

183

Chapter 15

Sol–Gel-Based Inorganic–Organic Composite Materials

H. Schmidt and H. Krug

Institut für Neue Materialien, Im Stadtwald, Gebäude 43,
66123 Saarbrücken, Germany

The sol-gel process allows the synthesis of inorganic non-metallic materials through a soft chemistry route and organic functions can be incorporated. While maintaining the phase size of the inorganic component on a molecular or nano range, inorganic molecular or nano composites can be fabricated. For this reason techniques that make use of surface interaction controlling ligands for colloidal sol-gel particles have been developed, allowing the inorganic part to be linked chemically to the organic one. Using these principles, new nanocomposites for optical application and for coatings with special properties (anti soiling, corrosion inhibition) have been developed.

Background

The sol-gel-process can be considered as a chemical route for the synthesis of inorganic nonmetallic materials such as glasses or ceramics (1-6). The formation of the inorganic backbone is based on a condensation step including the formation of metal/oxygen/metal bonds. The condensation step can take place at low temperatures, e.g. at the boiling temperature of organic solvents like ethanol. For the formation of densified glasses or sintered ceramics, high temperatures are required (e.g. T_g of glasses) and at these temperatures, in general, organic groupings are oxidized or pyrolyzed. However, as shown elsewhere (7-13) the presence of non-volatile organic groupings, especially if they are linked to the inorganic backbone, leads to an interesting type of materials (inorganic-organic composite ormocers, organically modified ceramics, polycerams or ceramers). Organic groupings can be used for basically three types of structural effects. They can be used for the modification of the inorganic backbone reducing the network connectivity and leading to processing temperatures low enough to fabricate dense materials without distroying the organics, or they can additionally be used for building up a second type of network by polymerizing or polycondensing appropriate organic groupings, or they can be used for achieving special functions (acids, bases, electron donating or accepting functions).

Using this basic principle, a wide variety of possibilities exists for synthesizing new materials. The material properties, of course, should depend strongly on the

structures produced. This includes the type of interaction between the inorganic and the organic components (chemical bonds or physical bonds) and phase size and phase distribution of the inorganic and the organic part. For these reasons it is very important to control the mechanism of the formation of the inorganic part by the sol-gel-process as well as e.g. in case of polymerization reactions, the organic part for the formation of the organic chains or even networks. In this paper some principle possibilities will be discussed, and it will be shown how far these principles can be used for the synthesis of composites with interesting properties for applications.

General Principles

Sol-gel reactions can be characterized by several reaction steps. At first soluble precursors in form of monomers, oligomers or clusters, e.g. in several alkoxides (14) are reacted to active species mostly by addition of water and the subsequent formation of reactive $\equiv\text{MeOH}$ (Me \equiv metal ion) groups. The reactivities depend on the thermodynamic parameters and on the electronegativity of the metal (15-17). The condensation rate of SiOH groups is slow (due to the electronegativity of the Si) compared to most other elements like aluminum, chromium, titanium or others. Spontaneous condensation reaction takes place in these cases started by a nucleation process and a subsequent growth reaction, which is, especially in not too highly concentrated solution, diffusion controlled. In general, the process leads to colloidal sols the particle size of which is dependant on the monomer concentration and the stabilization of the colloidal particles. Stabilization is necessary, otherwise the condensation process continues between the different particles leading to precipitates or gels.

In the case of silicon based compounds, e.g. organoalkoxysilanes the link between the inorganic and organic phase can be obtained by the SiC bond which is a very stable one. This principle, however, cannot be used for other elements since metal carbon bonds in general are not stable under hydrolytic conditions. As shown elsewhere, the use of double bond containing organoalkoxysilanes (methacryloxy or vinyl) leads to inorganic-organic composites on a molecular level, and coatings for various applications have been synthesized (18-20).

In case of titania or alumina the complexation of alkoxides with β -diketones containing polymerizable groupings has been proposed (21). The question arises how far this type of coordinative bond is stable against hydrolysis in synthesized sol-gel materials and how far within the resulting composites a molecular level distribution of inorganics and organics can be maintained. Another possibility for the complexation of alkoxides are carboxylic acids (16). As shown with methacrylic acid, complexes from zirconium alkoxides can be formed easily (22) and as shown further (23), after hydrolysis condensation and polymerization the resulting zirconia methacrylate composites are hydrolytically extremely stable. Using this principle nano scale particles can be formed from zirconia methacrylate systems by controlled hydrolysis and condensation and in combination with methacryloxy silanes they have been reacted to composites (24).

In Figure 1 the WAXS patterns are given for different compositions of this three component system. The scattering maxima correspond to particle sizes of about 2 nm showing that fairly narrow distribution can be established for various compositions. It has to be mentioned that the zirconia methacrylate colloids, having

been formed after hydrolysis and condensation of the complexed alkoxide do not show any shift of the C=O frequency of the carboxy group towards the free acid pointing out that in the colloidal form the complex type of bond is still present (24).

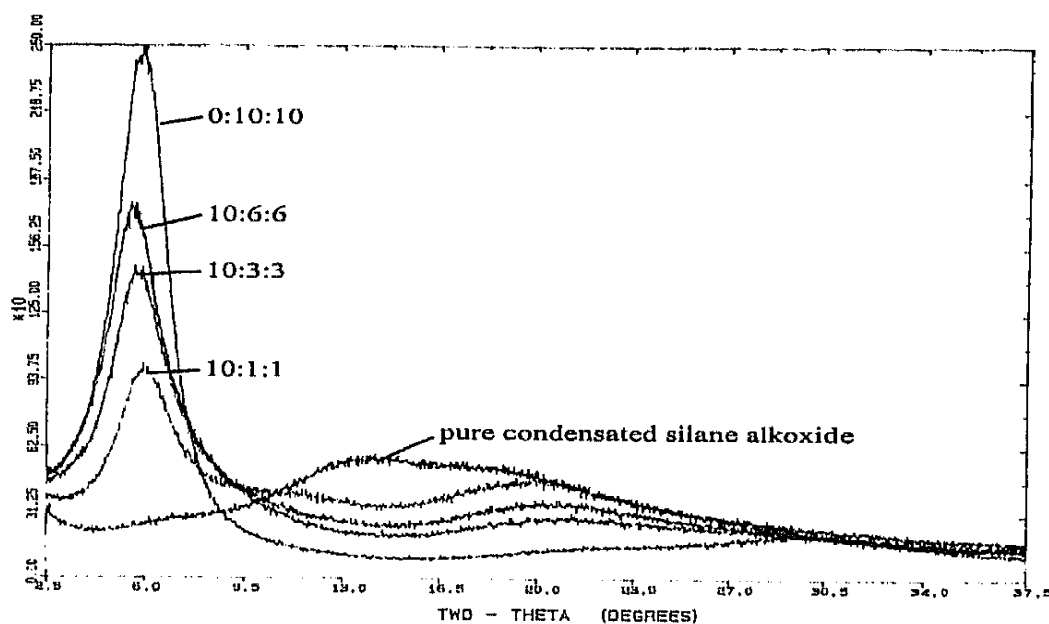


Fig. 1: WAXS-measurements of different composites (I/II/III) of a system alkoxisilane (I), Zr-alkoxide (II) complexed with methacrylic acid (III)

Similar results have been obtained from alumina with propionic acid (25, 26) even if commercially available boehmite with a particle size of 15 nm is used as starting material. Refluxing the boehmite for several hours in alcoholic solution with excess of propionic acid leads to a boehmite propionic acid surface compound which is hydrolytically stable and can be used as a stabilizer leading to sols with surprisingly high solid content (up to 40% by volume) without gelation. This type of surface modified boehmite has been incorporated into coatings for obtaining very high abrasion resistance (R. Kasemann, E. Wintrich, Institut für Neue Mat., 1993, priv. communication).

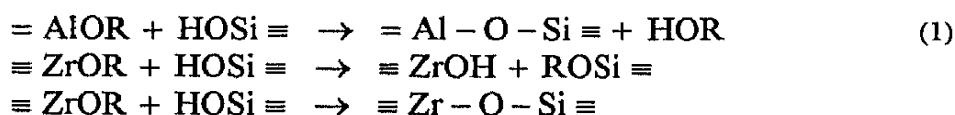
These examples show that colloidal systems produced by the sol-gel process can be surface modified by organics and to obtain a new type precursors with organic functions for further processing.

If the modifying agents are bifunctional, the newly created colloidal particles surface as in the case of zirconia, can be used for obtaining specifically designed properties, e.g. polymerizable particles to be incorporated into organic polymers or ormocers. This principle has been used for the modification of a variety of different sol-gel-derived or precipitated particles, even for metal colloids (27) or semiconductor quantum dots (28). The new type of „colloidal“ precursors are interesting candidates to synthesize new inorganic-organic nanocomposites where the ceramic, semiconductor or metal colloid provides special functions (e.g. mechanical, optical or electrical).

For material synthesis, hydrolysis and condensation as well as polymerization have to be controlled. For the control of hydrolysis and condensation, especially if

silanols are used, ^{29}Si -NMR spectroscopy in combination with the determination of water content are interesting methods. In the composition shown in figure 1 this method has been used to monitor the state of hydrolysis and condensation of methacryloxy or epoxy group containing silanols for controlling the water and silanol content of the system to avoid precipitation of highly reactive alkoxides of other elements. If precipitation from alkoxides of zirconia titania or alumina has to be avoided it is necessary to incorporate the hydrolysed species as fast as possible into a sol-gel network before nucleation and particle growth can take place.

For this reason, water required for hydrolysis has to be added in a very homogeneous or latent form. The problem can be solved in an elegant way by using silanols instead of molecular water. In this case, a cocondensation reaction between the silanol and the heteroalkoxide or a ligand exchange can take place, as shown in equation 1.



Whereas the formation of an $=\text{Al}-\text{O}-\text{Si}\equiv$ bond is very likely, and $\text{Si}-\text{Al}$ heteroesters (e.g. available from Dynamit Nobel chemical company) can be formed, in the case of zirconia, the formation of the corresponding bond could not be proved definitely. But it is well known that zirconia alkoxides or hydroxides are catalysts for the network condensation of silanes with a potential to immobilize the zirconia within the network to be formed on the level of very small particles or to maintain the colloidal distribution without further aggregation. This leads to a very specific strategy for the sol-gel reaction if alkoxy silanes are suitable for the formation of composites: at the point of the addition of the highly reactive alkoxide, the free H_2O content of the system should be as low as possible but should be present in the latent form as SiOH groups in concentrations as high as possible. In order to optimize the silanol group content, the hydrolysis and condensation reaction of methacryloxy group containing silanes (MTPS) has been monitored by Karl-Fischer titration and ^{29}Si -NMR spectroscopy. In Figure 2, the water balance of this system and the silanol concentration development are shown.

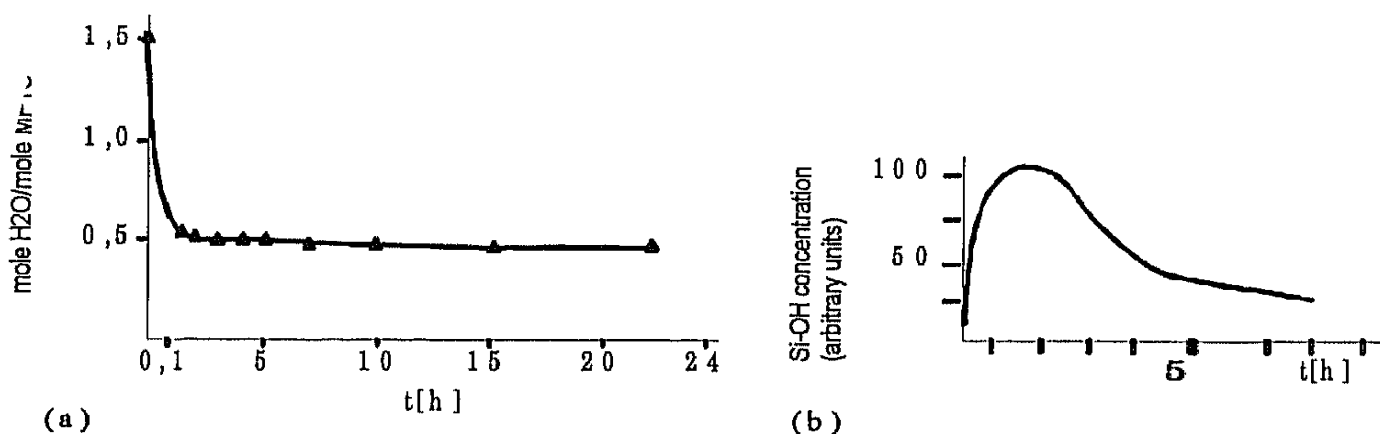
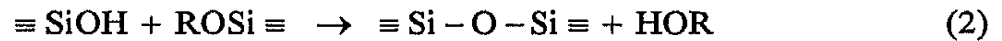


Fig. 2: H_2O and SiOH concentration in the hydrolysis reaction of MTPS-silane as a function of time in the hydrolysis reaction. (a): water content by Karl-Fischer; (b): SiOH by ^{29}Si -NMR.

As one can see, the water content decreases very rapidly at the beginning of the reaction and then stays almost constant, whereas the silanol concentration shows a maximum and then decreases slowly. The silanol concentration decrease even continues in the regime where the water concentration remains constant, which has to be attributed to the condensation reaction shown in equation 2.



For the addition of fast-reacting alkoxides, the regime with the lowest possible water content and the highest possible silanol content is desirable. As shown elsewhere (27) by using this principle, rather high concentrations of zirconia (up to 50 mole %) can be added to the prereacted silane without precipitation, and a wide variety of compositions becomes possible (Wilhelm, R., Ph. D. Thesis, INM, Saarbrücken, 1994, in print).

ZrO₂ containing composites are of interest for tailoring the refractive index for optical applications, e.g. waveguides. Another interesting feature is mechanical properties resulting from colloidal zirconia material particles which leads to mechanical surface properties not obtainable by pure polymers.

Whereas the sol-gel reaction can be considered to be the first part of the inorganic-organic composite synthesis, the second part of the synthesis reactions consists of the polymerization of double bonds, if an additional organic backbone has to be built up. Since the formation of the inorganic backbone, for example in the case of zirconia, is supposed to exist in form of a colloidal network interpenetrated by a siloxane network. If methacrylic acid complexes are used, a rather complex structure of the unpolymerized system should be present, characterized by entangling methacryloxy groups linked to the silane and methacrylic acid groups linked to the zirconia. A model is shown in figure 3.

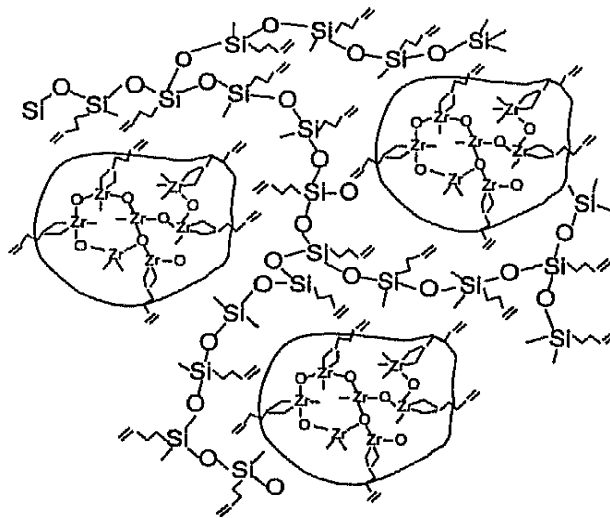


Fig. 3: Model for a colloidal organic-inorganic network interpenetrated by a siloxane network

The question arises how far it is possible to obtain conversion rates high enough to result in stable materials from these systems. For this reason, investigations

have been carried out to define the degree of conversion as a function of reaction conditions and temperature.

In case of radical chain polymerization, the conversion behavior is characterized by three different stages of the polymerization process. In an initial stage, conversion is inhibited by oxygen absorbed in the material. A second period of constant reaction rate for the radical formation follows. C-C bonds are generated and polymerization takes place up to the so called gel point. At the gel point, the radicals lose their high mobility as the medium gets highly viscous and the diffusion controlled conversion process slows down. The conversion rate after the gel point is only controlled by the diffusion rate of the remaining small radicals and reactive groupings. The effect of the gel-point, which can also be compared to the glass transition in pure organic systems, can be reduced by increasing the temperature, and conversion and degree of polymerization can be shifted to high values during the polymerization process. This conversion of the C=C double bonds of up to 90 % can be obtained by a temperature treatment during photopolymerization in ZrO_2 /methacrylic acid/methacryloxy silane systems, as shown in Figure. 4

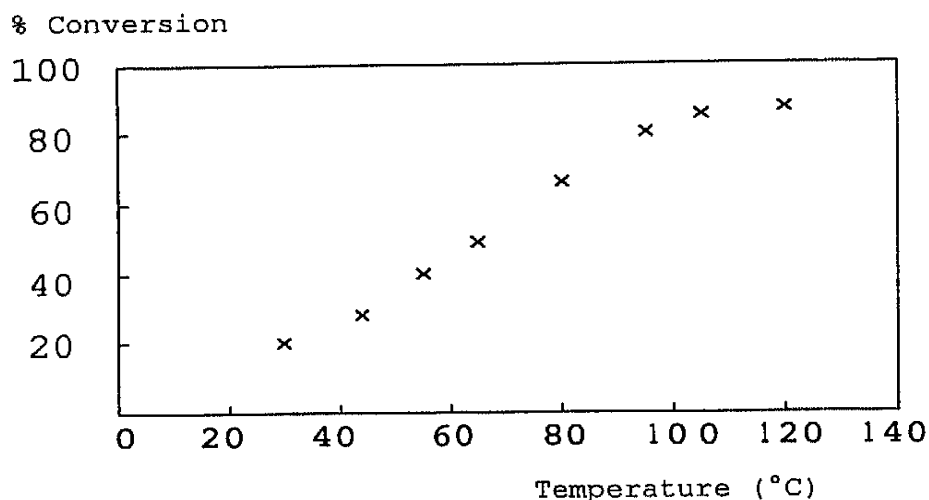


Fig. 4: Degree of conversion of C=C double bonds in dependance of temperature in the system ZrO_2 /methacrylic acid/methacryloxy silane 1/1/10 mole.%.

The results given in Figure 4 show that, at higher temperatures, surprisingly high conversion rates are possible in a system which was expected to be extremely inflexible from the three-dimensional inorganic crosslinking. Furthermore, it means that the diffusion rates of the double bond-containing units are rather high and should be in the range of monomers in organic systems during photopolymerization. In order to investigate the diffusion coefficients, an optical method was developed (29). The method is based on the generation of local polymerization areas in order to decrease monomer concentration by polymerization within these areas. This should enhance diffusion of non-polymerized monomers into these spots. If the polymerized areas exhibit a diffraction index different from that of the unpolymerized areas (which should be very likely in case that the polymerizable groupings are linked to zirconia), the increase of the diffractive index with time can be used as a parameter for determining the diffusion rate. In the case of photopolymerization, a diffractive

grating can be created by irradiating an area with a light beam the intensity of which is modulated by two wave mixing interference. The developing diffraction pattern can be visualized and the diffraction efficiency as a measure for the refractive index has been monitored as a function of time. The result of such a two-wave mixing experiment, which is also known as Forced Rayleigh scattering (FRS), is shown in Figure 5.

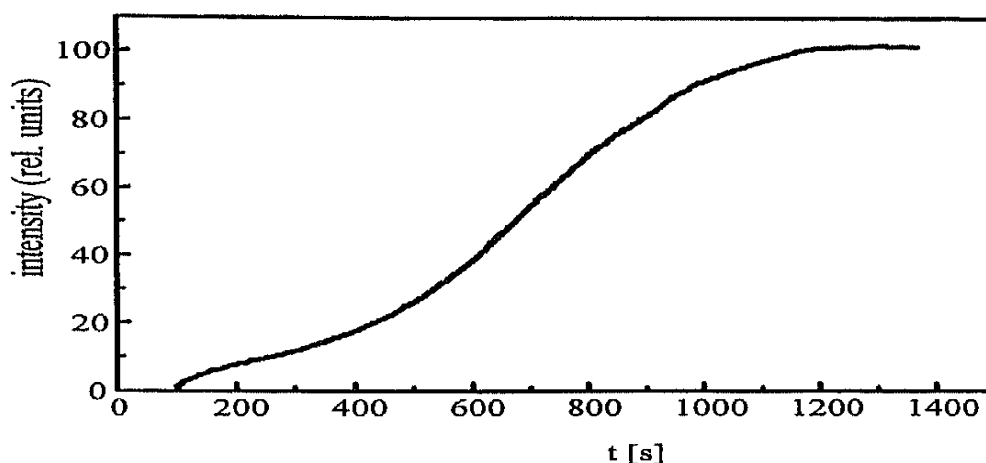


Fig. 5: Typical diffraction efficiency read in real time by FRS, system: ZrO₂/methacrylic acid/methacryloxy silane 1/1/10 mole.% (Oliveira, P., private communication, INM, 1993).

From the time dependant changes of the diffracted intensity $I(t)$ in the radical formation and conversion region (equation 4)

$$I(t) = \left(A + B \exp\left(-\frac{t}{\tau}\right) \right)^2 + C \quad (4)$$

where A and C are coherent and incoherent scattering backgrounds and B is a contrast factor, the characteristic relaxation time τ of the process can be calculated. This relaxation time is directly correlated to a Diffusion coefficient D (equation 5)

$$\tau^{-1} = 4\pi^2 D / \Lambda^2 \quad (5)$$

For a known grating period Λ of the diffraction grating, the diffusion coefficient D can be calculated and if the relaxing species has diffusive character, the diffusion coefficient will show an Arrhenius behavior of the form (equation 6)

$$\ln D = \ln D_0 - E_A / kT \quad (6)$$

and the activation energy E_A can be calculated. Figure 6 shows the experimental results of temperature dependant diffusion coefficients. For the described experiments, an activation energy of 29 kJ/mole is determined, which is typical for side chain relaxations of organic polymer systems (the diffusion coefficient calculated from equation 5 is in the order of magnitude of about $10^{-7} - 10^{-9} \text{ cm}^2 \text{ sec}^{-1}$ for the temperature range of 25-100 °C).

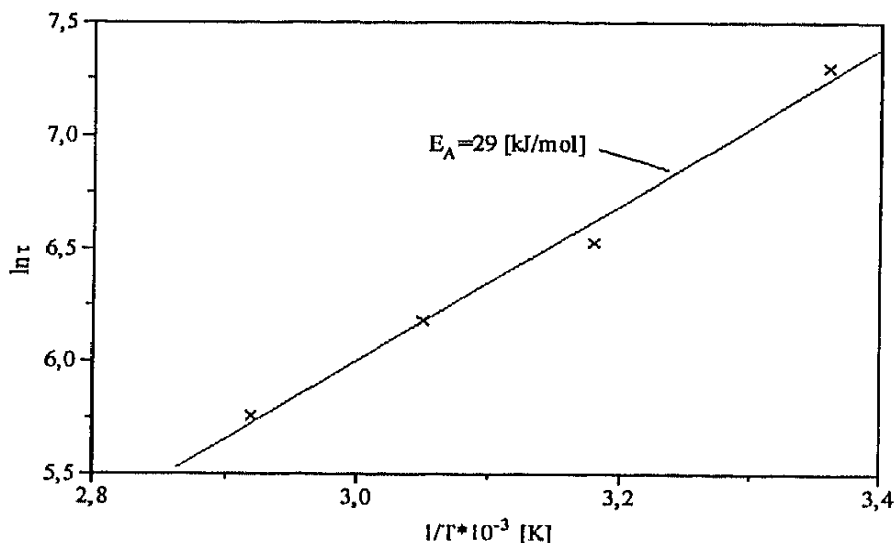


Fig. 6: Arrhenius plot of temperature dependant relaxation times in the system ZrO_2 /methacrylic acid/methacryloxy silane 1/1/10 mole. %.

These experiments show that it is possible to synthesize inorganic-organic nanocomposites by appropriate control of the sol-gel process in combination with photopolymerization. It has to be mentioned that this type of composites, due to the control of phase separation, which is in the lower nanometer range, shows excellent optical properties with respect to transparency and optical loss in the visible region.

Fabrication of Optical Waveguides. Direct laser writing (Figure 7) allows a locally well defined polymerization by a focused laser beam. By using a x-y stage as a sample holder, the experiment is very flexible and complex pattern can be prepared. After a development step, in which the unpolymerized material is removed by alcohol, a three dimensional structure is obtained. As can be seen from Figure 7, also rectangular waveguide pattern can be obtained if laser intensity and moving velocity of the x-y stage are correctly adjusted.

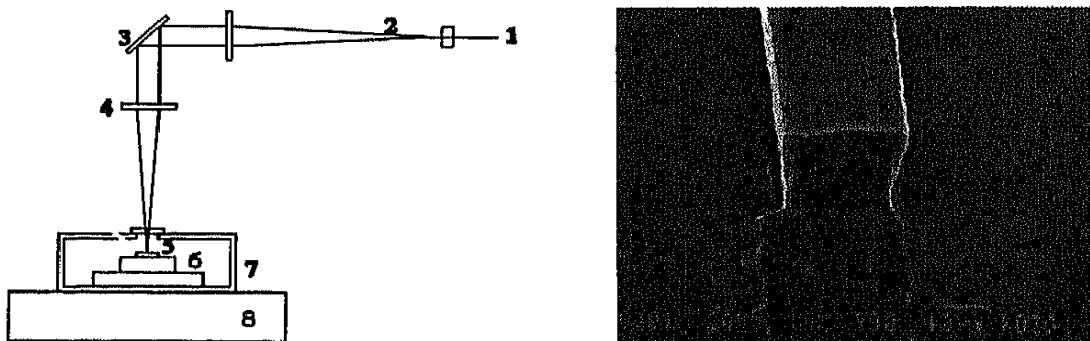


Fig. 7: Scheme of the direct laser writing experiment and SEM micograph a written waveguide after development. (1: laser beam, 2: beam expander, 3: mirror, 4: lens, 5: sample, 6: x-y stage, 7: closed chamber, 8: optical table).

Fabrication of Microlenses by Holographic Interference. The interference pattern of an object wave with a spheric and a planar wavefront results in concentric rings of maximum intensity. The sinusoidal form of this interference pattern leads to local changes of the degree of polymerisation of the same periodicity. After a development step, surface modulations are generated which act for inducing light as a Fresnel zone plate. The principal experimental setup and a patterned Fresnel lens is shown in Figure 8. The theoretical maximum diffraction efficiency of such Fresnel lens is about 34 %. The Fresnel lens by the described process shows a maximum diffraction efficiency of 29 % of the first order focus which is not far from the theoretical one.

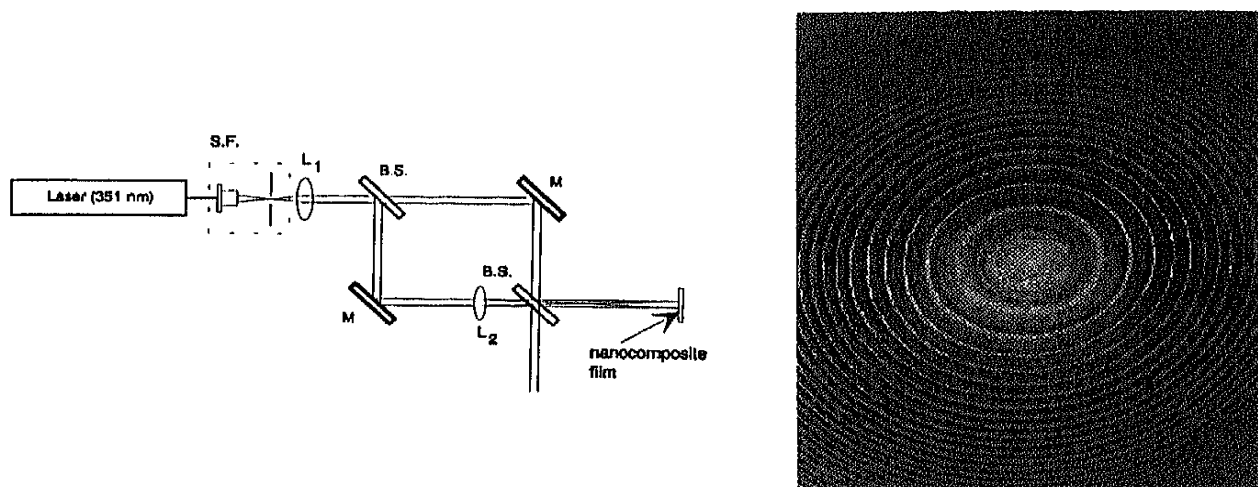
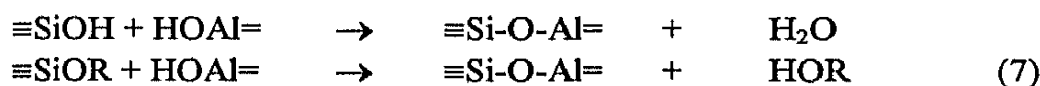
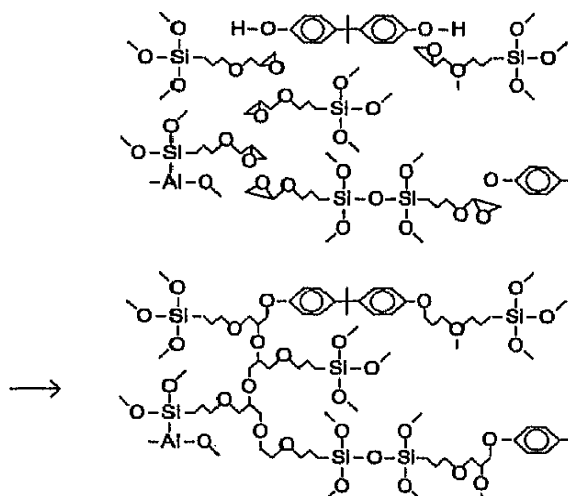


Fig. 8: Experimental setup for the fabrication of Fresnel lenses (L1,2:lens, M: mirror, BS: beam-splitter, SF: spatial filter) and developed Fresnel lens produced by this holographic interference technique (Oliveira, P., INM, 1993, private communication).

Protective Coatings. Corrosion protection of metals in most cases requires specially tailored interfaces. In the case of aluminum surface, the use of reactive silanes should lead to an interface characterized by the formation of chemical bonds. In the presence of wet atmosphere, Al-hydroxides are formed on the surface and SiOH and SiOR containing coating solutions should form a stable bond to the AlOH covered surfaces following equation 7



The cleavage of the Si-O-Al bonds as the reverse reaction should destroy the protective effect. For this reason, the immobilization of the silanes by organic crosslinking, as shown in (30), can prevent the interfacial degradation. In the present example, (a system based on an epoxy group containing silane, Si(OR)₄ and Al(OR)₃), the epoxy groupings have been crosslinked with bisphenoles, as shown in equation 8. The experimental details are shown in (30). The immobilized SiO-Al grouping should prevent the progress of the interfacial corrosion process and lead to stable interfaces.



(8)

Applied to Al surfaces, dense coatings having a very efficient corrosion protection are obtained. Figure 9 shows two Al plates after a 14 days salt spraying test. Before starting the test, a cross cut was carried out on the coated specimen in order to test whether underpinning takes place. The results show that no underpinning takes place.

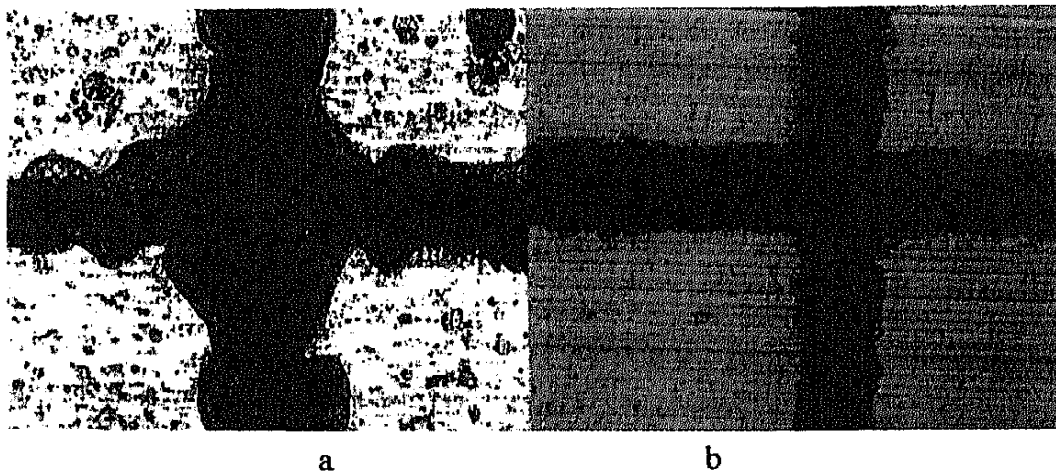


Fig. 9: Comparison of a conventional epoxy layer coated (a) and composite coated (b) Al plate after the salt spray test. Cross cuts show no corrosion along the interface and on the coated areas in the composite coated section.

The experiments demonstrate the high protection effect of the stable interface, especially since this type of coatings does not prevent the penetration of water molecules to the interface. If a corrosion reaction leads to the formation of aluminum hydroxides, as a stable solid phase, the reaction should, based on the rules of the mass balance law, continue in one direction. This is obviously not the case, so it has to be concluded that the reaction products, e.g aluminum hydroxide and silanols, cannot be removed from their "molecular" location, and the reaction stops at an equilibrium, representing an overall stable interface. The immobilization takes place by fixing the silane through the organic network. Colloidal Al_2O_3 particles have been

introduced into the coating system using Al alkoxides to obtain high scratch-resistance additionally.

Low Surface-Free Energy Coatings. The state of an interface or surface always tends to achieve the lowest free enthalpy value. This has been used to tailor the interface and the surface of a coating from multicomponent systems with components with assigned special functions to combine good adhesion, high transparency, high scratch resistance and low surface free energy as known from PTFE in one and the same system. For this reason liquid mixture containing components with silanol and SiOR groups of nano-scale particles from methacrylic acid complexed zirconia, silanes carrying perfluorinated carbon chains was used: if this sol is getting in contact with a polar surface as shows schematically in Figure 10 it can be expected that, thermodynamically driven, the polar groups (assumed that a sufficient diffusability is provided by the liquid phase) turn to a polar surface providing a good adhesion, and the perfluorinated groups turn to the atmosphere minimizing their surface-free energy and that the ZrO_2 /methacrylic acid particles remain distributed in the system randomly to be immobilized by subsequent polymerization.

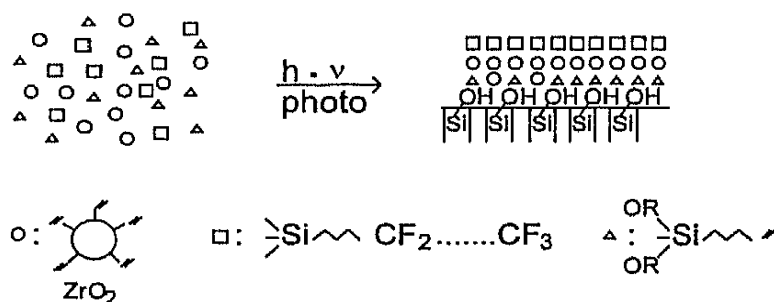


Fig. 10: Scheme of an organic-inorganic nanocomposite with polymerizable organic groupings

Experiments carried out with this type of systems (31) could prove that it is possible to obtain transparent coatings which are very scratch-resistant (zirconia colloids) with surface-free energy as low as 19 mJ/m^2 , which is even below the surface free energy of polytetrafluoroethylene. The coatings can be prepared with high transparency so that they can even be used on transparent plastics or glasses, not disturbing the light transmission. As proven by ESCA measurements, the concentration of perfluorinated groupings in the surface layer is by the factor of 7 to 10 higher in the surface layer than in the bulk. The low surface-free energy (due to the surface concentration effect) can be obtained with concentrations of the fluorinated silane as low as one mole-%. The coatings can be photocured or even thermally cured at higher temperatures and are used as anti-soiling coatings on glasses and a variety of other substrates.

Conclusion

The investigations show that, using very specific features of sol-gel and colloidal chemistry in combination with organic polymerization chemistry, it is possible to develop inorganic-organic nanocomposites with interesting properties for application.

It also has been shown that the control of the reaction is a key to the material property tailoring. It is of special interest that even with colloids very stable links between inorganic and organic phases can be provided, thus preventing agglomeration of colloidal particles, which is an indispensable requirement for using these nanocomposites for optical applications.

Literature Cited

1. „*Chemical Processing of Advanced Materials*“, Hench, L. L., West J.K. Ed.; Wiley John, New York (1992)
2. „*The Physics and Chemistry of Sol-Gel Processing*“, Scherer G.W., Brinker C.J. Ed.; Academic Press, New York Boston 1990
3. „*Sol-gel technology for thin film, fibers, preforms electronics and speciality shypes*“, Klein L. Ed., Noyes Publications, Park Ridge, New Jersey, 1988
4. „*Sol-Gel Optics I*“, Mackenzie J.D., Ulrich D.R., Ed.; Proc. SPIE 1328, Washington (1990)
5. „*Sol-Gel Optics II*“, Mackenzie J.D. Ed.; Proc. SPIE 1758, Washington (1992)
6. „*Chemistry, Spectroscopy and Application of Sol-Gel Glasses*“, Reisfeld R., Jorgensen C.K., Ed.; Springer-Verlag, Berlin (1992)
7. Uhlmann D.R., Boulton J.M., Toewee G.: SPIE 1328 (1990), 270
8. Novak B.M., Davies C.: *Macromolecules*, 24, (1991), 5481
9. Huang H.H., Orlor B., Wilker G.L.: *Macromolecules*, 20, (1987), 1322
10. Mackenzie J.D., Chung Y.J., Hu J.: *J. Non-Cryst. Solids*, 147, (1992), 271
11. Schmidt H.: *MRS Proc.*, 171, (1990), 3
12. Schmidt H. in: „*Ultrastructure Processing of Advanced Materials*“, Uhlmann D.R., Ulrich D.R., Eds.; John Wiley & Sons (1992), 409
13. Schmidt H., Wolter H.: *J. Non-Cryst. Solids*, 121, (1990), 428
14. Menrotra R.C., Bohra R., Gaur D.P.: „*Metal β -diketonates and Allied Derivated*“ Academic Press, London, (1978)
15. Sanchez C., Ribot F., Doeuff S.: In: „*Inorganic and Organometallic Polymers with Special Properties*“, Laine R.M., Ed.; Nato, ASI series, Kluwer Academic Pub., 206, (1992), 267
16. Bradley D.C., Mekrotra R.G., Gaur D.P., „*Metal Alkoxides*“, Academic Press, London, (1978)
17. Zelinski B.J.J., Uhlmann D.R.: *J. Phys. Chem. Solids*, 45, (1984), 1069
18. Schmidt H., Seiferling B., Phillip G., Deichmann KI., in „*Ultrastructure Processing of Advanced Ceramics*“, Mackenzie J. D., Ulrich D. R. Ulrich, Eds.; John Wiley & Sons, New-York, (1988), 651
19. Phillip G., Schmidt H., *J. Non-Cryst. Solids* 63, (1984), 283
20. Schmidt H., *DVS Berichte* 10, (1988), 54
21. Sanchez, C. in „*Proceedings on „First European Workshop on Hybrid Organic-Inorganic Materials*“, Bierville (France), (1993), 9
22. Popall M., Meyer H., Schmidt H., Schulz J.: *MRS Symp. Proc.* 180, (1990), 995
23. Schmidt H., Krug H., Kasemann R., Tiefensee F.: *SPIE Vol. 1590*, (1991), 36
24. Krug H., Tiefensee F., Oliveira P.W., Schmidt H.: *SPIE Vol. 1758* (1992), 448
25. Schmidt H., Nass R., Aslan M., Schmitt K.-P., Benthien T., Albayrak S., *Journal de Physique IV*, (1993), 1251