INORGANIC-ORGANIC COMPOSITES BY SOL-GEL TECHNIQUES

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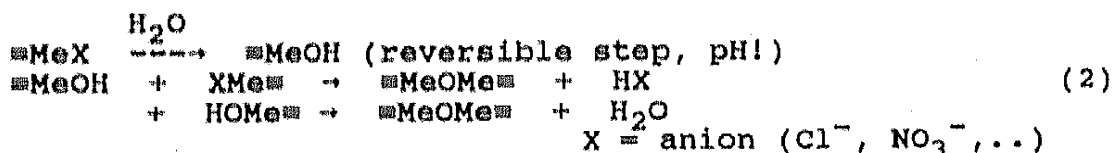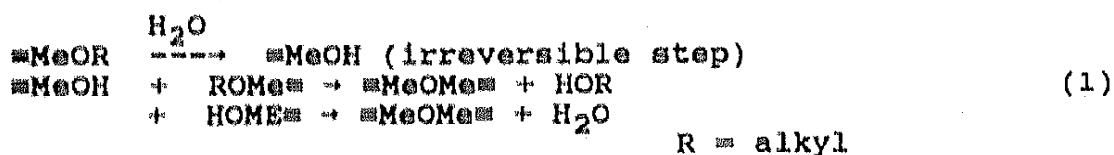Fraunhofer-Institut für Silicatforschung, Neunerplatz 2, D-8700
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ABSTRACT

The sol-gel process opens the possibility of combining in-organic and organic units to new hybrid polymers. Organic units can be used for structural modification of the inorganic back-bone, for creating new functions within an inorganic network and for building up organic polymeric chains. The materials show interesting perspectives with respect to structural (surface hardness, strength) and functional properties (e. g. diffusion, photocuring, incorporation of dyes, optical properties). A re-view over structural and functional properties of sol-gel de-rived inorganic-organic polymers (ORMOCERs = organically modi-fied ceramics) is given.

INTRODUCTION

The sol-gel process is a synthesis route to inorganic non-metallic materials. Reactive monomers, oligomers or colloids can be used as starting materials. They have to be "activated" in order to undergo a polycondensation step and to form poly-meric networks. This can be achieved by various means but, in general, by creating reactive ≡MeOH groups, which are able to form ≡Me-O-Me≡ bonds during the condensation step. A convenient route is the use of alkoxides as precursors which react with water to hydroxides, condensing spontaneously to polymeric spe-cies (1). Similar reactions are well-known from inorganic salts, forming hydroxides and precipitates (2) by pH change.

$$
\begin{aligned}
&\equiv\text{MeOR} \xrightarrow{\;\;\text{H}_2\text{O}\;\;} \equiv\text{MeOH} \text{ (irreversible step)}\\
&\equiv\text{MeOH} + \text{ROMe}\equiv \rightarrow \equiv\text{MeOMe}\equiv + \text{HOR} \\
&\qquad\quad + \text{HOMe}\equiv \rightarrow \equiv\text{MeOMe}\equiv + \text{H}_2\text{O}
\end{aligned}
\qquad (1)
$$

R = alkyl

$$
\begin{aligned}
&\equiv\text{MeX} \xrightarrow{\;\;\text{H}_2\text{O}\;\;} \equiv\text{MeOH} \text{ (reversible step, pH!)}\\
&\equiv\text{MeOH} + \text{XMe}\equiv \rightarrow \equiv\text{MeOMe}\equiv + \text{HX} \\
&\qquad\quad + \text{HOMe}\equiv \rightarrow \equiv\text{MeOMe}\equiv + \text{H}_2\text{O}
\end{aligned}
\qquad (2)
$$

X = anion (Cl$^-$, NO$_3^-$,..)

Another route is the destabilization of colloidal sols by pH change either in organic solvents or in water. All these reactions lead to gels, containing solvent or air after drying. Due to the (in general) high specific surface areas of these gels, they contain adsorbed molecules from the processing steps (water or organics) or, in the case of the alkoxide route, un-hydrolysed alkoxy groups. Organics are oxidized or pyrolyzed during heat treatments of gels, converting them into glasses or ceramics. Heat treatments are necessary to enhance diffusion

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processes (for crystallization) or to decrease viscosity (for glass formation) in gels. The viscosity of inorganic gels is high due to the three dimensional crosslinking of the inorganic building units (e. g. SiO_4^{4-} tetrahedron) leading to the typical brittleness of ceramics.

Decreasing network connectivity by introducing organic groupings can cause a remarkable decrease of viscosity of systems with pure inorganic backbones and leads to dense materials at temperatures between 50 and 150 °C, as shown in [1-2]. An analogue effect can be observed in inorganic glasses where the introduction of inorganic network modifiers leads to lower viscosities compared to fused silica. The combination of organic groupings with ceramics can take place via various routes, e. g. mechanical mixing, infiltration and chemical synthesis as indicated in figure 1. Mechanical processes are the most common and most economical processes, but the chemical routes offer new and interesting perspectives. Linking organic units to inorganic
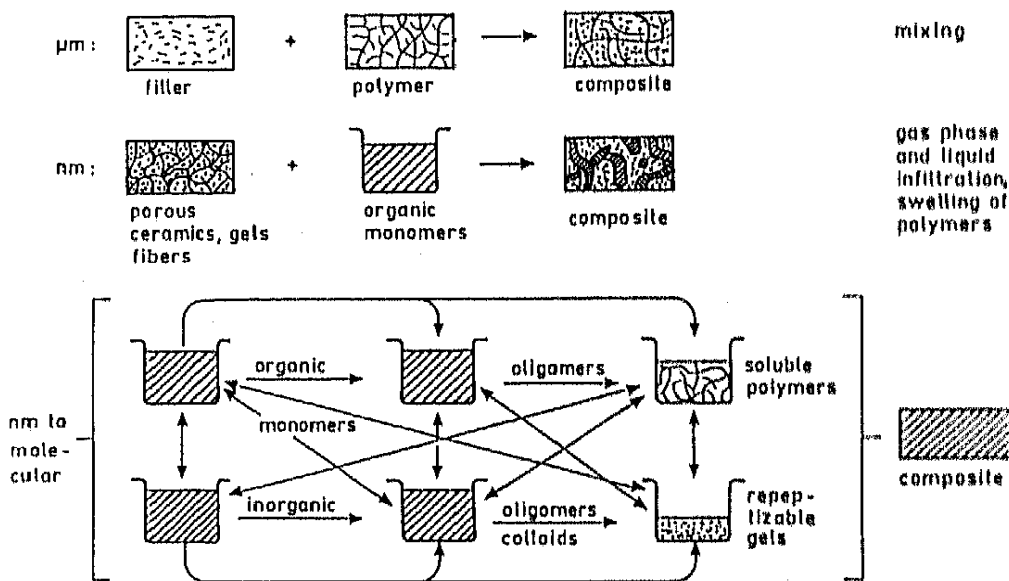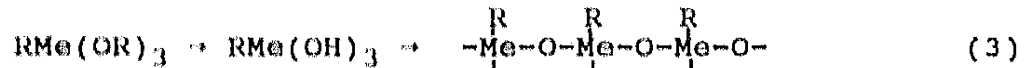

Figure 1. Routes to inorganic organic composites.

ones provides the possibility of controlling the size scale of inorganic and organic domaines in the final product but also to keep them on the liquid-liquid mixing level (molecular or oligomer). Therefore, crosslinking and phase separation mechanisms have to be controlled. The simplest way to prevent separation of inorganic from organic units is to have them attached together by chemical bonds, for example in precursors like substituted alkoxy silanes, with appropriate functional groupings, alkoxides with complex formers or salts of organic acids (figure 2).

≡Me-C≡	Me = Si, Sn, Ge ...	σ bond
≡Me-O-C≡	Me = Si, ...	σ bond
≡Me⁺⁻OCO-C≡	Me = Al, Zr, Ti, ...	ionic bond
≡Me ←L-C-	Me = Al, Zr, Ti, Cu, Pt ...	coordination bond

Figure 2. Chemical links between
organic and inorganic units.

Then, the inorganic crosslinking reaction can take place by
hydrolysis and condensation of the alkoxy group via a typical
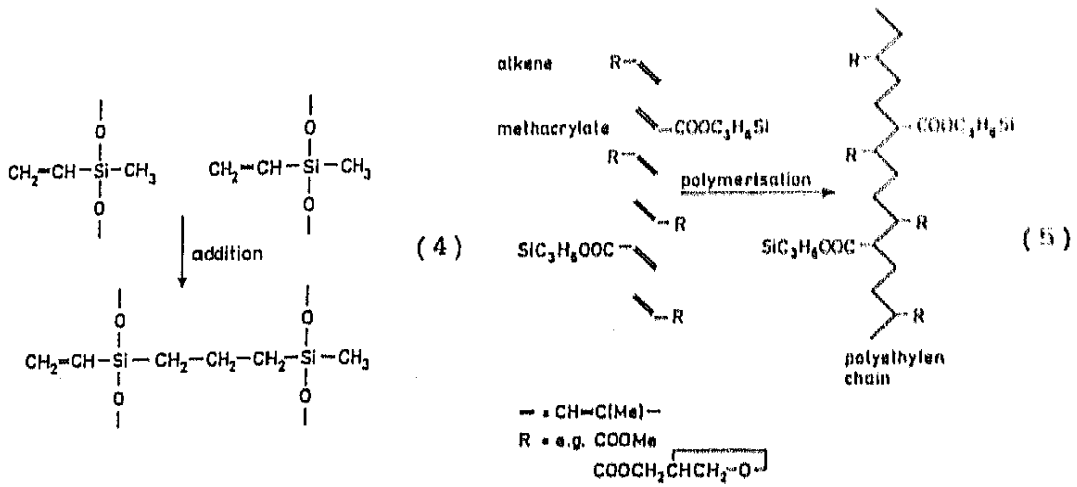sol-gel reaction (equation 3). The properties of the reaction

$$RMe(OR)_3 \rightarrow RMe(OH)_3 \rightarrow \begin{array}{ccc} R & R & R \\ | & | & | \\ -Me-O-Me-O-Me-O- \\ | & | & | \end{array} \qquad (3)$$

product depend strongly on the type and the number of R per in-
organic unit. In silicones, RSi≡ and $R_2Si=$ units are used [3].

The ≡Si-C≡ bond can be used as a general link between the
inorganic and the organic side. For R corresponding to a non-
reactive organic group, a pure organic network modification
results. This principle is used for spin-on glasses [4] which
can be densified at temperatures as low as 200 - 300 °C, com-
pared to 800 - 900 °C of sol-gel silica and applied in thick-
nesses of more than 20 µm. This type of material represents the
group of organically network modified glasses and ceramics.

For R corresponding to a functional organic group, chemical
functions can be introduced into these networks, leading to spe-
cial properties like adsorptive properties [5], reactive sur-
faces to special molecules [6] or sensors [7]. This group repre-
sents the type of organofunctional modified glasses or ceramics.
Functional groups which are able to be polymerized lead to the
additional organic chains within the inorganic network and to
hybrid polymers (inorganic-organic polymers), equation (4). This
principle can be varied by incorporation of organic monomers as
indicated in equation (5).

The construction principles shown above are all character-
ized by a chemical bond between the inorganic network and the
organic group. A lack of this bond leads to two independent or
interpenetrating networks. In opposition to the "chemically
linked" case, the possibility of separation of the "organic"
from the "inorganic" phase exists, leading to a composit type
of material, as indicated in figure 1. Examples, therefore, are
given by Mark and Wilkes [8-9] and [10]. These inorganic-organic
phase separated materials show a drastic change in mechanical
properties compared to the original organic polymer (e. g. in-
crease of tensile strength and modulus of elasticity).

$CH_2=CH-\overset{\overset{\displaystyle O}{|}}{\underset{\underset{\displaystyle O}{|}}{Si}}-CH_3$ $CH_2=CH-\overset{\overset{\displaystyle O}{|}}{\underset{\underset{\displaystyle O}{|}}{Si}}-CH_3$

↓ addition   (4)

$CH_2=CH-\overset{\overset{\displaystyle O}{|}}{\underset{\underset{\displaystyle O}{|}}{Si}}-CH_2-CH_2-CH_2-\overset{\overset{\displaystyle O}{|}}{\underset{\underset{\displaystyle O}{|}}{Si}}-CH_3$

alkene   R~

methacrylate   ~COOC₃H₆Si

R~   polymerisation →

SiC_3H_6OOC ~

~ R

~ R

(5)

SiC_3H_6OOC ~

~ R

~ R

polyethylen chain

~ = CH=C(Me)—
R = e.g. COOMe
COOCH₂CHCH₂—O—

ASPECTS OF PROPERTIES

General aspects

As indicated above, the introduction of organic groupings into an inorganic network leads to structural variations. On the average a decrease of the network connectivity number decreases Tg and increases the thermal expansion coefficient (TCE) α. Figure 3 shows Tg and α as a function of different "organic-inorganic" bonds ≡Me-R (x) per total number of inorganic groupings. There is a clear tendency showing that for these properties x is the dominating parameter.
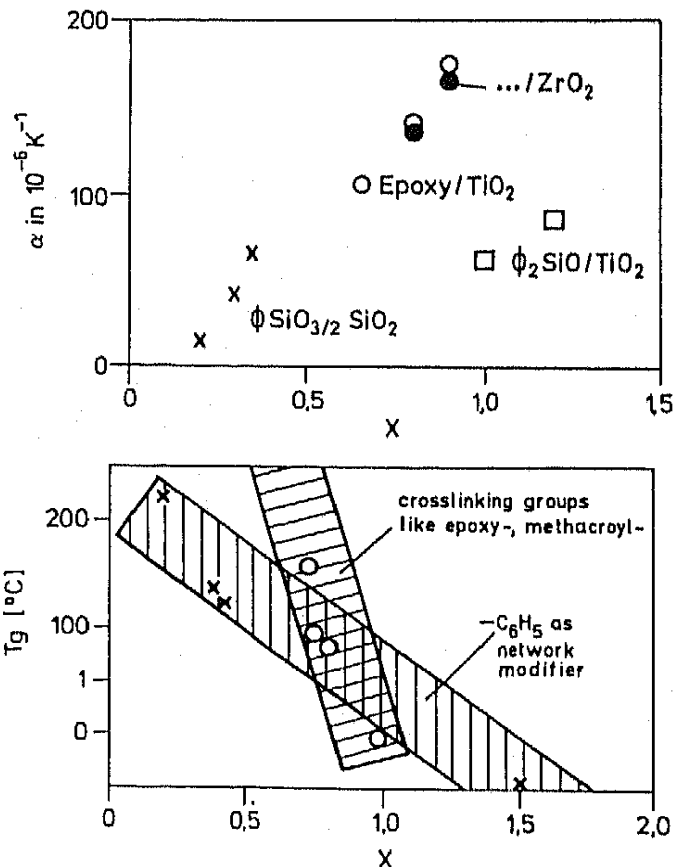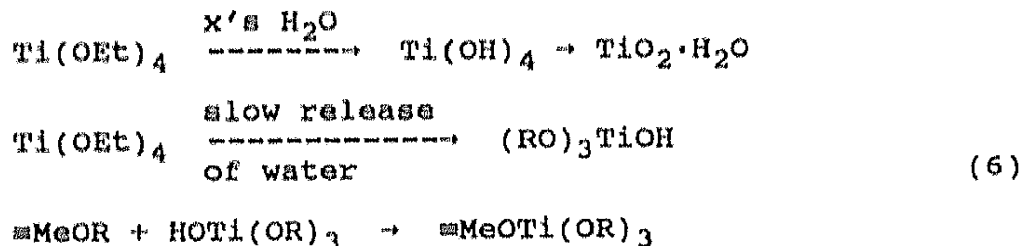

Figure 3. α and Tg depending on x.

$x = \dfrac{\equiv Me-x}{\equiv Me-O-}$

The influence of the type of the organic group does not seem to play the most important role, but a tendency to a steeper slope of the Tg function with increasing concentration of cross-linking organic units (figure 3) is observed; for x = < 0.7 no Tg values could be measured below decomposition, probably due to the increasing immobilization of the organic group within the inorganic network.

The densities (compared to the pure inorganic materials) decrease drastically as a result of the organic modification. As pointed out in [11], the computed densities (between 2 and 3 g/cm^3) differ from the measured ones remarkably which are between 1.35 and 1.65 g/cm^3. This indicates the existence of a free volume similar to organic polymers [12]. In [13] neutron scattering experiments show that the glass transition can be correlated with the chain movement, supporting the hypothesis of a free volume based low density. The investigations were carried out with amino modified SiO_2 condensates.

Homogeneity is an important property if optical applications are of interest. In a single component system without intergranular interfaces optical transparency should be obtained easily. Organic polymers, however, tend to form crystalline phases thus disturbing optical transparency. This can also be induced by ageing, thermal or mechanical stresses and leads to the question of structural stability. Basically, a three-dimensional inorganic network should be stable and no structural rearrangement should be possible after sufficient curing. For the preparation of sol-gel derived multicomponent systems one has to take into consideration phase separation effects based on different rates of reactions of the precursors, e. g. Ti and Si alkoxides. Adaption of rates is limited and cannot successfully be used to enable a simple addition of water to a mixture of $Ti(OEt)_4$ and $(CH_3O)_3Si-CH_2-CH_2-O-CH_2-CH-CH_2-O$ (Si-epoxy): If water is added, TiO_2 precipitates. Controlled release systems for water in order to avoid high concentration, accompanied by heavy stirring leads to a partial hydrolysis of the fast reacting components and to a condensation via the alkoxide substitution (6).

$$Ti(OEt)_4 \xrightarrow{\text{x's } H_2O} Ti(OH)_4 \rightarrow TiO_2 \cdot H_2O$$

$$Ti(OEt)_4 \xrightarrow[\text{of water}]{\text{slow release}} (RO)_3TiOH \qquad (6)$$

$$\equiv MeOR + HOTi(OR)_3 \rightarrow \equiv MeOTi(OR)_3$$

This is in accordance with Livage's electronegativity driven reaction scheme [14]. In a composition (molar ratio) of about 30 $Ti(OEt)_4$, 65 Si-epoxy and 5 $Si(OEt)_4$, the addition of only 1/16 of the total amount of water is necessary to be added by a controlled release process (CCC according to [15] or H_2O doped silica) to prevent precipitation after addition of the full amount. The reaction scheme is shown in figure 4. The hydrolysis rates increase in the order $Si(OEt)_4$ < Si-epoxy < $Ti(OEt)_4$. The preparation leads to a homogeneous liquid with a general structure proposed in figure 4 which can be used for coatings [16].

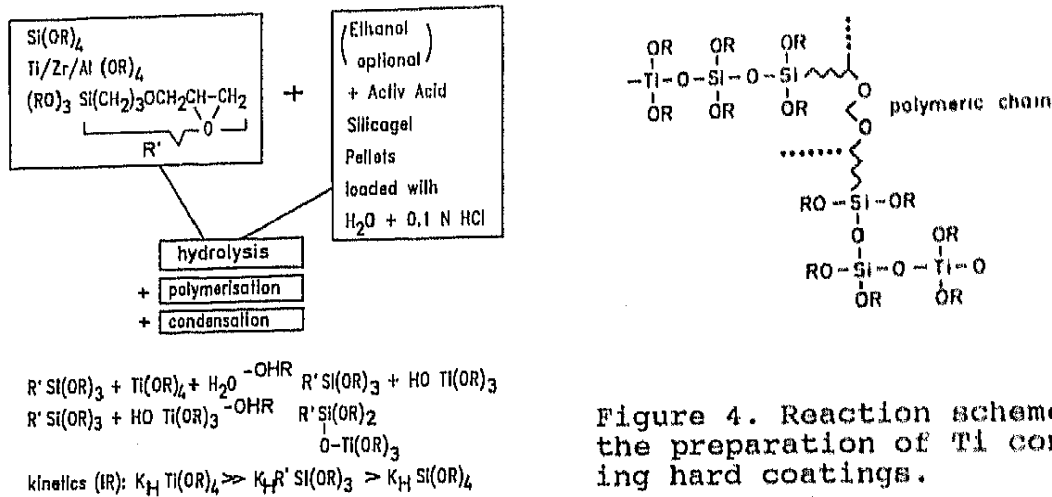The material does not show any phase separation down to 1 nm (resolution of the TEM).

Figure 4. Reaction scheme for the preparation of Ti containing hard coatings.

Similar techniques can be used for combinations with other alkoxides like $Al(OR)_3$, $Zr(OR)_4$ or $Sn(OR)_4$. This demonstrates that homogeneous multicomponent materials can be prepared by an appropriate chemical processing.

Structural properties and aspects

One of the most interesting properties of these groups of compositions is the abrasion resistance if used as coatings [16]. Haze measurements after taber abrader tests show values close to those of float glass surfaces. The moduli of elasticity are between 1 and 7 GPa, that means remarkably lower than those of glass and ceramics. However, the low moduli are an important prerequirement for coating organic polymer surfaces. First, the lower modulus can help to overcome stresses resulting from TCE differences between substrate and coating (high CTE of the coating materials according to figure 3 is helpful, too). Second, for practical use, coating thicknesses for abrasion resistance have to be in the range of ≥ 5 μm, a thickness which can be achieved for densified inorganic sol-gel coatings only by a multiple coating process and which leads to cracks caused by stresses due to the CTE mismatch dependent on the preparation technique. As a consequence, there are no pure inorganic thick protective coatings on soft plastics available. The comparison of the behavior of ORMOCER coatings on ceramic coatings is schematically illustrated in figure 5.

The modulus is very sensitive to the concentration of inorganic units and to the type of inorganic network formers and increases in the order Zr < Ti < Al. The abrasion resistance corresponds to this order. Based on these findings, various scratch resistant systems have been developed, as described in [16-17], for example for CR 39, polycarbonates, PC, PMMA, but also for metals, like brass.
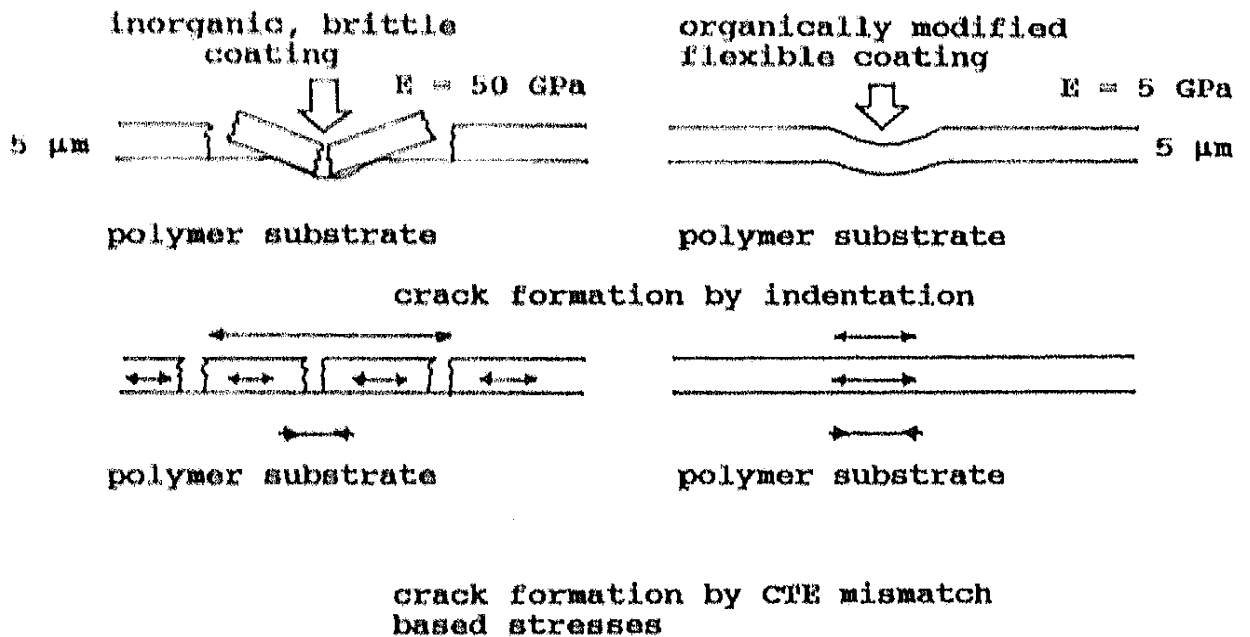
Figure 5. General behaviour of low and high moduli coatings on plastics.

Other mechanical properties like bending strength depend, as expected, very much on the degree of organic crosslinking. In table I, the results of 3-point bending experiments are given.

Table I. 3-point bending experiments on various polymers.

Type	Curing	σ_B(MPa)
A SiO_2/Si-epoxy/ TiO_2	thermal (130 °C)	3
B SiO_2/Si-epoxy Si methacryl/TiO_2*	thermal (130 °C) + photo	4 - 5
C SiO_2/Si-epoxy/Si-methacryl/TiO_2 MMA*	thermal (130 °C) + photo	8 - 9
D SiO_2/$(C_6H_5)_2SiO$/ $CH_3(CH_2=CH)SiO$**	thermal (200 °C) + photo + thermal (130 °C)	30
E ZrO_2 (methacrylic acid (MA) Si-methacryl***	photo + thermal (100 - 150 °C)	80 - 90

* according to [18]   ** according to [2]
*** complexation of $Zr[o-prop]_4$ with methacrylic acid (1:1) and subsequent hydrolysis and condensation by photocuring with Irgacure 184 (Ciba Geigy)
[19]

In composition A the epoxy is reacted to a glycol group that means no organic crosslinking takes place. The materials are brittle, they are cured in polypropylene moulds, the surface quality of which is defining the number and size of surface flaws (influence of flaws on strength has not been investigated). The number of organic crosslinking units increases from A to E, but all materials are brittle with negligible plastic deformation. According to this data, a clear connection between strength and organic crosslinking exists. The first results obtained from methacrylic acid condensates show bending strength values, already suitable for structural applications, even if the systems are not optimized so far.

Another example for property changes is the building up of inorganic networks within already formed organic polymers, for example ethylvinyl acetate copolymer (EVA) according to [10] where the extremely low EVA modulus increases to about 5 GPa by addition of 50 wt.% $Ti(OEt)_4$ to the polymer solution in toluene. Depending on the route of addition of water, phase separated (figure 6a; H_2O is added rapidly via atmosphere) or non-phase separated polymers (figure 6b, H_2O is added via a controlled chemical condensation process [16]; phase separation not visible within the resolution of the instrument = 2 nm).
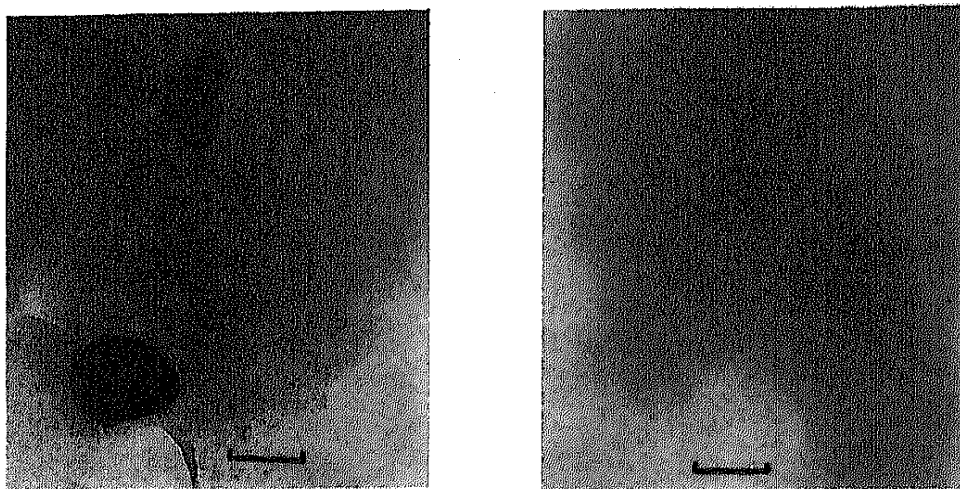

Figure 6a and 6b. TEM of a TiO_2/EVA copolymer. 6a: phase separation about 100 nm; 6b: no phase separation or separation ≤ 2 nm; bar: 100 nm.

Functional properties

Despite the fact that the investigation of structural properties of ORMOCERs (except abrasion resistance) is at its beginning, the question arises whether they can be combined with functional properties. Developments of special functional properties have already been published elsewhere. Table II gives a survey over various developments.

As one can see from these examples, the introduction of functions into ORMOCERs can lead to interesting properties and potentials for applications.

Table II. Development of functional ORMOCERs and corresponding organofunctional groups.

Property	Application	Chemical Function	Reference
hydrophobicity	contact lenses	epoxy to glycol	[18]
reactive surfaces	carrier for enzymes radioimmunoassay	$\sim$NH$_2$, $\sim$COOH	[20]
adsorption of CO$_2$	heat pump	-CH$_3$, $\sim$NH$_2$	[5]
SO$_2$ adsorption	SO$_2$ gas sensor	$\sim$NR$_2$	[7, 21]
mild abrasion	acne ointment	$(CH_3)_2SiO/SiO_2$	[23]
adhesion to glass surfaces	protective coatings on medieval glasses; sealing agent	$(C_6H_5)_2Si\begin{smallmatrix}O^-\\OH\end{smallmatrix}$ $\equiv$SiOR	[24-25]
NIR absorption	solar protection	V^{4+}	[26]
H$^+$ conductivity	solid state electrolytes	$\sim$NH$_3$$^+X^-$	[27-28]
low ϵ, high resistance	dielectric materials	SiO$_2$, hydrocarbons	[29]
low hydrocarbon diffusion	gas tanks	$\equiv$Si-O- -Al$\begin{smallmatrix}O-\\ \end{smallmatrix}$	[29]
micro patterns by photolithography	SMT technologies, laser writing, resists	$\equiv$Si-methacryl $\equiv$Si-vinyl $\equiv$Si-epoxy	[30]
fluorescent coatings	solar collectors	fluorescent organic dyes	[31]
thermoplasticity	hot melts	$(C_6H_5)_2SiO$	[32]
refractive index	optical coatings	Ti, Zr, aryl	[33]

CONCLUSIONS

The combination of functional with structural properties in most cases can be achieved and functions can be transferred to hard coatings. Of special interest is the question, how far these materials are able to play an important role for key technologies. Their ability of being patterned is important for microelectronics or microsystems, especially in combination with other properties like sensor properties, low or high dielectric constants, low H_2O diffusion or temperature stability. Therefore, the knowledge of structure to property relations has to be improved. The high homogeneity shows an interesting potential for optical applications, especially in combination with other functions like dye incorporation. The properties of nanocomposites based on ORMOCERs are hardly investigated up to now despite the possibility to tailor such composites by controlled phase separation.

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