ORGANICALLY MODIFIED CERAMICS

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ABSTRACT

For the synthesis of composites on a nano or molecular level, chemical or physical methods have to be used since mechanical procedures cannot be employed for these systems. If organics have to be included, low temperature processing has to be used for the synthesis of the inorganic component in order not to damage the organic component. Sol-gel techniques are an appropriate means to synthesize oxidic networks by soft chemistry, and various systems of organically modified ceramics (ORMOCERS) have been developed so far. It has been shown that the synthesis parameter can be used to tailor the material properties in a wide range. A review over the chemistry and chemical properties of ORMOCERS and several examples of material developments will be given.

INTRODUCTION

The aim of this paper is to point out special chemical aspects of organically modified ceramics of the ORMOCER type, mainly developed in the Fraunhofer-Institut für Silicatforschung in Würzburg, FRG. Due to the limited amount of space and with respect to the review, in several cases details were not reported here, but are foreseen for later publication or are found in the cited literature.

In numerous cases of materials application in technology one-component systems do not meet the complex practical requirements and, therefore, composites have to be used. The vast majority are so-called macroscopic composites like laminates or fiber reinforced materials. The lower limit of the component size in these cases is the μm range and is limited by mechanical processing (e.g. mixing, coating, blending). For coatings, layer thicknesses in the nano range can easily be achieved by deposition techniques and, as shown in [1], composites consisting of several hundreds of thin layers can be prepared by microwave assisted chemical vapor deposition. That means layered composites with one very small dimension can be obtained. Particulate phases, e.g. ceramic phases in ceramic matrices, are obtained by nucleation and crystallization processes at high temperatures. It is difficult to obtain very small grain sizes if one starts from conventional crystalline raw materials like oxides. Amorphous gels, however, can be transformed into ceramics with extremely small particle sizes [2]. If growth and agglomeration processes can be controlled

particulate raw materials for ceramics in the nano range can be prepared [3]. In controlled sol-gel reactions, fine particles can be formed by a controlled growth mechanism in solution.

To obtain glasses or ceramics from gels or from ultrafine particles, the material has to be densified by heat treatment during a sintering process. The densification mechanism can either be a viscous flow, e.g. in glasses, as described in [4] or a diffusion controlled mechanisms, similar to sintering mechanisms of ceramics [5]. In ceramic multicomponent compositions, the diffusion paths can be extremely short if the particle size is small, leading to reduced crystallisation temperatures [6]. The high temperatures necessary for densification are a result of a molecular property of the inorganic units. They form a three-dimensional network since the number of bonds per unit, as a rule, is ≥ 3 . Lower network connectivity numbers enhance densification as known from organic polymers. The organic modification in sols and gels should have the same effect. This idea was used for an improvement of the processing properties for fiber drawing from SiO_2 sols in [7]. In this case, a $\equiv\text{SiOC}_2\text{H}_5$ grouping represents the determining function. Other examples for chemical modifications are shown in [8]. In this case, the complexation of Al-alkoxides leads to ultrafine particles, suitable for fiber drawing or coating. In these examples, the organic modification is only used to overcome disadvantages of the three-dimensional crosslinking in processing steps before densification and afterwards the organics are burnt out. But if organics are carriers of special functions it might be of interest to keep them within the final product. In this case, hybrid materials with inorganic backbones and organic components are obtained and the organic component may act as a chemical or structural modification of the inorganic network. Therefore, the sol-gel process provides a means for the preparation of ultrafine dispersions for the inorganic phase and, in addition to this, organic groups can be included which enhance relaxation and densification of the network.

GENERAL ASPECTS OF ORGANIC MODIFICATION OF ORMOCERS

Various material syntheses by sol-gel techniques in combination with organic groups have already been described [9-14]. Different basic types of ORMOCER materials can be distinguished:

- organic groups act as non-reactive network modifiers, e.g. alkyl or aryl groups covalently bond to Si. There is a strong effect on T_g shown in fig. 1 (x, with phenyl groups as an example).

This type can be considered as a modified glass structure with organic groups as network modifiers instead of alkali ions. Curve (o) represents the case of a second type of structure:

- organic groups are linked together and can stabilize the "gel network" mechanically by forming flexible links.

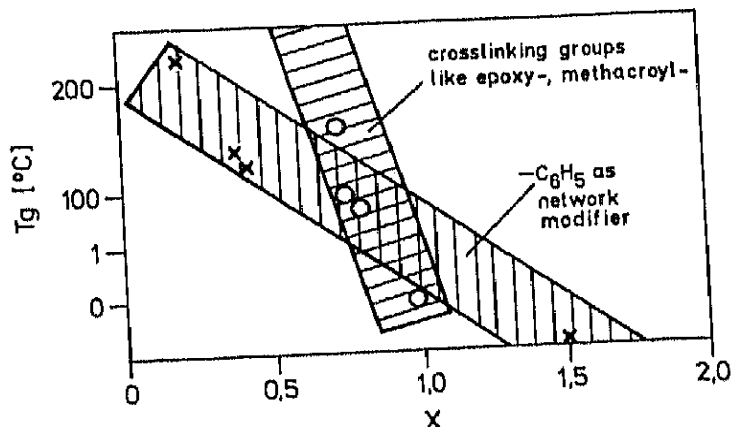


Fig. 1. Effect of organic groups on T_g in organically modified ceramics according to [10].

In this case, a steeper slope (o, fig. 1) results, as pointed out in [10]. No T_g can be determined if the ratio of network modifier carrying groups to network modifier-free groups becomes 0.7. Materials with $r > 0.7$ can be easily densified to bulks without cracking.

If one considers this behavior from the organic polymer point of view, it can be explained as a structure stabilizing effect of the inorganic components, too. Stabilized structures like this do not only show higher T_g , but show also special chemical properties like reduced diffusion for e.g. organic molecules. In fig. 2, the permeation rates $P = S \cdot D$ (S = solubility; D = diffusion coefficient) of coated and uncoated high density polyethylene (HDPE) are compared with a standard test gasoline fraction as permeate [15].

Another aspect of structural stabilization in combination with special properties is described in [16] in materials derived from $(\text{CH}_3\text{O})_3\text{Si}-(\text{CH}_2)_3\text{NH}_2$. Hydrolysis and condensation results in transparent monolithic condensates stable up to 150°C . Doping with HClO_4 or $\text{CF}_3\text{SO}_3\text{H}$ leads to protonic solid state electrolytes with no change in conductivity by ageing time or temperature influences, indicating a high structural stability compared to organic polymers like polyethylene oxide. It is assumed that the inorganic backbone stabilizes structures according to fig. 3.

The proton transport can be explained by a chain motion mechanism, since the conductivity rises sharply at the glass transition temperature. Both findings, low permeation rates as well as stable conductivity behavior support the thesis of a structural stabilization effect of the inorganic backbone. From the ceramic point of view and according to fig. 1, the T_g values are substantially lowered compared to corresponding inorganic compositions (the inorganic backbone with the organics to be removed) and the densification behaviour should be affected, too.

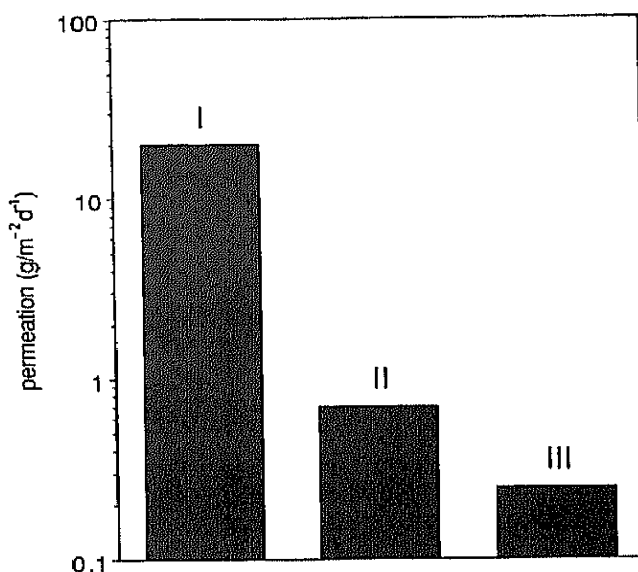


Fig. 2. Permeation of hydrocarbons through coated and uncoated HDPE. I = uncoated HDPE; II = coated with a polymer obtained from $\text{Al}(\text{OBus})_3 : (\text{CH}_3\text{O})_3\text{Si}-(\text{CH}_2)_2\text{OCOCH}(\text{CH}_3)=\text{CH}_2 : (\text{C}_2\text{H}_5\text{O})_3\text{Si}-(\text{CH}_2)_2\text{CH}_3 : (\text{CH}_3\text{O})_3\text{Si}-(\text{CH}_2)_3\text{NH}_2 = 20:50:30:4$ (molar ratio) by hydrolysis and condensation and photocuring after coating with IRGACURE 184 (commercial photoinitiator from Ciba Geigy company); III = same polymer, but methacrylate grouping substituted by the epoxy grouping $(\text{CH}_3\text{O})_3\text{Si}-(\text{CH}_2)_2\text{OCH}_2\text{CH}=\text{CH}_2\text{O}$, thermally cured after coating at 90 °C. Coating thickness: 5 μm .
P: equilibrium rates after 50 hrs.

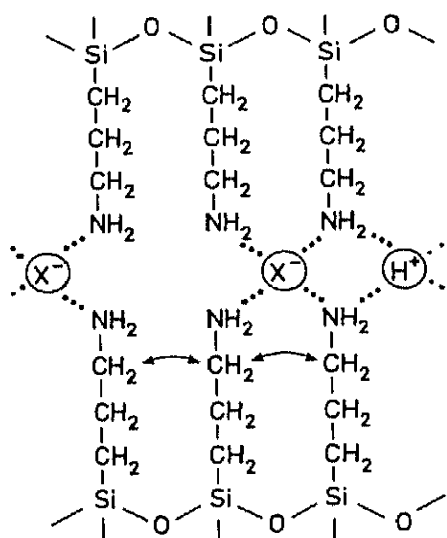


Fig. 3. Model of a proton conductive modified glass according to [17].

As shown in various examples [16,18], dense and crack-free bulk materials can be prepared very easily with ORMOCERs and especially by use of a two step process including organic polymerization (fig. 4). The advantage of the two step process results from the separation of the sol-gel reaction (mainly controlled by H₂O and catalysts) from the organic polymerization reaction (thermally activated or photoactivated). The organic crosslinking affects the chemical properties, too. Whereas structures with ≡Si-O-bonds as backbones and without polymeric crosslinking are sensitive to alkaline or hydrolytic attack, polymerized materials are chemically much more stable. This behavior can be used for pattern development by photolithography (fig. 5) [19]. Without stabilization by polymerization an ORMOCER film can be removed after drying at room temperature completely by diluted NaOH. By this, patterns can be developed after UV light exposure with appropriate masks.

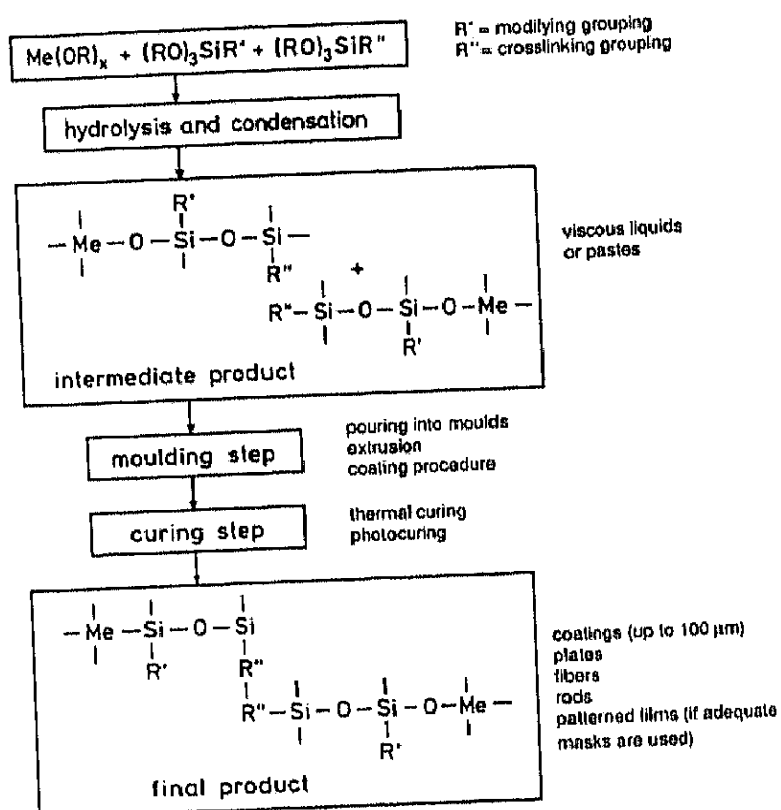


Fig. 4. Typical two step processing of organically crosslinked ORMOCERs; R': alkyl, aryl; R'': vinyl, methacryl.

The sensitivity against NaOH decreases with increasing degree of organic polymerisation and can be affected by composition, too. If epoxy-free compositions are used and the methacrylate is substituted by vinyl, one can synthesize "silicates" extremely stable against alkaline attack, as shown in [20,21]. In addition to this, for example, coatings of the system SiO₂/(C₆H₅)₂SiO/CH₃-vinyl-SiO = 5:35:60 (molar ratio) show a low permittivity constant ε of about 2.7 (which does not change after weathering due to a very low H₂O take up), and a high

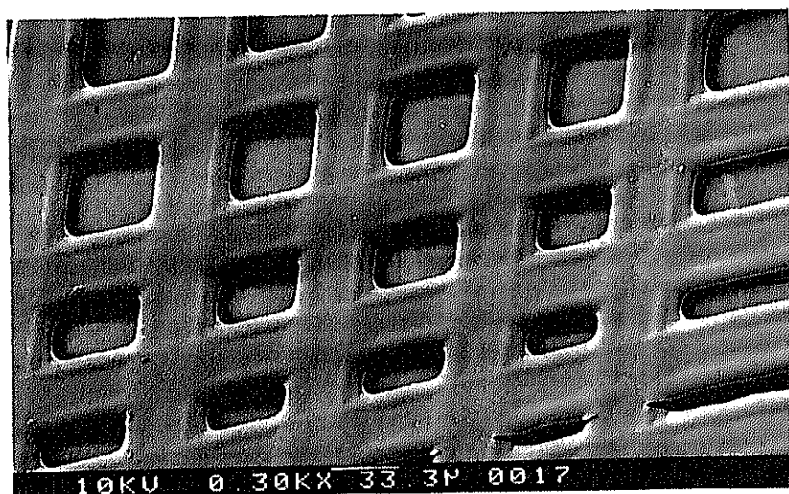
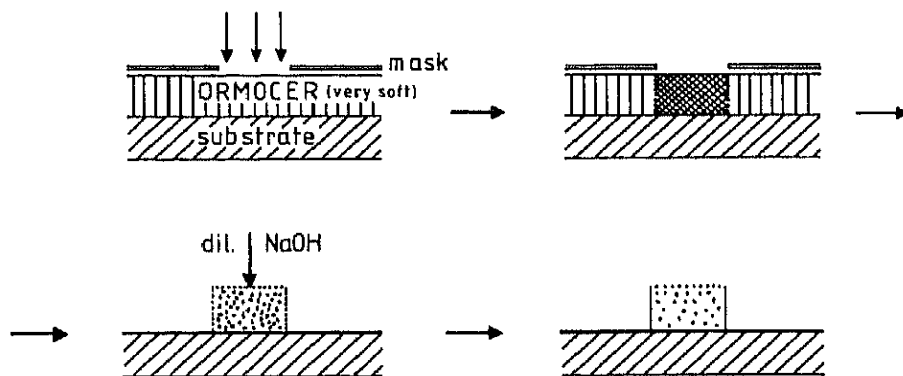
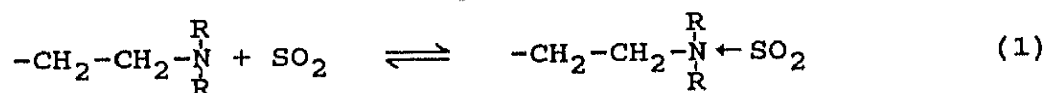


Fig. 5. Photolithography of ORMOCERs by polymerization stabilization.

a) ORMOCER composition:
 $\text{SiO}_3/2(\text{CH}_2)_3\text{OCOCH}(\text{CH}_3)=\text{CH}_2$: 38.6)
 $\text{SiO}_3/2(\text{CH}_2)_3\text{OCH}_2\text{CHCH}_2\text{O}-$: 38.6) molar ratios
 $\text{SiO}_3/2\text{CH}=\text{CH}_2$: 18.9; SiO_2 : 3.9)
 Photoinitiator: IRGACURE 184 (Ciba Geigy)

b) Developed patterns; UV exposure by direct laser writing. chemical stability against concentrated bases, which is quite unusual for silica based materials. The material can be used for dielectric coatings.

In opposition to a high chemical stability, a high sensitivity for special compounds can be useful, too. As pointed out in the introduction, organofunctional groups can dominate the chemistry of ORMOCERs in a wide range. The use of aminogroups as charge carriers for solid state electrolytes already has been shown in fig. 3. They also can be used for complex formation for SO_2 [22]. In this case, secondary or tertiary amino groups react reversibly with gaseous SO_2 (1)



The complex formation is a function of the SO₂ partial pressure. The ORMOCER is dense, but SO₂ can diffuse into the structure. The adsorption process can be monitored by IR as shown in fig. 6 but more efficiently by other techniques. In fig. 7a and 7b the response of a coated piezo quartz and of an interdigitated capacitor is shown [23]. The frequency shift of the quartz is linear to the vapor pressure of SO₂. The capacitance device shows an extremely high sensitivity (<< 1 vpm SO₂)

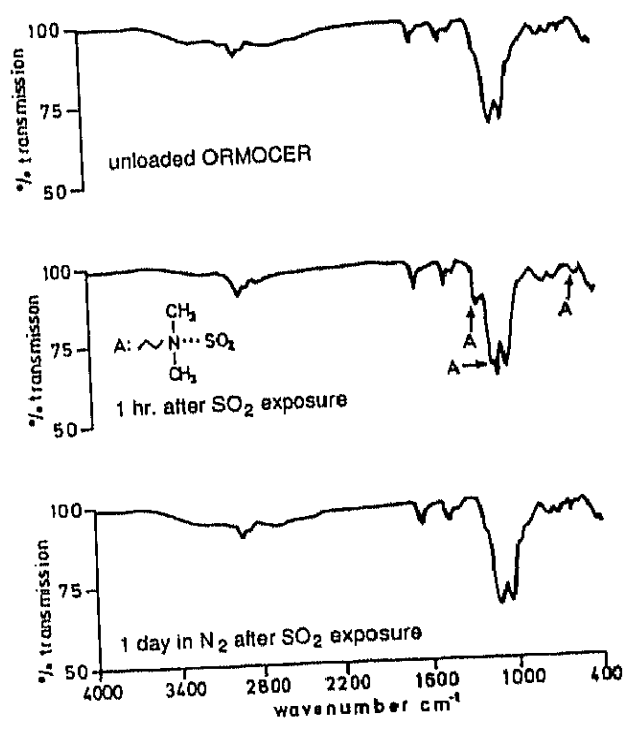


Fig. 6. Adsorption of SO₂ on a tertiary amine. The amine is covalently bond to a silane: (CH₃CH₂)₂N(CH₂)₃Si(OR)₃ and incorporated into the ORMOCER NND (34/1) according to [22].

spectra of a NND (34/1) layer on KBr-crystal
 top: before SO₂-treatment
 middle: loaded with SO₂
 bottom: after SO₂-treatment

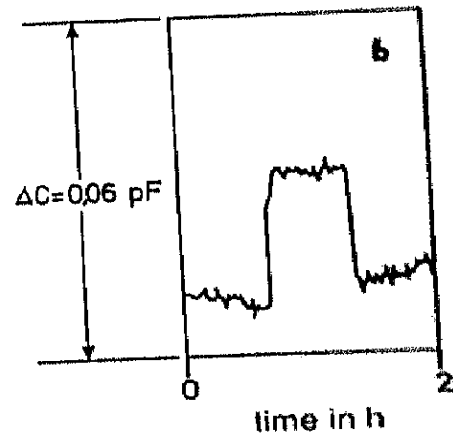
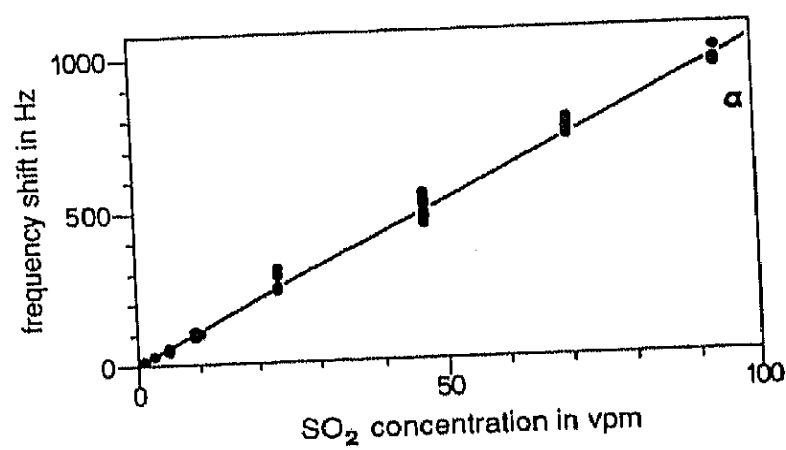


Fig. 7a-7b. a) Frequency shift of an ORMOCER coated piezo quartz as a function of the SO₂ partial pressure. b) Capacitance shift of an interdigitated capacitor coated with an ORMOCER by exposing 1 vpm SO₂ in N₂.

The examples described above demonstrate some special chemical properties of ORMOCERS. These properties are related to structural features and, in this connection, it seems to be of importance that the materials are of high homogeneity and no resolution of phases can be observed in the TEM (≈ 1 nm resolution). That does not necessarily mean that the homogeneity is on a molecular scale, but no correlation between the size of inorganic and organic domains could have been drawn so far.

CHEMICAL PROCESSING OF ORMOCERS

In the previous chapter mainly the question of chemical properties was discussed (on the basis of composition). But independent on composition, the properties are influenced by processing, too. In the following, several synthesis processes for different types of ORMOCERS and the influence on properties are described. As published elsewhere [9], a family of scratch resistant coatings was developed from an ORMOCER contact lens composition. The hardness of these materials was attributed to the inorganic backbone. These materials have to be prepared by a special condensation process according to [24] in order to obtain sufficient homogeneity. γ -glycidylpropyltrimethoxysilane (epoxy silane) was used as organic modifier, which is able to form a polyethylene oxide chain by polymerization. One disadvantage of these materials is their brittleness, which prevents their application on flexible substrates like rubber or thin foils to be bent with small curvature radii. The elongation limit of these coatings is in the range of about 1 - 2 %. The question arises, whether flexibility can be improved by reducing the concentration of inorganic units without losing scratch resistance.

The simplest way to reduce the amount of inorganic backbone is the elimination of pure inorganic network formers and to start with the one-component system "epoxy silane". The synthesis process is described in details in [25]. For the hydrolysis of the epoxy silane two different concentrations of water were used: 1.5 mole H_2O /mole silane and 3.0 mole H_2O /mole silane. In fig. 8 the residual H_2O concentration after 10, 50 and 200 minutes hydrolysis at pH 9 after 16 hrs prehydrolysis at pH 5.5 is shown (at pH 5.5 only a small fraction of water is consumed).

The analysis of the epoxy groups shows that with 3.0 mole H_2O the residual epoxy group content is remarkably lower. After pH 9 hydrolysis, ≈ 30 % of the epoxy groups are changed to glycol groups indicating that a part of H_2O is used for the epoxy ring opening instead of hydrolysis. With 1.5, almost no glycols are formed. This should have a serious effect on the epoxy crosslinking: For the 3.0 system, a weaker crosslinking and a more hydrophilic matrix is expected.

Coating experiments on metal and PET foils show significant differences. The 1.5 system shows after an amino-catalysed curing (= epoxy polymerization to PEO chains) a surprising flexibility compared to the 3.0 system, as indicated in fig. 9, which is attributed to the higher PEO chain content of this

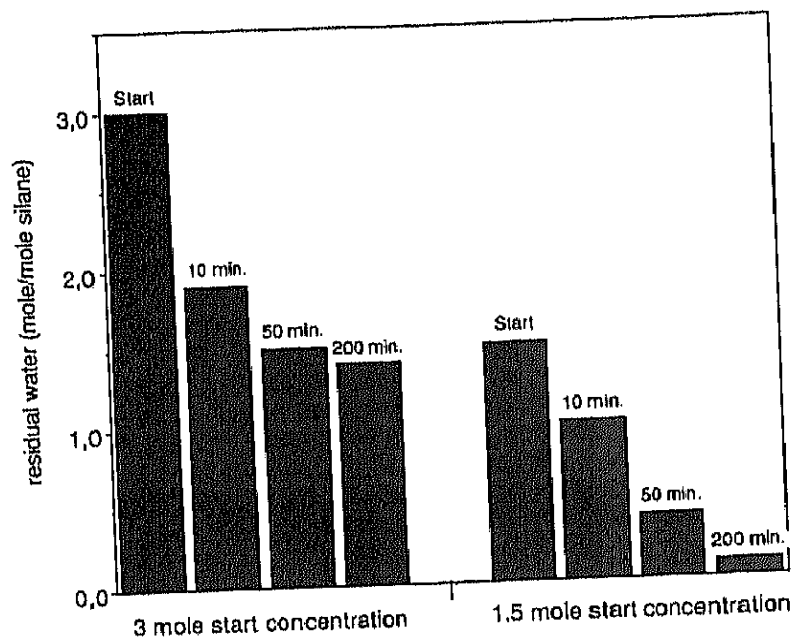


Fig. 8. Comparison of the hydrolysis kinetics of 3.0 and 1.5 mole H_2O concentration of the epoxysilane at pH 9; 16 hrs at pH 5.5.

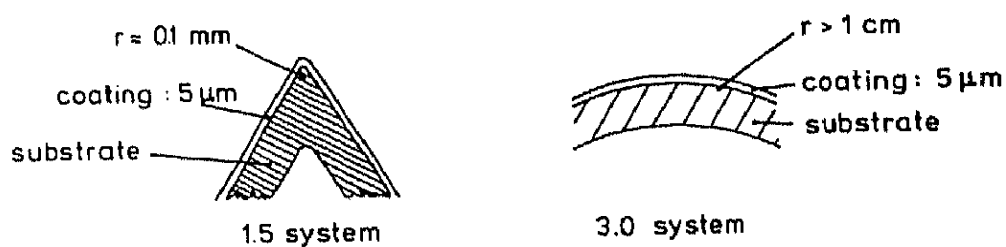
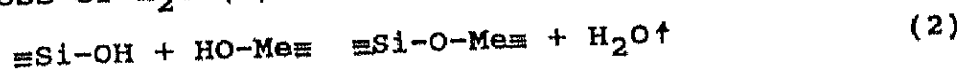


Fig. 9. Differences in flexibility of the 1.5 and the 3.0 system.

chain content of this system. Humidity tests confirm the result: The 3.0 system shows crack formation after 14 days treatment at 40 °C in 100 % r.h. due to its higher water take up, whereas the 1.5 system remains unchanged. The results clearly show the strong impact of hydrolysis and condensation conditions on the material properties.

These materials can be easily employed as thick coatings (up to 50 μm) without cracking. Cracking in general occurs during the thermally induced condensation step by shrinkage due to the loss of H_2O (2) or closing of pores.



If no pores are present, shrinkage is only based on the loss of H_2O if the precursor is solvent-free and hydrolysis is complete. The elimination of $\equiv Si-OH$ groups should lead to an improvement of the shrinkage behavior. Therefore, in a

composition with 30 SiO₂ (from TEOS), 30 C₆H₅SiO_{3/2} (from C₆H₅Si(OEt)₃) and CH₂=C(CH₃)COO(CH₂)₃SiO_{3/2} (from the ethoxide), an average of 1.5 ≡Si-O bonds at the phenylsilane was substituted by F (fig. 10). This was carried out by introducing C₆H₅SiF₃, which hydrolyses to an average of 1.5 F during hydrolysis and condensation [26]. In fig. 11, the NIR spectra shows the disappearance of the SiOH groups by the introduction of F.

Thermal treatment shows remarkable differences between the two systems. The fluorinated system (after photocuring the MMA groupings) undergoes a weight loss of only a few % between 100 and 280 °C with almost no shrinkage, whereas the non-fluorinated system loses already remarkable weight accompanied by crack formation in 10 μm thick coatings. Employed as coatings, the fluorinated materials can be used up to 250 °C without shrinkage

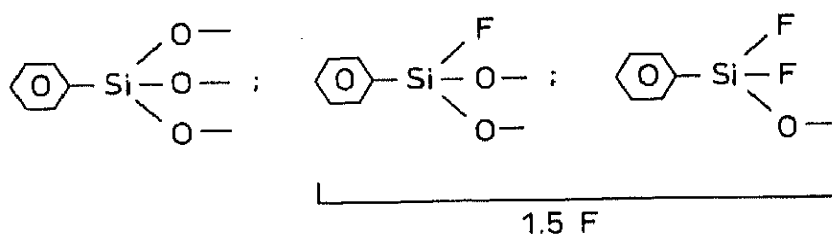


Fig. 10. Substitution of ≡Si-O- by ≡Si-F.

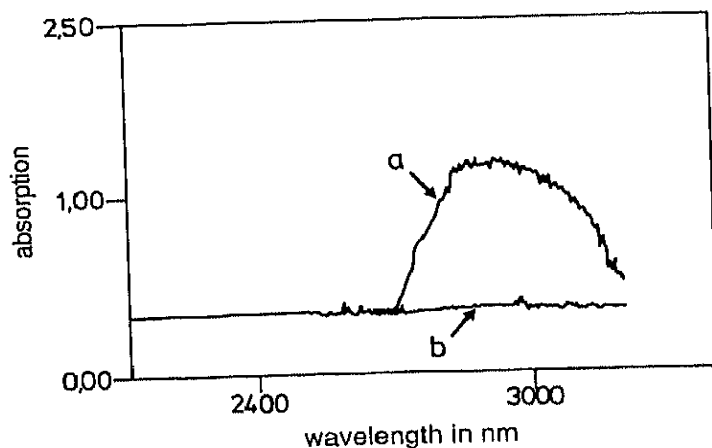


Fig. 11. NIR spectra of SiOH groups of the fluorine-free (a) and the fluorinated system (b).

and cracking. They are highly transparent and show a good scratch resistance, too. They are not effected by humidity in the weathering test. The behavior can be explained by the lack of thermally activated condensation of SiOH groups in the flexible network.

Another interesting variation by chemistry can be used to incorporate metal oxides into polymers on a molecular or nano scale by complex formation. For example, $Zr(prop^1)_4$ complexed with methacrylic acid (MA) can be used for polymerizing the acid with olefins to form ZrO_2 containing polymers. The complex formation can be followed by IR (fig. 12), excess of MA ($r/ZrO_2: MA > 2$) leaves uncomplexed acid. Polycondensation and polymerization of the complexed $Zr(OR)_4$ with methacryloxysilane (1:9 molar ratio) leads to bulk materials with interesting mechanical properties [27]: Solid rods can be prepared with a bending strength up to 80 MPa. This can be interpreted by an internal reinforcement of the modified PMMA crosslinked ORMOCER.

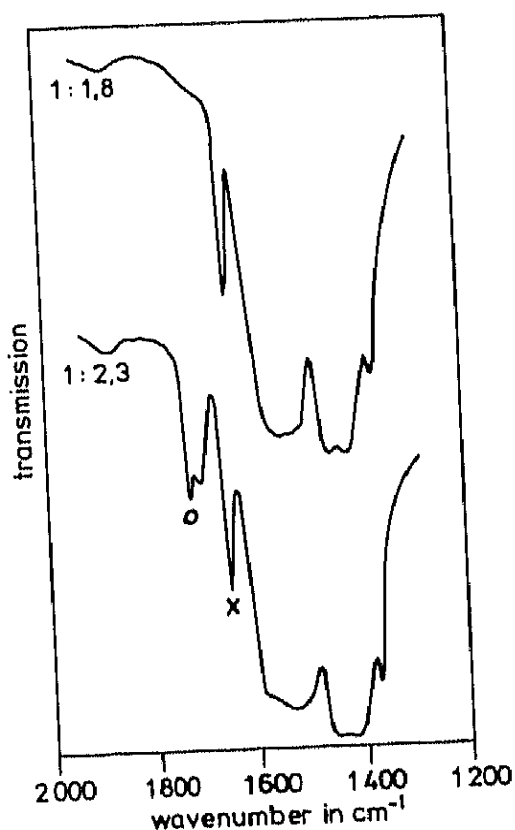


Fig. 12. Consumption of MA by complex formation with $Zr(prop^1)_4$; MA:Zr = 1:1.8 (upper curve) and 1:2.3 (lower curve, molar ratios). x \equiv C=O vibration of complexes, o \equiv C=O vibration of the free acid.

CONCLUSIONS

Sol-gel chemistry in combination with organic modification can lead to new materials with interesting properties. Chemical properties can be changed in a wide range. But for the understanding of the properties, the understanding of the synthesis chemistry is necessary. This can be difficult, especially if multicomponent systems with differences in the reactivity of the different components occur. Investigations in many cases are only at its beginning but show already very hopeful results. The second point necessary to be investigated is the size effect of the inorganic-organic domains on the properties of the materials.

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