

Heteropolysiloxanes by Sol-Gel Techniques: Composite Materials with Interesting Properties

Helmut K. Schmidt

Institut für Neue Materialien gem. GmbH

Im Stadtwald, Geb. 43 A, D-66123 Saarbrücken, Germany

1 Introduction

Chemical synthesis methods are not only used for the synthesis of chemical compounds, but also for materials. Examples are silicones, polymers, adhesives and ceramic powders [1]. But if one compares the potential of chemical synthesis with the number of materials produced by these routes, one has to say that the potential of chemical synthesis is only used to an extremely small extent. The focus of chemical research still is mainly directed to "new chemistry", generating new compounds. So far, sol-gel chemistry as an interesting route for material synthesis never has come to a real breakthrough in application and even is rarely used in silicon chemistry, although a large methodical overlap exists [2, 3].

The modification of silicon-type polymers by hetero atoms, for example, titanium, has been investigated by Adrian [4], but the expected increase in thermal stability could not be realized. Swelling of silicones with titanium alkoxides or silanes, as carried out by Mark [5], showed interesting effects on the mechanical properties of these systems, but did not lead to industrial materials. The use of siloxane precursors in sol-gel techniques has led to the concept of inorganic-organic composites with a variety of interesting material developments [6–13]. The basic principles of these synthesis routes are the use of alkoxy silanes together with alkoxides or colloidal systems from oxides of other elements and the formation of inorganic molecular composite networks. An interesting feature in this connection is the question of the phase dimension of these composites.

Whilst in silicones the "inorganic" and "organic" phases are present within one molecule (intramolecular composite), the ormocer type of composite as described in [7, 8, 14] can be considered as a molecular level type of composite (intermolecular inorganic-organic composite). However, in this type of composite, the inorganic unit is not present as an inorganic phase, i. e., it does not maintain properties related to the inorganic solid state. The main function of the inorganic phases in the intramolecular

composite is to act as a network modifier, introducing hardness or stiffness into the system, and several interesting properties resulting from these structural functions have been developed, such as hard coatings for plastics [14, 15]. It has been shown recently [16] that by controlling the synthesis parameters, it is possible to tailor the phase dimensions of the inorganic phase in a way that nanosized phases can be obtained and that this principle can be employed to obtain nanoscale metal, semiconductor and ceramic phases.

This leads to another interesting material development principle. In the present paper, several molecular composites as well as nanocomposites are presented and synthesis routes and properties will be discussed.

2 General Considerations

If one considers so-called molecular composites, one can distinguish between three basic types. As schematically indicated in Fig. 1, systems with inorganic backbones and organic groups directly linked to it, for example by covalent ($\equiv\text{Si}-\text{C}\equiv$) or chelate bonds, organic molecules dispersed in the inorganic backbone, for example, organic dyes dispersed in gels [17–19] or structures in which organic crosslinking units fixed to the inorganic backbone are present. It makes sense that the chemical nature of the link between the inorganic and the organic unit are of high importance for structure as well as for properties.

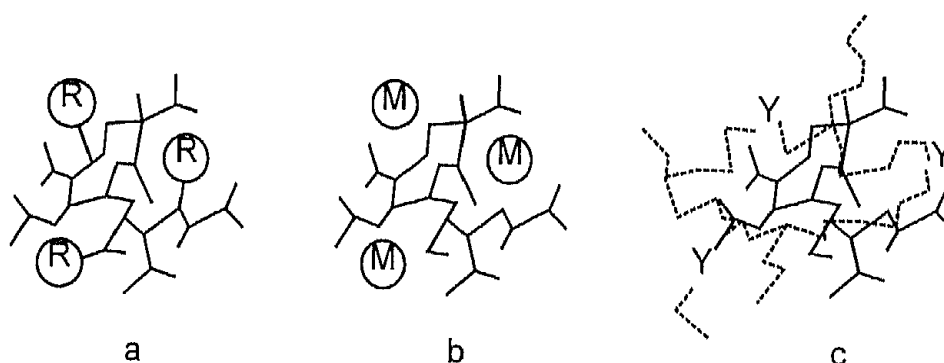


Fig. 1. Model of different types of inorganic-organic composites:

- a) organic groups modifying the inorganic backbone (R = organic or organofunctional groups like alkyls, aryl, acids, bases and others)
- b) organic molecules dispersed in inorganic networks (M = dyes, acids, bases, complexes and others)
- c) inorganic-organic composite with interpenetrating networks (Y = chemical link between the inorganic and organic backbone, for example chelates or covalent bonds); *broken line*: organic chains; *full line*: inorganic backbone)

In Fig. 2 some examples for chemical links between inorganic and organic groups are given. As one can see, there is a variety of possibilities, which, of course, could be extended.

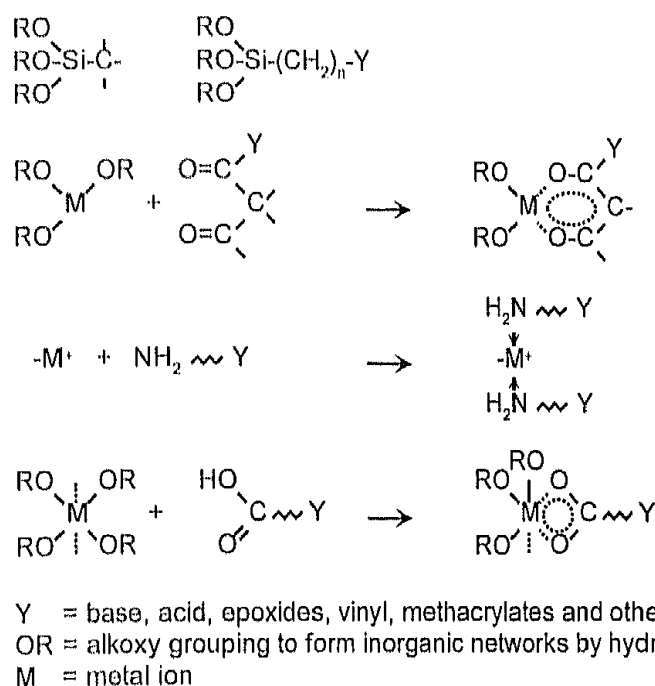


Fig. 2. Some examples for chemical links between inorganic and organic units

The given examples are well-known from chemistry, [1, 20] they are well investigated, but not used as principal routes for material synthesis. In the following, some examples are given how these principles can be used for making materials.

3 Composites

3.1 Molecular Composites

3.1.1 Transparent Coatings with a Tailored Index of Refraction

One of the advantages of the molecular type of composite is the high optical transparency of these materials. For this reason, they have been successfully applied as hard coatings for eye glass lenses from CR³⁹ as polymeric material [21]. Hard coating systems have been prepared from epoxy group containing silanes together with titanium alkoxide, leading to a refractive index between 1.52 and 1.55, depending on the amount of titania added to the system. The titania acts as a condensation catalyst, leading to a very dense, hard network, but can cause damage by UV light on extensive exposure due to its photocatalytic activity. Substitution of titania by alumina, which has been described elsewhere [22], leads to a coating

system with similar mechanical properties and, if aluminum oxide nanoparticles are added, to properties superior to the cited system. However, the index of refraction is decreased substantially, which leads to problems due to interference if used as a hard coating for polymer substrates with a higher index of refraction, for example, 1.6, which is at present introduced into the market. For this reason, investigations have been carried out, the experimental details of which are described elsewhere [23]. The basic idea of the system to be developed was to use epoxy silanes as a basic network-forming unit and to substitute TiO_2 as a high refractive index component by organic groups such as phenyl or sulfide groups. In Fig. 3 the basic function of the used epoxy silane is shown. It can be polymerized by base catalysis to form a polyethylene oxide network. In addition to this, the alkoxide groups can be used for the formation of the inorganic backbone. Moreover, the epoxide group can also react with activated OH groups, for example, with phenols. If these phenols are used, an additional type of crosslinking between the epoxide units can be carried out.

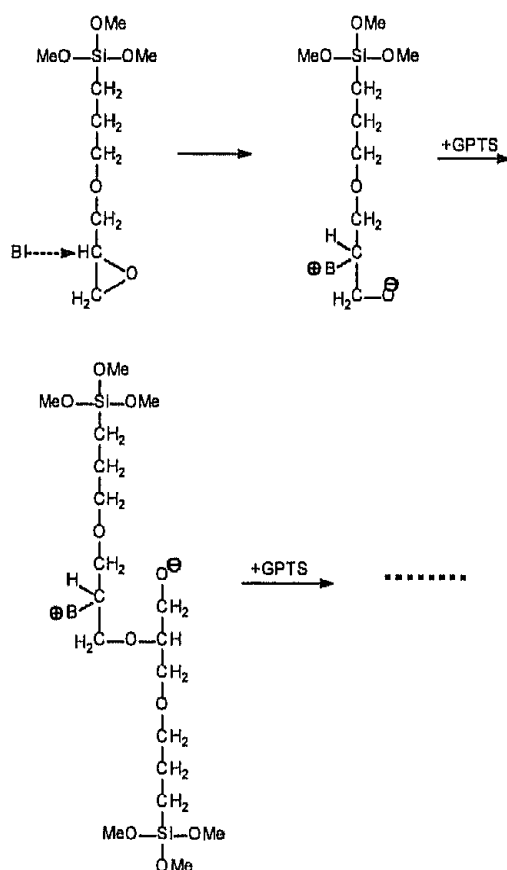


Fig. 3. Basic reaction of glycidyloxypropyl-trimethoxysilane (GPTS) to form polyethylene oxide chains

In this case, also bases like methyl imidazole can be used. In Fig. 4 a structural model of the reaction of GPTS with bisphenol A to form an inorganic-organic composite structure is shown.

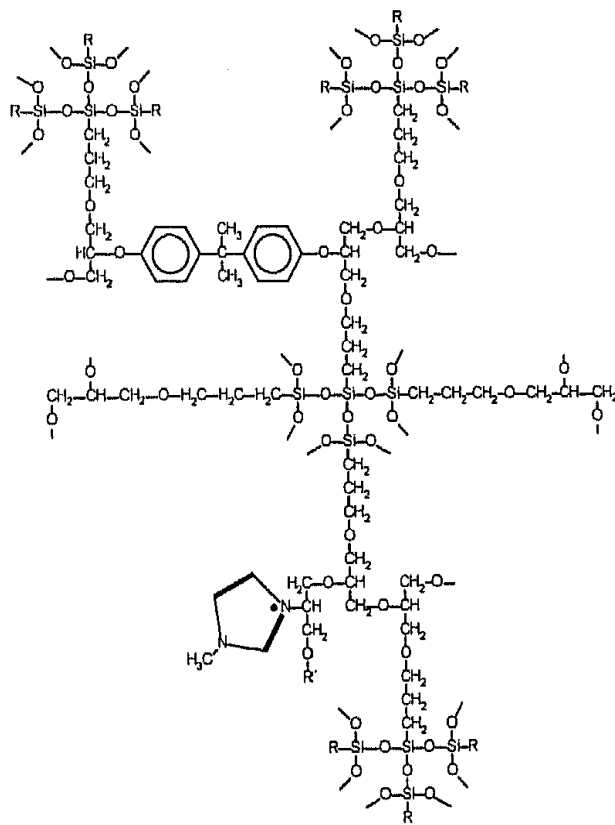


Fig. 4. Model of a structure of a composite formed from GPTS bisphenol A and using methyl imidazole as a catalyst; R = glycidyloxypropyl group

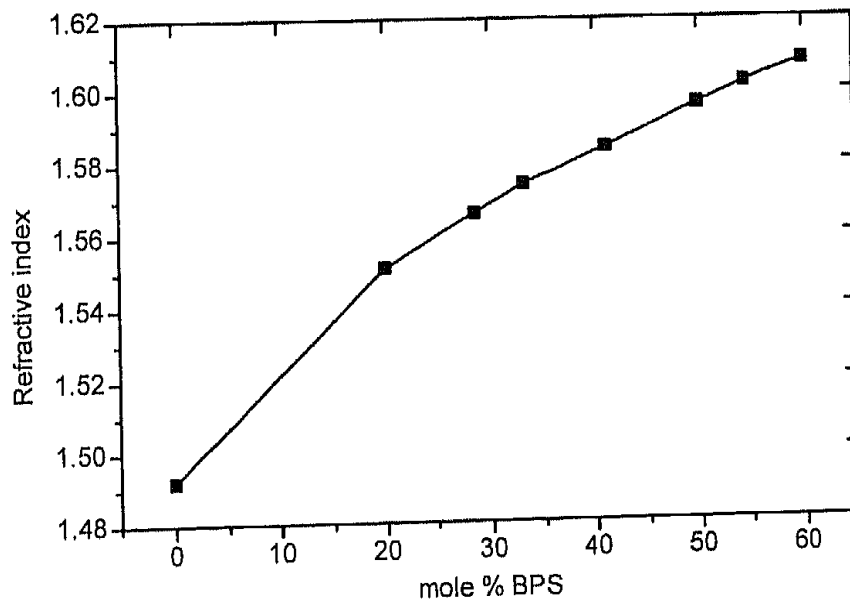
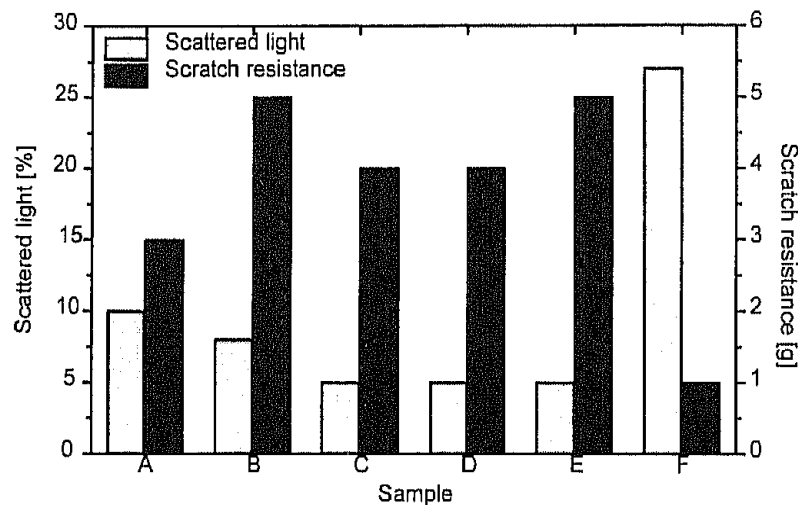


Fig. 5. Dependence of the refractive index of a bisphenol S composite on the BPS content, ref. [23]

In the same way, bisphenol S ($\text{HO}C_6H_4\text{SO}_2C_6H_4\text{OH}$, BPS) can be used as a crosslinking agent. Systematic investigations have been carried out to study the influence of BPS on the refractive index on the above described composites. The result is shown in Fig. 5.

As one can easily see, the refractive index can be varied from 1.49 up to 1.65 just by the variation of the percentage of BPS. The coating systems are prepared by hydrolyzing GPTS under acidic conditions to a viscous liquid and then adding the bisphenol including the catalyst. For the testing of the materials with respect to mechanical properties and abrasion resistance, a taber abrader test according to DIN 52347 (100 cycles, 500 g load) was carried out, and the haze was measured (% loss of transmission). In addition to this, a scratch test using a Vickers diamond scratching over the surface was used. The load in g causing the first visible scratch is registered as scratch resistance. Since the two-component system GPTS/BPS shows a rather poor performance with respect to abrasion and scratch resistance, tetraethyl orthosilicate and propyl triethoxy silane were used, acting as three-dimensional crosslinking agents. The results are shown in Fig. 6.



Sample	GPTS	BPS	TEOS	PTEOS
A	1	0.2	0	0
B	1	0.4	0	0
C	1	0.5	0	0
D	1	0.4	0.2	0
E	1	0.4	0	0.2
F	uncoated polycarbonate			

Fig. 6. Composition and scratch and abrasion resistance of various compositions

As one can clearly see, the composition E shows the best performance: low scattered light as a measure of the low abrasion and high scratch resistance at the same time. The refractive index of 1.56 of this composition is sufficient not to show disturbing interferences on CR³⁹ as coating.

3.1.2 Molecular Composites with Tailored Adhesive Properties

As shown in the previous chapters, the chemical synthesis principles allow the introduction of a variety of functional groups into the composite materials and, by controlling the dimensionality of the network crosslinking tailoring of mechanical and thermal properties, too. As shown elsewhere [24], thermoplastic systems have been developed by using diphenyl silane diols, vinyl methyl silanes and EOS as starting materials. Systems containing more than 25 mol% of the diphenyl silane and more than 50 mol% of methyl vinyl silane show thermoplasticity and are stable against temperatures up to 250 °C, still having remarkable OH group contents after several hours of curing at these temperatures, but only if acids are used as catalysts. An infrared spectrum of the system containing 27.5 % of the phenyl (Ph) component, 70 % of the methyl vinyl (mevi) component and 2.5 % of the SiO₂ component is shown (Fig. 7).

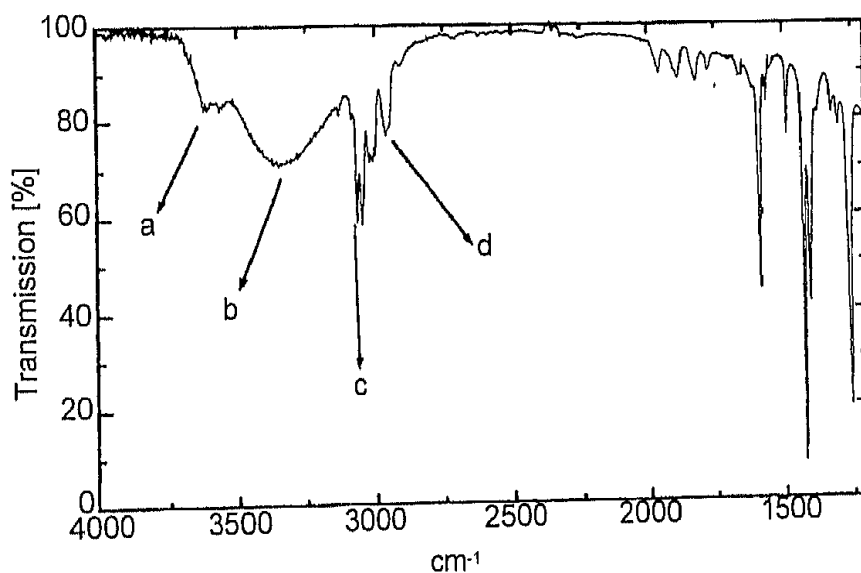


Fig. 7. IR spectrum of a condensate: 70 % mevi, 27.5 % Ph, 2.5 % SiO₂
a & b) free and bridged SiOH groups
c) aromatic and
d) aliphatic CH groups, ref. [25]

Investigations [25] have shown that these systems show good adhesion as a hot melt to all types of surfaces (glass, metals), if the free and bridged OH groups do not decrease below a certain level, determined as the ratio between the OH and the phenyl concentration, determined from the infrared peaks a-c (Fig. 8).

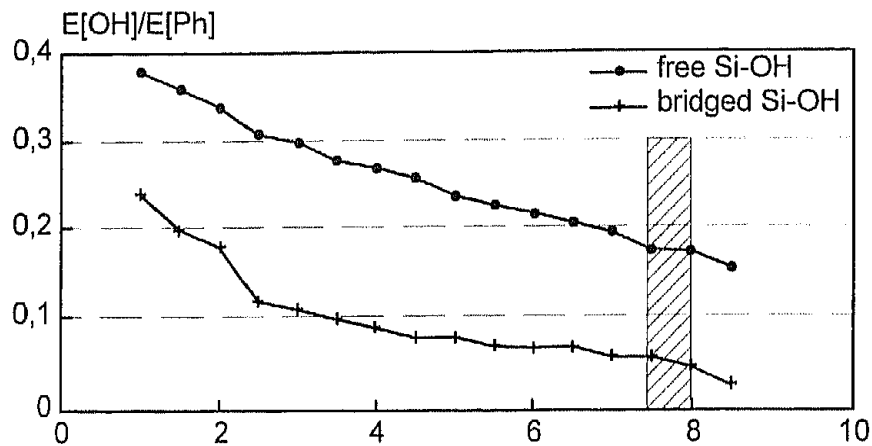


Fig. 8. Dependence of the OH group contents (free and bridged) as a function of curing time at 230 °C; hatched area: optimized adhesion, ref. [25]

It could be shown by the adhesion strength experiments that the best results are obtained if the ratio of free SiOH:phCH = 0.18 and bridged SiOH:phCH is less than 0.05. Higher and lower values lead to a decrease of adhesion, however, the overall adhesion is only in the range of about 3–3.5 N cm⁻¹, determined as peel strength. Investigations of the fracture mechanism show that the seal shows a brittle fracture behavior, as indicated in Fig. 9.

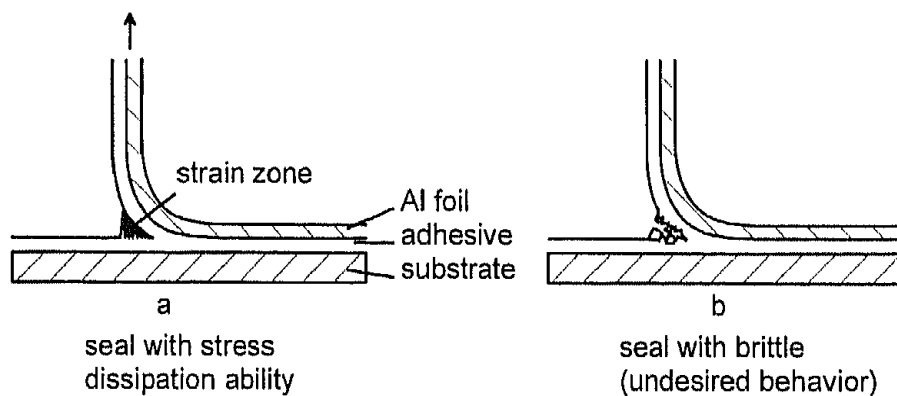
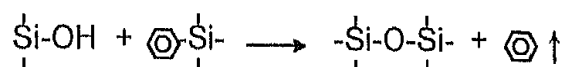


Fig. 9. Schematics of a peel strength experiment indicating good and undesired (brittle) behavior

It was found that after the curing time, three-dimensional crosslinking of the system has been increased due to a benzene elimination mechanism, as shown in Eq. 1.



Eq. 1.

This could be proved by solid-state NMR analysis, showing that the T3 content increases with curing time at the expense of the diphenyl T1 content (index means the number of oxygen bridges to other silicon atoms of the considered silicon atom). It was of interest to investigate how far the stress dissipation ability of the seal can be improved without reducing the sealing properties. Moreover, it was of further interest for practical reasons how far these systems are able to be adapted to polyimide surfaces in connection with copper as a counterpart.

Preliminary tests of using this system as a seal between copper and polyimide showed that a seal strength up to 4.2 N cm^{-1} could be obtained with systems containing 70 mol% phenyl silane, 27.5 mol% methyl vinyl silane and 2.5 mol% EOS. Fracture investigations show that a cohesion rupture is also dominating in this case, confirming the above mentioned result that the brittleness of the seal is too high.

Several routes were investigated to improve the behavior. One route was to incorporate additional network modifiers in order to reduce the brittleness. For this reason, an additional silane (amino group containing silane, for example γ -aminopropyl triethoxy silane or γ -aminopropyl methyldiethoxy silane, AMDES) were introduced as a crosslinking agent for diepoxides acting as "flexible" chains between the highly crosslinked composite network.

At the same time it was assumed that interaction of the amino groups of the silane should act as additional adhesion promotor to the polyimide surface. The use of the γ -aminopropyl methyl triethoxy silane together with diepoxides (Araldite[®] GY 266) did not improve the brittleness remarkably. The use of AMDES, however, should lead to less brittle systems due to the only two-dimensional crosslinking ability of the diethoxy silane. The basic structure formation features are given in Fig. 10.

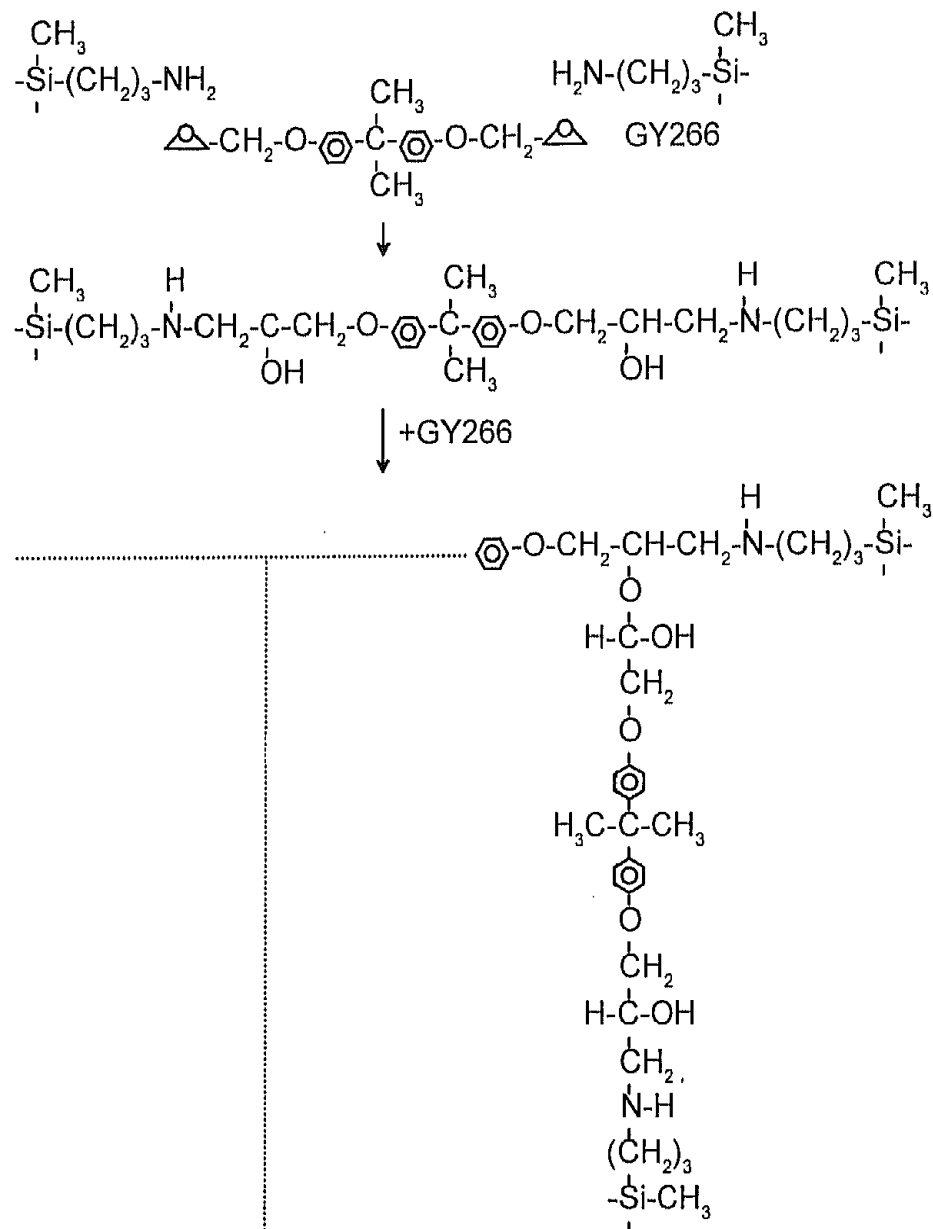


Fig. 10. Reaction model of amino silanes with diepoxides

In order to improve the condensation of the silane to the backbone of the basic composition, the curing time of the system was reduced in order to increase the OH group content. It could be shown that with ratios of the free SiOH:phCH of about 3.6 and of the bridged SiOH:phCH of 0.6 a crosslinking of the amino silane to the phenyl groups was possible. This was proven by ^{29}Si NMR spectroscopy [25]. If the amine was used in the ratio of 1:1 of the diepoxides (molar ratio), the peel strength was even decreased (2.5 N cm^{-1}), but when the ratio amine to epoxide was changed to 1:2, the maximum peel strength obtained as a function of the total content of the amine was above 10. The optimum seal strength was obtained by adding about 30 wt. % of the amine to the basic system. The results are shown in Fig. 11.

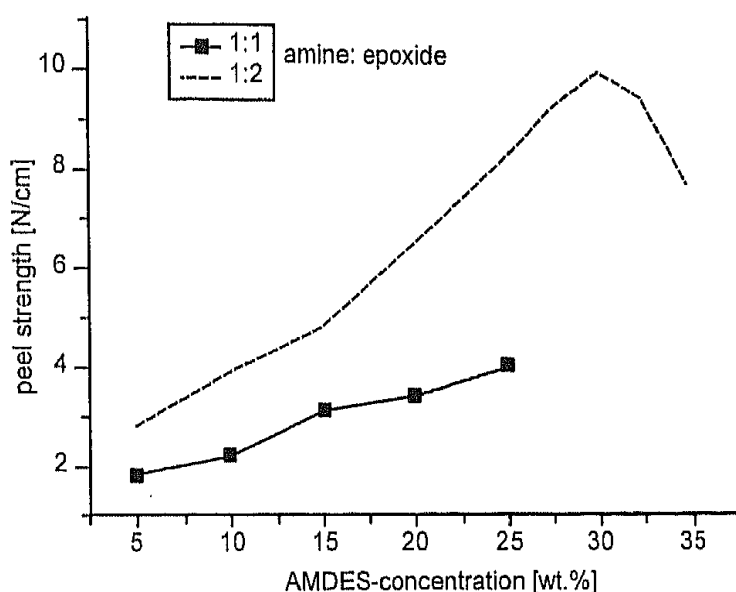


Fig. 11. Dependence of the peel strength on the amine content of the seal using two different amine-to-epoxide ratios

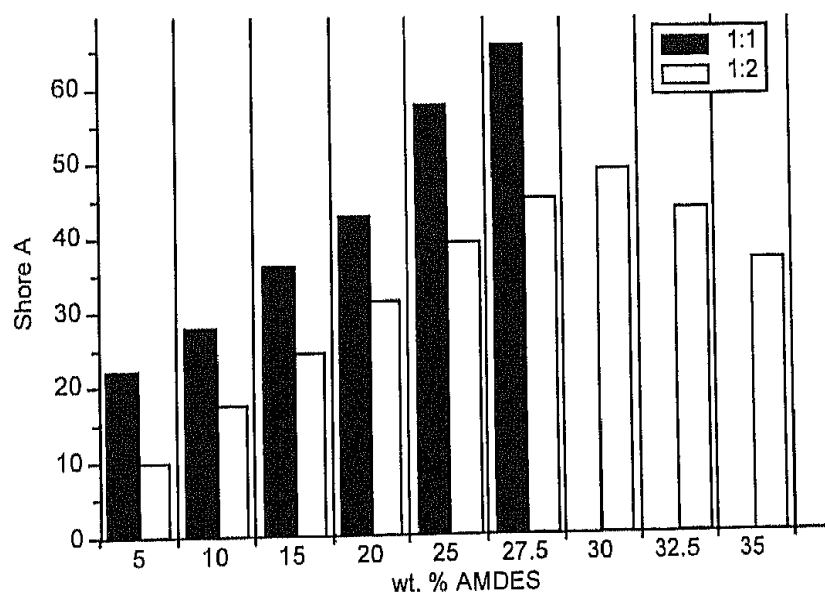


Fig. 12. Shore A hardness of composites with different AMDES/GY 266 contents

The investigation of the shore hardness of the different systems shows that the shore increases with the amino content, but the shore hardness of the 1:2 composition is still below that of the 1:1 composition. It is interesting that the shore hardness shows the same tendency as the adhesive strength (Fig. 12). An interpretation is that with increasing amount of amino groups the adhesive strength to copper as well as polyimide is increased due to the better adhesion to the different surfaces, but at the same time the shore hardness has to be kept low enough not to prevent stress dissipation. With too high amino contents the

shore hardness decreases, but now the mechanical strength of the seal decreases, too (Fig. 12). The lower shore hardness of the 1:2 system indicates a better stress dissipation ability than the 1:1 system. The seal strength of 10 N cm^{-1} is an excellent value compared to the state of art (3–4 with silicones used in application).

The electrical properties of the system are shown in Table 1.

System	Resistivity ρ [$\Omega \text{ cm}^{-1}$]	Breakthrough Voltage D [V cm^{-1}]	DK 1 kHz	$\tan \sigma$ 1 kHz – 1 Mhz.
17	1.1×10^9	10^5	3.9	2.8×10^{-2}

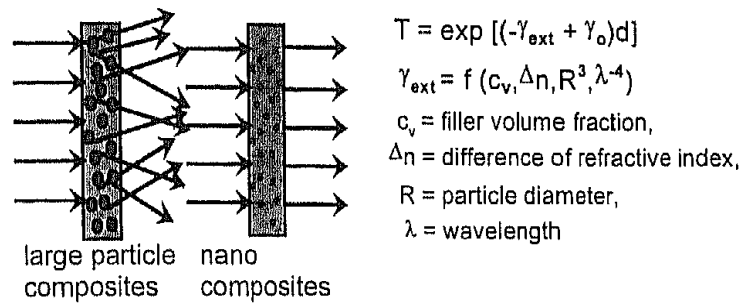
Table 1. Electrical properties of the optimized system

The values are within the limits for electronic application. The seal is thermally stable up to $180 \text{ }^\circ\text{C}$. The investigations show that by tailoring chemical structures of sol-gel derived organically modified hetero polysiloxanes, mechanical and adhesive structures can be tailored for needs of application.

3.2 Nanocomposites

3.2.1 General Considerations

In the previous sections, two examples of the synthesis and material development based on molecular composite systems have been described. However, in these systems, due to the absence of inorganic extended networks (amorphous or crystalline), solid-state properties attributed to these extended networks cannot be introduced. These properties, however, are of interest for a variety of reasons, for example, mechanical properties, optical properties (linear and non-linear properties) or quantum size effects, if the phase dimension of these inorganic units can be kept in the nano range. Keeping the phase dimension in the nano range makes these composites interesting for optical purposes since Rayleigh scattering can be neglected. The combination of the nanophases with a molecular composite matrix as described above leads to a new type of nanocomposite based on hetero polysiloxanes. In Fig. 13, an overview over the potential of this type of nanocomposite materials is shown. The transparency T is a function of the coefficient of extinction in which Rayleigh scattering is included, and in this case the coefficient depends on the third power of the particle size. The interesting part is that passive as well as active functions can be generated by small particles in composites.



- passive "functions": refractive index (n_E)
 mechanical properties
 interface properties
 absorptive properties
- active "functions": semiconductor properties
 (band gap, intermediate electron location
 \Rightarrow NLO)
 plasmon properties
 photochromic, electrochromic properties

Fig. 13. Overview over some properties to be derived from inorganic-organic hetero polysiloxane nanocomposites and potential applications

For the synthesis of the nanocomposites, additionally to the reaction principles described above, nanoscale particles have to be generated within or added to the hetero polysiloxane composite matrix. As described elsewhere [26], the sol-gel process, is a suitable means. It can be considered as a growth process from solution where a controlled growth reaction takes place, that leads to a stabilized colloidal system and thus avoiding precipitation.

The sol-gel reactions have mainly been investigated in alcoholic solution, which is a reaction medium easily allows electrostatic stabilization by appropriate choice of the pH. This type of stabilization can only be used in a few cases as a means for incorporating the colloidal particle agglomerate-free into tailored matrices, since these matrices, as a rule, destroy the electrostatic "coating" around the particles. As a consequence, agglomeration takes place, and the high transparency required for optical application is lost.

For this reason, another type, the so-called short organic molecule stabilization by tailored surface modification for colloidal particles, has been developed, the principles of which in comparison to the electrostatic stabilization is schematically shown in Fig. 14.

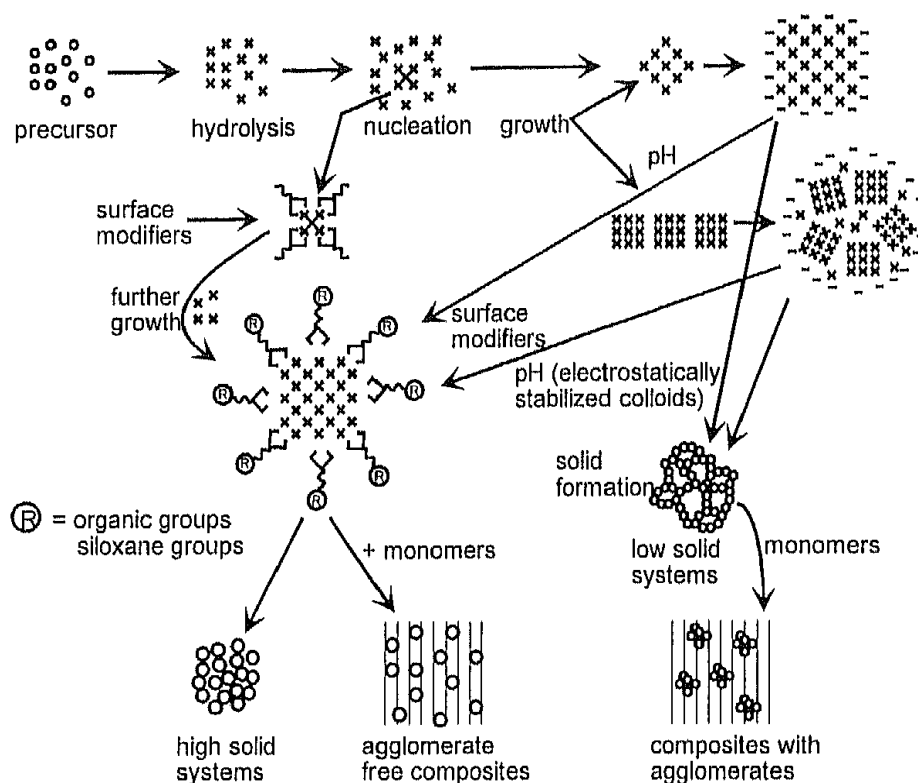


Fig. 14. Reaction paths for the stabilization and fabrication of nanocomposites using growth reactions controlled by surface modifications

The use of this route, of course, opens some interesting questions, for example, how far the surface-modifying molecules interfere with a growth reaction or how far bonds with the desired stability to the surface of the growing particles can be obtained. The interesting potential of this method is that by controlling the surface free energy of the growth process, a tailoring of particle size should be possible. Additionally to this, if it is further possible to tailor the bond strength to the surface, reactive colloids may be prepared by using so-called bifunctional molecules. In these molecules one function is used to link the molecule to the surface and the second function is used to create a desired activity like hydrolyzable and condensable groups of silanes, double bonds or epoxides for further polymerization or polyaddition reactions. These principles have been investigated in detail elsewhere [27–29].

3.2.2 ZrO₂ Containing Composites for Optics

Using zirconia as a model, it could be shown that if zirconium alkoxides are used as starting compounds in the presence of chelating agents like carboxylic acids [27] or β -diketones, [30] the

precipitation of zirconia can be avoided through hydrolysis and condensation. In Fig. 15 the schematics of this reaction are shown.

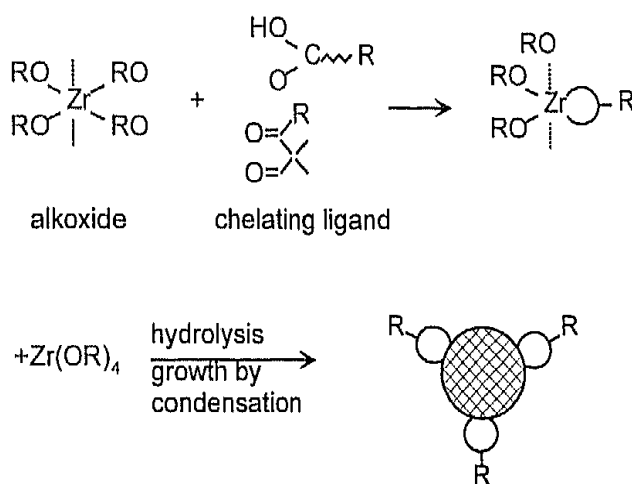


Fig. 15. Reaction model of the formation of ZrO_2 colloids covered by methacrylic acid (ma) through a surface-controlled growth process

If, for example, methacrylic acid is used as a complexing agent, particles of about 2–5 nm in diameter can be generated by hydrolysis and condensation, and if, in addition to this, methacryloxy group containing hydrolyzable silanes are used in combination with the zirconia colloids, transparent composite systems have been synthesized.

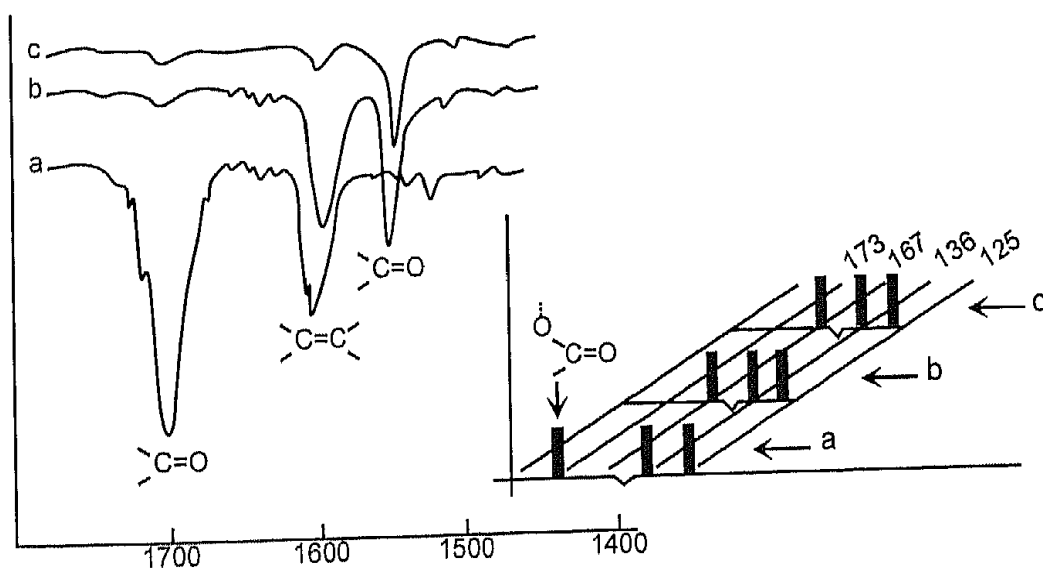


Fig. 16. Analysis of complexation and solidification of zirconia ma colloids by IR and ^{13}C NMR:

- a) methacrylic acid
- b) zirconia ma complex
- c) zirconia ma complex after hydrolysis, condensation and polymerization, before and after curing and exposure to water, according to [32]

As shown in [31], after curing at 120 °C these composites contain nanocrystalline monoclinic zirconia particles. IR and NMR analysis (as shown in Fig. 16) show that the carbon CO frequency obtained by complexation is still maintained after hydrolysis of the colloid and after polymerization of the double bonds together with methacryloxy silanes, no change in the carbonyl frequency can be observed. Even after using these systems as coatings, after two weeks exposure to water no change is observed. Similar results are also obtained by ^{13}C NMR analysis of the carboxylic carbon atom, as shown in Fig. 16.

In Fig. 17 a structural model of the composite before polymerization is given.

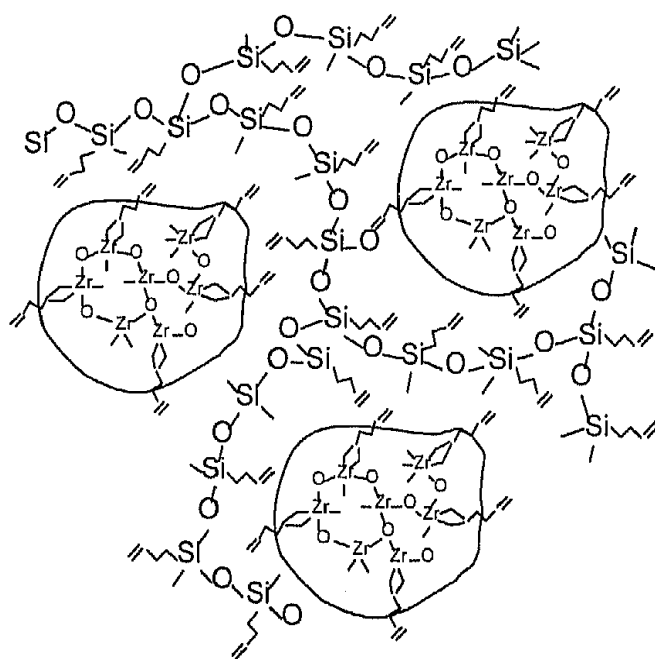


Fig. 17. Model for a colloidal organic-inorganic network interpenetrated by a siloxane network

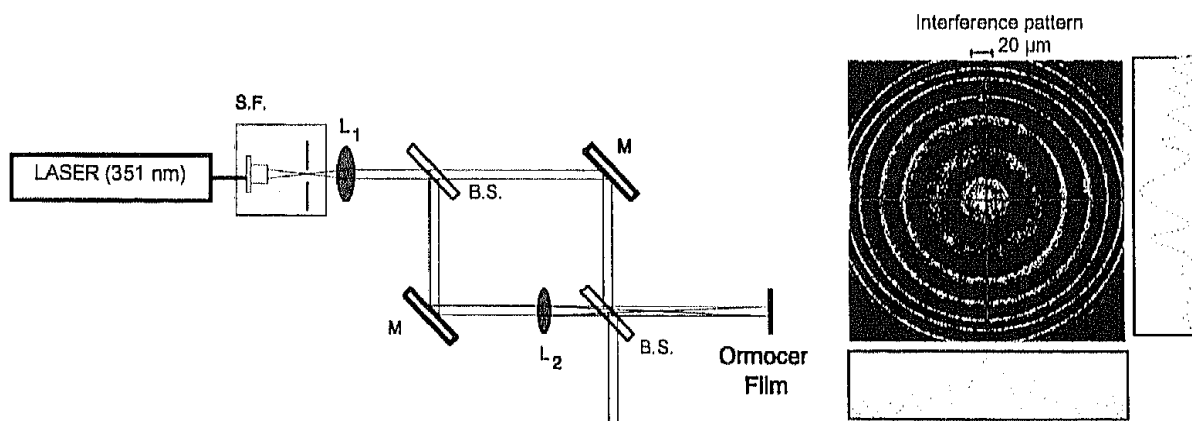


Fig. 18. Schematics of the fabrication of micro fresnel lenses by two-wave mixing, [35]

As shown by [31, 33, 34], these complexes can be polymerized to polymers by photo and thermal initiation, and at 120 °C conversions above 96 % have been obtained. By use of photoinitiators and two-wave mixing systems by a laser light source resulting in concentric interference patterns, these coatings can be used to create Fresnel lens micropatterns by partial polymerization and subsequent development by dissolving the unpolymerized parts by organic solvents. Suitable optical properties can be obtained by controlling the interference patterns and the refractive index by the zirconia content. An example of Fresnel lens micropattern fabrication is given in Fig. 18.

Using this principle, optical gratings and channel waveguides already have been developed [35].

3.2.3 Third-Function Coatings

The incorporation of other functions into these systems can be used for developing other interesting properties. As shown in [36], the addition of silanes carrying perfluorinated side chains as additional precursors leads to liquid systems with the fluorinated components homogeneously distributed through the material. As soon as these liquids are spread onto a surface in form of thin films (several μm in thickness), a phase separation takes place leading to a gradient material with the fluorinated side chains directed to the surface and the polar groups of the system directed to the substrate interface. In Fig. 19, the basic function of the system is shown [36].

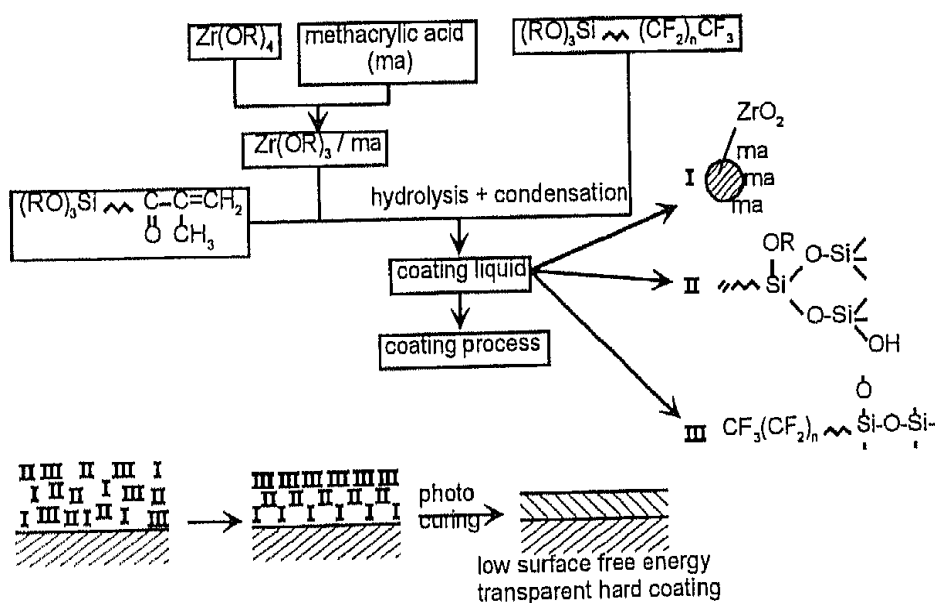


Fig. 19. Schematics of the thermodynamically driven alignment effect of the ZrO_2 /perfluorinated silane composition

The alignment of the different components is driven by the reduction of the surface and interfacial free energy. This general principle can be extended to other colloidal systems as components, and by appropriate choice of composition, colloidal concentration and particle size, the gradient of the fluorinated system can be tailored in a wide range [37]. If SiO_2 is used instead of zirconia, surface-modified by methyl silanes, high-temperature systems up to $400\text{ }^\circ\text{C}$ are obtained, also having the gradient effect. These systems have been developed for glass surfaces due to the low surface free energy. All these systems are dust- and soil-repellent, highly transparent and scratch-resistant compared to polymers.

In Fig. 20 the ESCA spectrum of the surface and of the bulk after two minutes argon sputtering is shown.

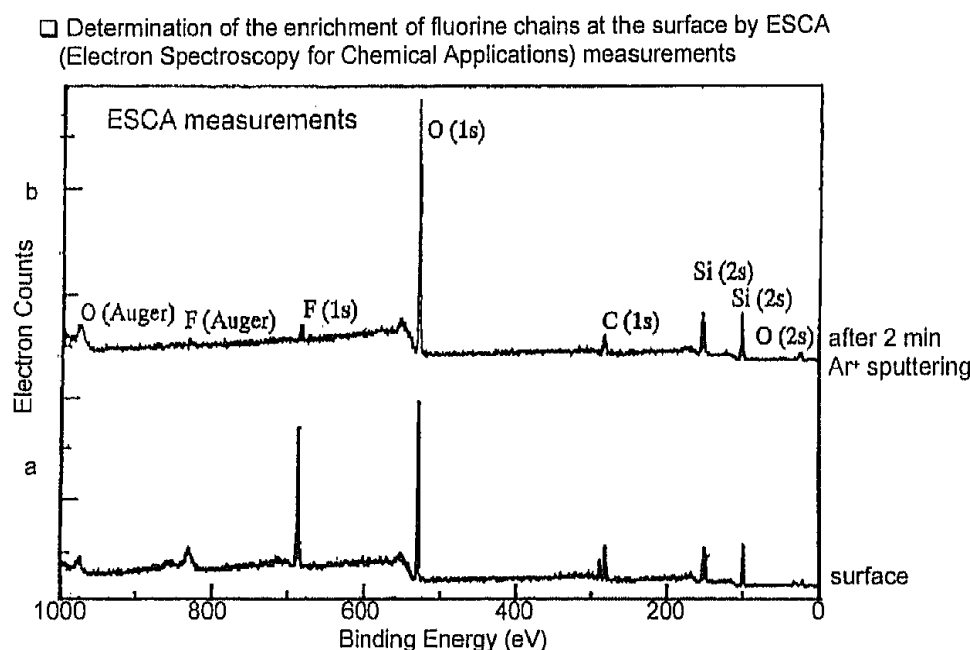


Fig. 20. ESCA spectrum of a coating of the ZrO_2 /perfluorinated silane system

- a) surface
- b) bulk

As one can see, the concentration of fluorine is strongly enhanced on the surface. ESCA profiling shows that even in the ESCA machine the contamination content (adsorption of hydrocarbons) is extremely low compared with that of other samples (glasses, metals polymer surfaces). These systems already are successfully used in industry to avoid sticking to steel conveyor belts during production, for food containers as easy-to-cleaning inner coatings, for metal pipes in analytics to keep the carry-over with liquids near to zero and for the glass industry for keeping glass panes clean.

Summarizing, the in-situ growth of nanoscale particles in hetero polysiloxane type of matrix systems leads to an interesting type of nanocomposites, which is of special interest for application due to its

possibility for photocuring in combination with high optical transparency (microoptical systems, waveguide systems).

The incorporation is of special interest for a variety of applications. One of them has been described in the previous sections, others are the incorporation of semiconductors [38] of metal colloids [39, 29] or silver halides [40].

3.2.4 Systems with Nanoparticles Added to a Matrix System

Another possibility mentioned above is the addition of nanoscale particles to a liquid matrix system where the nanoscale particles are grown outside of the system. Experiments have been carried out with boehmite in a matrix derived from $\text{Si}(\text{OR})_4/\text{Al}(\text{OR})_3$ and glycidylxypropyl triethoxy silane (GTPS) [22]. Even the addition of 5 % by volume of γ -alumina or boehmite leads to systems which show a remarkably increased scratch-resistance compared to the unfilled material. The optical transparency is not influenced if the particle size of the boehmite is below 20 or 30 nm. In Fig. 21 the scratch resistance by the Vickers diamond test of the unfilled system is compared to the filled system and, as one can see, the scratch resistance is increased remarkably.

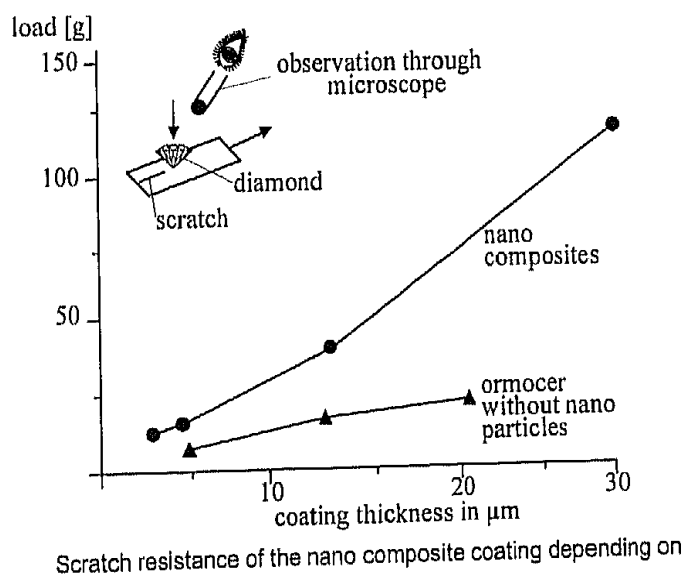


Fig. 21. Scratch resistance of the nanocomposite coating depending on the thickness in comparison to a conventional Ormocer coating, ref. [22]

This effect cannot be simply explained by the low degree of filling. Detailed investigations of the reaction mechanism of the composite formation by ^{27}Al , ^{29}Si , ^{13}C NMR spectroscopy, and NIR infrared spectroscopy show that in this system the boehmite acts as a condensation catalyst for the epoxide

polymerization. At the same time, an $\equiv\text{Si}-\text{O}-\text{Al}=\text{}$ bond is formed by the epoxy silane to the boehmite particle surface, which also can be shown by NMR spectroscopy (Fig. 22).

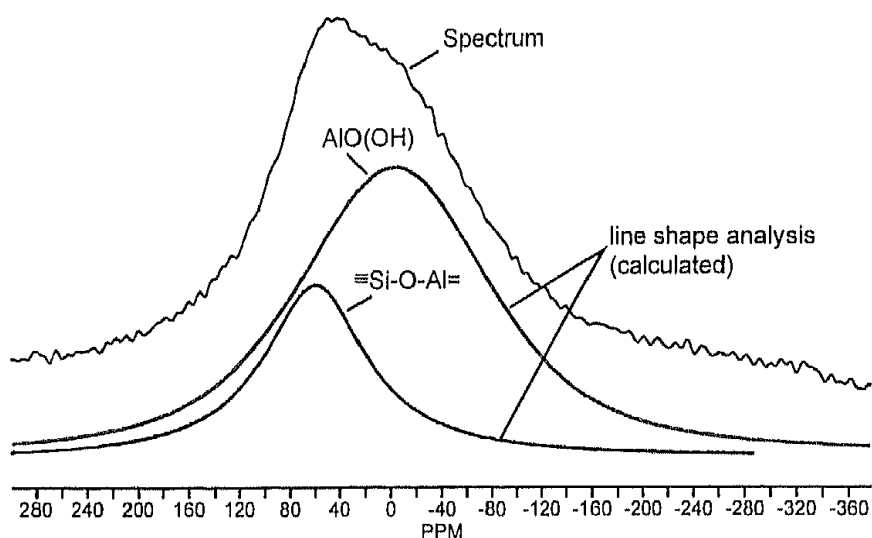


Fig. 22. ^{27}Al NMR spectrum of the $\equiv\text{Si}-\text{O}-\text{Al}=\text{}$ bond formation in the GPTS/- $\text{SiO}_2/\text{Al}_2\text{O}_3/\text{boehmite}$ nanocomposite

For the described reason, a special structure is proposed, which is schematically shown in Fig. 23. In this figure, the structure is compared with a filled polymer structure (SiO_2 filled polysiloxanes, very often used as hard coatings for eye glass lenses). The figure also depicts the results of a so-called tumble test. In this test the coated eye glass lens is tumbled in a tumbler filled with a special composition of abrasive materials. As one can see from the figure, the haze produced from coatings with a new nanocomposite is distinctively lower than that from other materials in use. This behavior is attributed to the special structures. NMR and IR data suggest that poly(ethylene oxide) chains are concentrated around the aluminum oxide particles, providing a flexible suspension of these particles in the stiff network and thus leading to a mechanical behavior showing a specific hardness on the one hand, but due to the suspension, the ability of not being broken out so easily by mechanical impact on the other hand. These systems have also been further developed to be used on other polycarbonates very successfully.

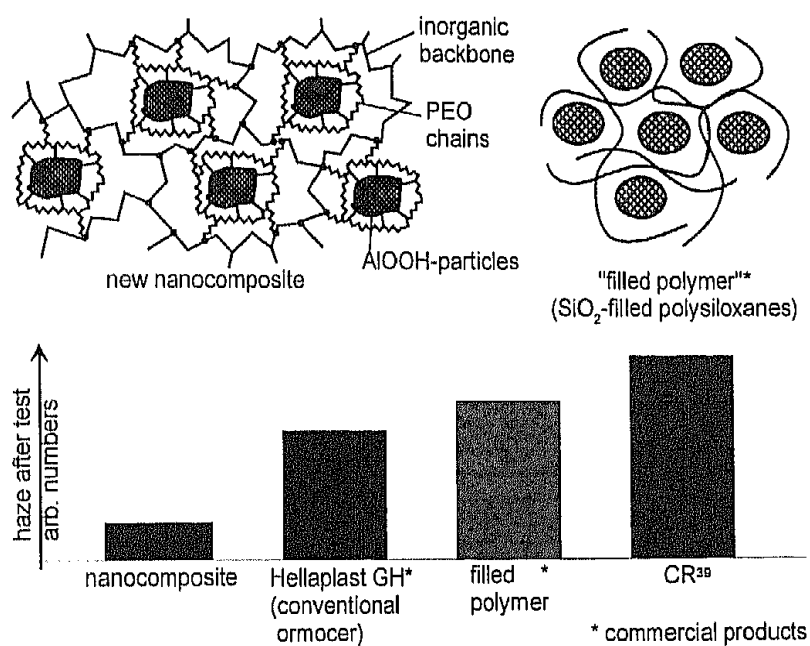


Fig. 23. Comparison of several coatings used on CR³⁹ eye glass lenses by the tumble test and structural model of the nanocomposite coating

These few examples show how the use of nanocomposite systems with hetero polysiloxane type of matrices leads to interesting properties for applications. Further developments using these basic systems are transparent controlled release coatings for anti-fogging systems [41], anti-corrosive systems for metal protection [42], and nanocomposite optical bulk materials [43].

4 Conclusions

The development of materials based on hetero polysiloxanes in combination with or without nanoparticles is an interesting route to new materials with interesting aspects and applications. These materials, especially in the initial phase, cannot play the role as mass commodity materials to be produced in large quantities by chemical industry. This might be one of the reasons that the penetration of this type of material into industrial application is still at its infancy, but anyway, for creating special functions or special innovation in the field of materials users, this type of materials has already proven its usefulness for practice.

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