

Section 4. Physical and chemical properties of shaped materials: (f) Composites

ORGANICALLY MODIFIED CERAMICS AND THEIR APPLICATIONS

Helmut SCHMIDT¹ and Herbert WOLTER

Fraunhofer-Institut für Silicatforschung, Neunerplatz 2, D-8700 Würzburg, FRG

ORMOCERs (organically modified ceramics) are inorganic-organic composites on a molecular or nano level. The inorganic backbone can be synthesized by sol-gel techniques from inorganic molecular precursors, for example alkoxides or soluble oxides. Organic components can be introduced by Si-C bonds, coordinative bonds, or ionic bonds. Introduction of organic polymeric chains leads to a second type of network. This network can be chemically linked to the inorganic backbone or act as an interpenetrating network. Properties of the materials can be varied in a wide range due to composition, reaction conditions and processing. They can reach from thermoplastic materials (e.g. sealings) to brittle coatings (hard coatings). Various functions such as photocuring, scratch resistance, special dielectric properties, or barrier functions can be introduced. Especially low permittivity constant in combination with thermal stability and low conductivities lead to the development of dielectric coatings for electronic applications.

1. Introduction

Sol-gel techniques have attained strong interest because of the potential for development of new or better ceramics or glasses. The main potential of the process is the low temperature processing of non-metallic, inorganic solids (gels or powders), which can be processed to final materials or shapes at temperatures which are, in general, substantially lower than conventional processing conditions. Scientific interest in the sol-gel process has led to an increase of fundamental knowledge especially in silicate systems. The number of sol-gel products is still comparatively small but increasing. The proceedings of the sol-gel related congresses [1-10] and books [11] provide a survey over the state of the art. From the standpoint of application, glass coatings and ceramic powders [12-13] are most important directions. In these cases, organics remaining within the gels have to be removed carefully. On the other hand, organics remaining in the solids can modify the materials substantially and can be used to create new functions. Some examples are the incorporation of organic dyes in gels [14,15], introduction of

methacrylate or epoxy groups into silica gels [16], modifying organic polymers by in situ sol-gel derived components [17], or materials modified with organics linked to zirconia atoms by complex formation [18,19]. In these investigations, the sol-gel process is used to build up an inorganic network in the presence of organics at temperatures low enough not to destroy them. In refs. [20-24] a survey is given by sol-gel materials including organic components. Two groups of ORMOCERs have been of special interest. Systems which show excellent mechanical surface properties, which can be used as hard coatings [25] and materials which exhibit thermoplastic properties and can be used as functional or protective coatings [26-28].

2. Hard coatings and diffusion barriers

It is possible [29] to combine properties of ceramics with those of polymers. Hard coatings are based on Al₂O₃, ZrO₂, TiO₂, or SiO₂ as network formers and epoxy or methacrylate groupings bound to Si via a ≡Si-C≡ bond. They can be thermally cured at low temperature and thus can be applied to organic polymers. Abrasion tests show substantial improvements over uncoated plastics.

¹ Present address: INM gem. GmbH, Universität des Saarlandes, Gebäude 43, D-6600 Saarbrücken, FRG.

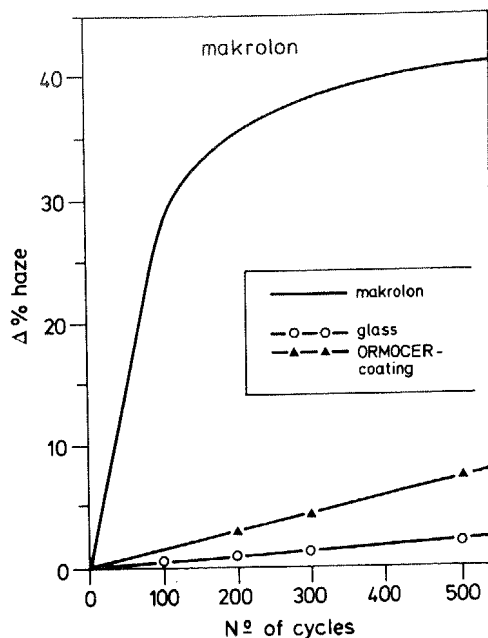


Fig. 1. Effect of ORMOCER coating on polycarbonate (abraded test).

Figure 1 shows the change in haze as a function of scratch cycling for an ORMOCER coating on a coated polycarbonate plate (Makrolon, from Bayer) in comparison with an uncoated sample and to a float glass sample [30]. The coating system is based on an $\text{Al}_2\text{O}_3/\text{SiO}_{3/2}$ -epoxy composition with a propyl group as third component. The preparation of the system takes advantage of the CCC process [31] which uses a small amount of water to create OH-groups at highly reactive alkoxides, e.g. at $=\text{AlOR}$ to $=\text{AlOH}$. These $=\text{AlOH}$ groups then condense spontaneously to available $=\text{SiOR}$ groups, leading to a homogeneous distribution of species with very different reaction rates. The system is composed of $\text{Al}(\text{O}i\text{Bu})_3$, a trimethoxy epoxysilane and a triethoxy propylsilane as precursors in the molar ratio 2:5:3. The propyl component reduces the water take-up leading to coatings with high moisture resistance in the humidity test (40°C , 100% RH for two weeks). The coating is crackfree, has a thickness of $5\ \mu\text{m}$ and is prepared by a one step dip coating process.

The results show clearly that the abrasion resistance of the system is close to that of float glass. This improvement is attributed to the effect of the

inorganic network, which resists the cutting impact of the grinding wheel particles better than the polymeric chain of the polycarbonate. The low curing temperatures resemble properties typical of organic polymers. However, it is well-known that the condensation process in sol-gel reactions takes place spontaneously during the evaporation of solvents at low temperatures. In the case of the described coating, the densification and curing takes place at $90\text{--}130^\circ\text{C}$. This curing can be attributed to the effect of the organic chains, which provide sufficient relaxation behavior to generate mobility of the $=\text{Al-OH}$ and $\equiv\text{SiOH}$ units which allows further condensation up to complete densification. Figure 2 points out the high network flexibility on a possible structural model.

The complete densification at low temperature of those systems demonstrates another coating. The permeation behavior of a coating of the composition $\text{Al}_2\text{O}_3:\text{SiO}_{3/2}\text{R}:\text{SiO}_{3/2}\text{-propyl} = 2:5:3$ (R = epoxy, methacryl; γ -aminopropyl triethoxysilane was added in amounts up to 5 mol% as adhesion promoter) was measured. Therefore, the coating was employed on a high density polyethylene (HDPE) subpolymerizable groupings (in the case of methacrylate containing coatings, coating A) or thermally cured as reported above (coating B). The effect of the coatings on the hydrocarbon permeability is shown in figure 3.

As one can clearly see, the coating reduces the permeation to a very low level. Porosity within the

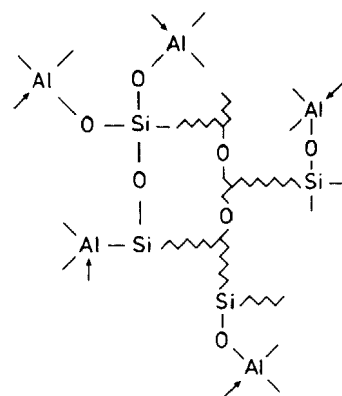


Fig. 2. Structural model of an $\text{Al}_2\text{O}_3/\text{Si}$ -polyethylene oxide composite.

coating would lead to higher values. The results can be interpreted again from the structural point of view. The inorganic backbone leads to a low solubility of hydrocarbons since no swelling effect could be observed. The high abrasion resistance is maintained.

3. Systems for dielectric applications

3.1. General introduction

The systems described above use a $R'Si(OR)_3$ grouping (monofunctional silanes with R' as the functional grouping) as a means for introducing organics. The use of additional difunctional silanes (e.g. $(C_6H_5)_2Si(OR)_2$) changes the properties substantially, as described in refs. [26,27]. Therefore, in addition to the $(C_6H_5)_2SiO$ unit, the use of a polymerizable system is described, e.g. the $\equiv S-CH=CH_2$ (vinyl) unit. Thus, one can use the diphenyl unit as a *linearizing inorganic* backbone and the vinyl unit as a *crosslinking organic* unit. Since these systems contain high concentrations of hydrophobic groupings, the water stability should be high and the water take-up low.

These systems can be combined with tetrafunctional network formers, as described in ref. [26]. The basic features of the system, its stability

against water and acids, suggested a potential for applications as a dielectric material for electronic purposes. Therefore, the system $(C_6H_5)_2SiO/CH_2=CH(CH_3)SiO/SiO_2$ was chosen as basis, since these components should exhibit a low dielectric constant ϵ if the OH-group content can be kept at a low level.

General requirements for dielectric electronic materials are low ϵ values (< 5.5), high stability against humidity (humidity 10 test $> 92\%$ RH at $40^\circ C$ and > 4 days), high electrical resistance ($< 10^{10} \Omega$), low loss factors ($\tan \delta < 35 \times 10^{-3}$) and high temperature stability ($> 250^\circ C$). If the material is applied as a coating, a suitable coating viscosity has to be adjusted and adhesion to the substrates to be used is required. As starting material, the composition of the system described in ref. [27] was chosen, since it exhibited excellent adhesion to surfaces of inorganic materials and shows a very good performance with respect to humidity and freezing/thaw cycles.

The system is based on the composition $(C_6H_5)_2SiO/(CH_2=CH(CH_3)SiO/SiO_2/TiO_2/ZrO_2$. The system can be cured thermally as well as by photopolymerization (based on the vinyl groupings). The influence of synthesis parameters with respect to OH content, physical and electrical properties was the main objective of the investigations.

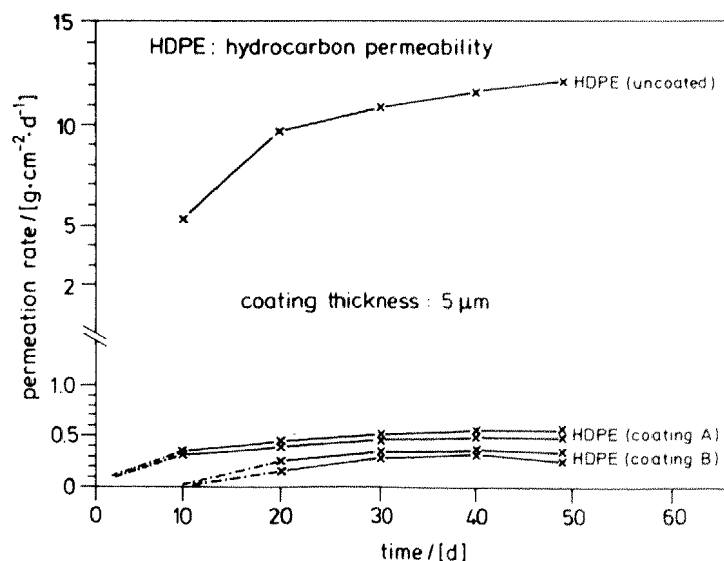


Fig. 3. Effect of ORMOCER coatings on the hydrocarbon permeability of HDPE.

3.2. Experimental

For the preparation $(C_6H_5)_2SiCl_2$, $CH_2=CH(CH_3)SiCl_2$ (MeVi) and TEOS were used as starting materials. The molar ratio was varied from $(C_6H_5)_2 : SiO : MeViSiO : SiO_2 = 65 : 32.5 : 2.5$ to $32.5 : 65 : 2.5$. Toluene and ethylacetate were used as solvents. For electrophoretic deposition of the coatings, γ -aminopropyl triethoxy silane was added up to 5 mol% and a water based emulsion was prepared containing 5.0 wt% polymer, 0.7–0.9% xylene, and 20 mol% CH_3COOH (with respect to the total amino content). The emulsion was obtained by a rapid stirring process.

The reactive precursors were converted by a hydrolysis and condensation step under acid conditions and in ethanolic KOH as solvent and catalyst. Precipitated KCl under basic conditions can be separated from the solution by filtration. After evaporating the solvent, an organic pre-crosslinking step forms a well-fitted polymer rheology. The mixture can be cured by a thermal process (1 h, $260^\circ C$) without an initiator. Photocuring was carried out with a photoinitiator (Irgacure 184, Ciba Geigy). Viscosity measurements were carried out by rotation viscosimetry during the curing process. The viscosity controlling device is shown in fig. 4.

Since the curing liquid does not show Newtonian behavior, the measured viscosity depends strongly on the device geometry. From these reasons, no viscosity calculations were carried out and the torsional moment, i.e. shearing strength τ^* was used for calibration. Aluminium plates were coated by dip coating (60 wt% solid content). Humidity tests were carried out at $40^\circ C$ and 100% RH for 4 days.

3.3. Results

The hydrolysis and condensation reactions were carried out by addition of water (acid conditions) and by addition of excess of KOH solution (basic conditions). Due to the chlorides as precursors,

* Determination of electric properties were carried out at SEL laboratories (Standard Electric Lorenz Company), Stuttgart, FRG.

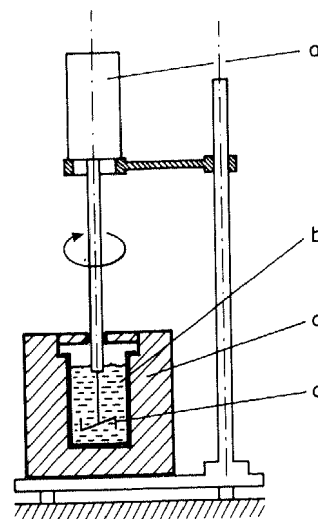


Fig. 4. Device for viscosity controlled pre-crosslinking. (a) rotation speed controlled motor with torsional moment measuring unit included = shearing strength = resin rheology; (b) ORMOCER resin; (c) heating medium ($220^\circ C$); (d) wing rotator.

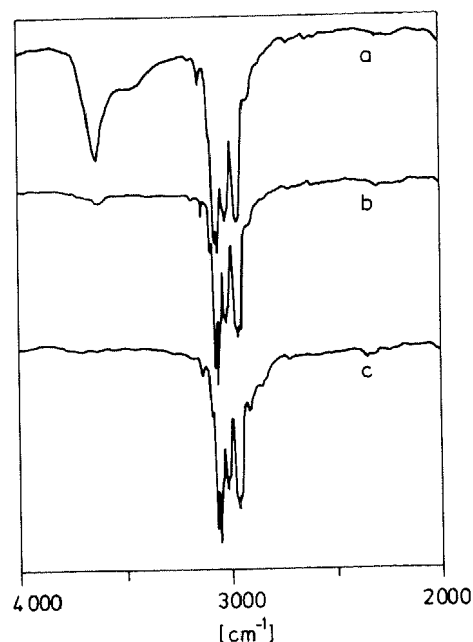


Fig. 5. IR spectra of the compositions with 65 mol% $(C_6H_5)_2SiO$. (a) acid conditions, thermal $250^\circ C$ for 8 h; (b) a + addition of 10^{-5} mol/l KOH, heating at $125^\circ C$ for 1 h; (c) neutralization after solvent removal; addition of 10^{-5} mol KOH/l, $125^\circ C$ for 1 h.

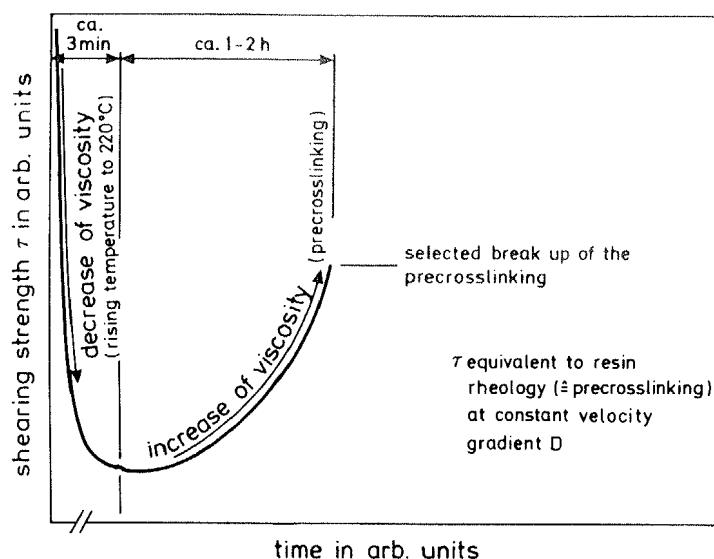
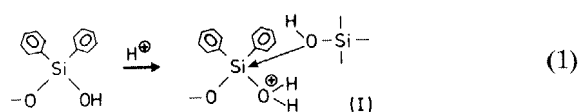


Fig. 6. Viscosity curve of the ORMOCER pre-crosslinking process.

the addition of water during the hydrolysis and condensation leads to a highly acid medium. After removal of the solvent, the remaining condensate is a viscous liquid. Thermal treatment leads slowly to a further condensation even at elevated temperatures and long times as long as traces of H^+ are present. Figure 5 shows the effect of the thermal treatment under different conditions.

It is surprising that despite the low viscosity at

250 °C during the curing process, a high water content remains in the liquid even after several hours. The acid based condensation mechanism



does not seem to work quickly with the diphenyl system. An interpretation could be the steric

Table 1
Properties of the ORMOCER coating on Al substrates

	Climate I ^{a)}		Climate II ^{b)}	
	without amino groups	with amino groups	without amino groups	with amino groups
Surface resistance				
R_0 (Ω):	$> 10^{14}$	4.2×10^{13}	4.4×10^{12}	5.5×10^{12}
Bulk resistance				
R_D (Ω cm):	4.5×10^{16}	7.6×10^{15}	6.8×10^{15}	3.1×10^{15}
Dielectric strength				
E_D (V/cm):	8.7×10^5	8.5×10^5	n.d. ^{c)}	n.d. ^{c)}
Permittivity constant ϵ_R :	3.23	2.85	3.45	2.71
Loss factor $\tan \delta$:	3.97×10^{-3}	7.7×10^{-3}	7.6×10^{-3}	7.6×10^{-3}
Resistance to soldering heat (10 s, 260 °C):	without problems			

^{a)} I dry climate: 30% and 50% RH and 24 °C (4 days).

^{b)} II humid climate: 92% RH and 40 °C (4 days).

^{c)} n.d.: not determined.

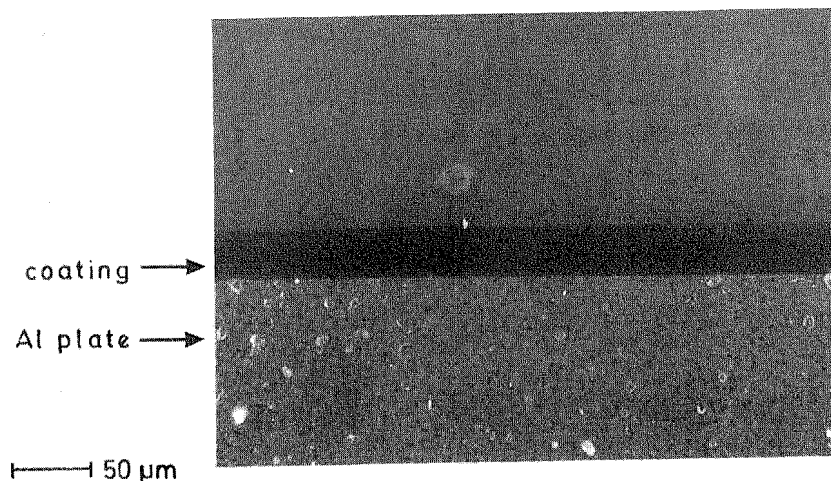
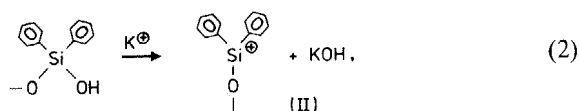


Fig. 7. Electrophoretically coated Al plate.

hindrance of the two phenyl groups, which do not favor a pentavalent transition state and the SN_2 mechanism. Addition of KOH probably supports the SN_1 mechanism with a trivalent transition state, which could be stabilized by the two phenyl groups (eq. (2)):



(II) is more accessible for condensation than (I).

After several hours of thermal curing at 250°C , the materials become solid at room temperature but still remain soluble in toluene or ethyl acetate. The same behavior can be observed after basic curing according to figs. 5(b) and 5(c). Coatings prepared from compositions with 65 mol% $(\text{C}_6\text{H}_5)_2\text{SiO}$ show good adhesion on Al, but are very brittle after drying at 250°C and thus have inadequate mechanical properties. Therefore, the ratio $(\text{C}_6\text{H}_5)_2\text{SiO}:\text{MeViSiO}$ was changed from 2:1 to 1:2. This change should lead to more flexibility due to the increase of organic chains to

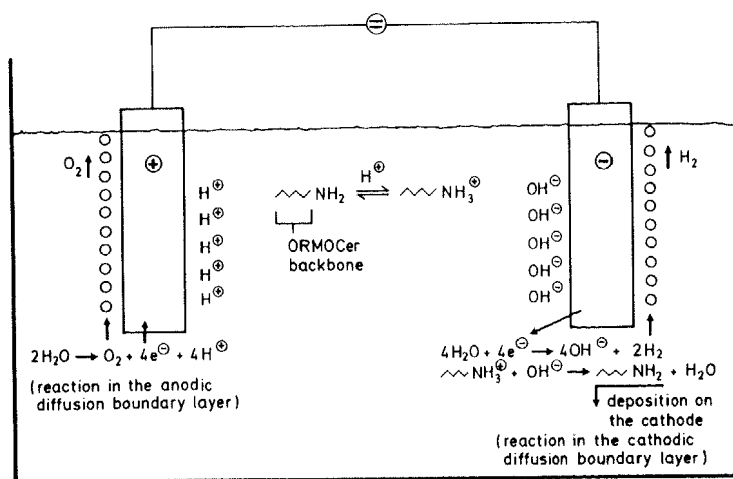
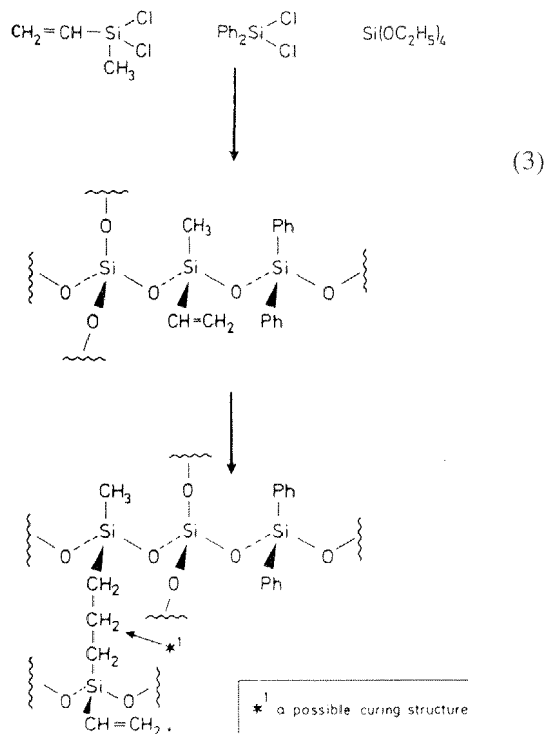


Fig. 8. Scheme of the electrophoretic deposition process.

be built up according to eq. (3):



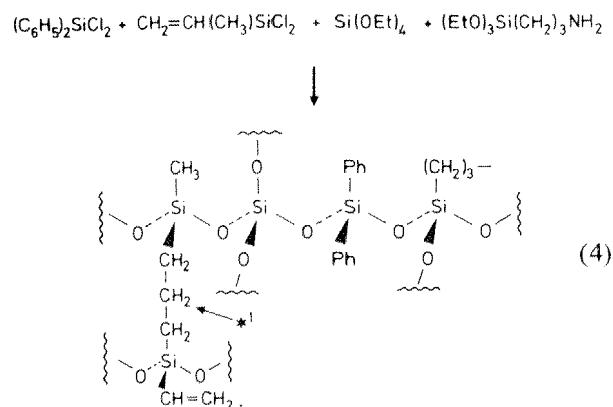
To achieve constant coating properties, it is necessary to cure to a desired constant viscosity. This curing is important to obtain smooth, dense coatings without pinholes to achieve coating thickness of 30 μm in one or two step coating. Figure 6 shows the shearing strength curve during the thermal pre-crosslinking process.

This process was mechanized in order to provide reproducible pre-crosslinking. The pre-crosslinked materials were dissolved in toluene and Al plates were dip coated and cured at 200°C for 10 min 260°C for 1 h to obtain, for example, 30 μm coatings on Al. The tests were carried out with the composition $(\text{C}_6\text{H}_5)_2\text{SiO}/\text{MeViSiO}/\text{SiO}_2 = 32.5:65:2.5$ (molar ratio). The results are shown in table 1.

Additional tests were carried out for chemical stability. These show that with 5% NaOH and 5% H_2SO_4 at 50°C no change takes place. It requires 40% KOH at 50°C to etch the surface, which demonstrates very good chemical stability for a silicate material. The tests also show that the material offers excellent electrical and weathering properties. The low value of ϵ and the high surface

and bulk resistance even after weathering are interesting for dielectric applications. The temperature stability of 260°C is suitable for soldering processes.

The dipcoating process can be applied only for simple geometries. In order to apply the coating material to more complex geometries, the possibility of an electrophoretic deposition process was investigated. Two requirements have to be fulfilled: charge carriers have to be introduced and an emulsion has to be prepared. As charge carriers, the γ -aminopropyltrimethoxysilane was chosen, which can be built into the network by condensation (eq. (4)):



Investigation of the photocuring behavior shows that it is strongly influenced by the amino grouping. The reaction time could be reduced substantially. The mechanism for this finding is not known. Amino components up to 5 mol% do not change the electrical properties.

An emulsion could be prepared from the pre-crosslinked material, xylol, acetic acid and water by rapid stirring. From this emulsion, coatings of 20–30 μm thickness can be deposited within 3 min at 40–50 V. Figure 7 shows a coated Al plate with an electrophoretic deposited ORMOCER and fig. 8 shows the scheme of the deposition process. The deposited coating has to be cured at 270°C for 1 h.

4. Conclusions

It has been shown that the sol-gel synthesis of organically modified ceramics leads to materials

with interesting properties. On the one hand, mechanical properties close to those of pure inorganic materials can be obtained, overcoming serious problems related to inorganic coatings such as high curing temperatures and crack formation at thicknesses over 1 μm . The improved densification behavior is due to the increased relaxation ability from the organic chains. The addition of functions such as diffusion inhibition for special permeates or special low water take-up, chemical or electric properties is also possible. This shows clearly the potential of these materials for tailoring materials for special application.

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