Chapter 26

Inorganic–Organic Hybrid Coatings for Metal and Glass Surfaces

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Inorganic-organic composite materials have been tailored by sol-gel synthesis with different properties for different applications. A composite from SiO_2, diphenyl silanes and methylvinyl silanes was modified by an amino silane and crosslinked by diepoxides, leading to a sealing strength of more than 10 N/cm when used as a hot melt for sealing copper to polyimide. An ormocer type of coating was modified by nanoscaled γ-Al_2O_3 or boehmite, leading to a low-curing transparent coating material with very high scratch resistances and a ZrO_2 nanocomposite modified with silanes with perfluorinated groupings having high transparency combined with low surface free energy with 18 mJ/m² was synthesized.

The combination of properties related to ceramic materials and polymeric materials is an attractive conception and allows the tailoring of material properties in a wide range. For this reason, composite materials have been developed and applied for many purposes. In general, ceramic-polymer composite materials are prepared by mechanical mixing. With a few exceptions, ceramic filler components are produced by mechanical processing which restricts the particle size to the µm range. The exception is fumed silica which is available with smaller particle sizes (50 nm), but, in general, is rather agglomerated. If particles in the lower nano range are of interest, other methods have to be considered. The synthesis of inorganic components, starting from molecular precursors by a growth process and stopped at the desired particle size, seems to be an adequate route. In the sol-gel synthesis, as a rule, molecular precursors are used which react in a growth process to colloidal systems ranging from one to several 100 nm [*1 - 5*]. If these reactions are carried out in the presence of organic groupings or organic grouping-carrying molecules (e.g. organofunctional silanes), a variety of different types of composites can be synthesized (ormosils, ormocers, polycerams, ceramers) [*6 - 9*]. Using these principles, materials with

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special optical [*10*], mechanical [*11*] or protective properties on various surfaces can be tailored. For example, the mechanical properties can be influenced by the type of crosslinking (three-dimensional versus two-dimensional) or the phase dimensions of the inorganic and the organic phase. Depending on the dimension of the inorganic phase, one can distinguish between so-called molecular-type and nano-type of composites, however, this differentiation is hardly done in the literature. In the present paper three examples for material development are given using inorganic-organic sol-gel processing with the objective of tailoring very special, but different surface properties: a high surface free energy system with adhesive properties based on a molecular type of composite, a low surface free energy system and a system with a very high abrasion resistance. Furthermore, in this paper, the material development aspect using sol-gel synthesis principles is emphasized.

Results

Materials with Tailored Mechanical Properties for Adhesion of Metal Foils to Polyimide

In order to achieve a good adhesion, adhesive materials have to show two basic properties: a good wetting behavior to the surface and mechanical properties leading to stress dissipation under peeling stress. If such materials have to be used in a hot-melt process, wetting is of extremely high importance since no solvents can be used which, in general, provide a good wetting behavior. If, in addition to this, high temperature stability and good sealing properties to surfaces with very different chemical properties (e.g. copper to polyimide for electronics) are required, the material basis becomes very narrow, and silicones are the most interesting materials at present. As already shown in [*11*], a hot-seal system has been developed by sol-gel techniques from diphenyl silanes ($(RO)_2Si(C_6H_5)_2$ (I)), methylvinyl silanes ($CH_3(CH_2{=}CH)Si(OR)_2$ (II)) and tetraethylorthosilicates ($Si(OR)_4$ (III)). As starting compound, the corresponding dichlorides can be used also. This system, however, developed for sealing aluminum foils to glass and having excellent properties with respect to moisture resistance, shows a relatively low peel strength of about 3 N/cm in the peel test. The sealing medium shows a typical brittle behavior under stress, since the strain zone cannot be dissipated by the system, as schematically shown in Figure 1. The experimental details are given elsewhere [*12*].

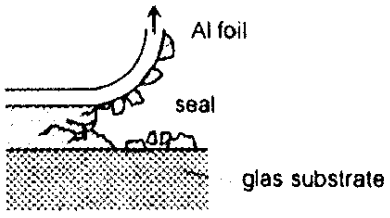


Fig. 1 Schematics of a peeling test with a too brittle sealing agent [after *11*].

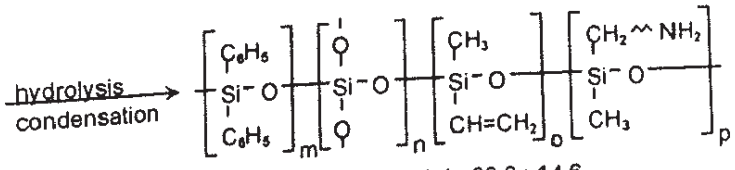
The brittleness of the system can be explained by a high degree of three-dimensonal crosslinking based on a condensation process taking place at 150 °C through benzene elimination,

$$\equiv Si\text{-}C_6H_5 + HO\text{-}Si\equiv \rightarrow \equiv Si\text{-}O\text{-}Si\equiv + C_6H_6, \qquad (1)$$

which has been proved by IR spectroscopy as well as by analysis of volatiles during the curing process, forming stiff "units". Nevertheless, the resin-like systems show a thermoplastic behavior, which is attributed to the low molecular weight "units" (3000 - 5000 a.m.u., as proved by molecular weight measurements), stabilized at low temperatures by hydrogen bounds of ≡SiOH groupings still present in the material. The most interesting property of the system is its excellent wettability to various surfaces (glass, metals, polymers) and a good hot-melt behavior. The wetting behavior is attributed to the polarity of the system caused by a relatively high content of SiOH groupings to be controlled by IR. The wettability decreases drastically if the ratio $E_{3620\ cm^{-1}}$ (SiOH) : $E_{3070\ cm^{-1}}$ (phenyl CH) ≤ 0.19.

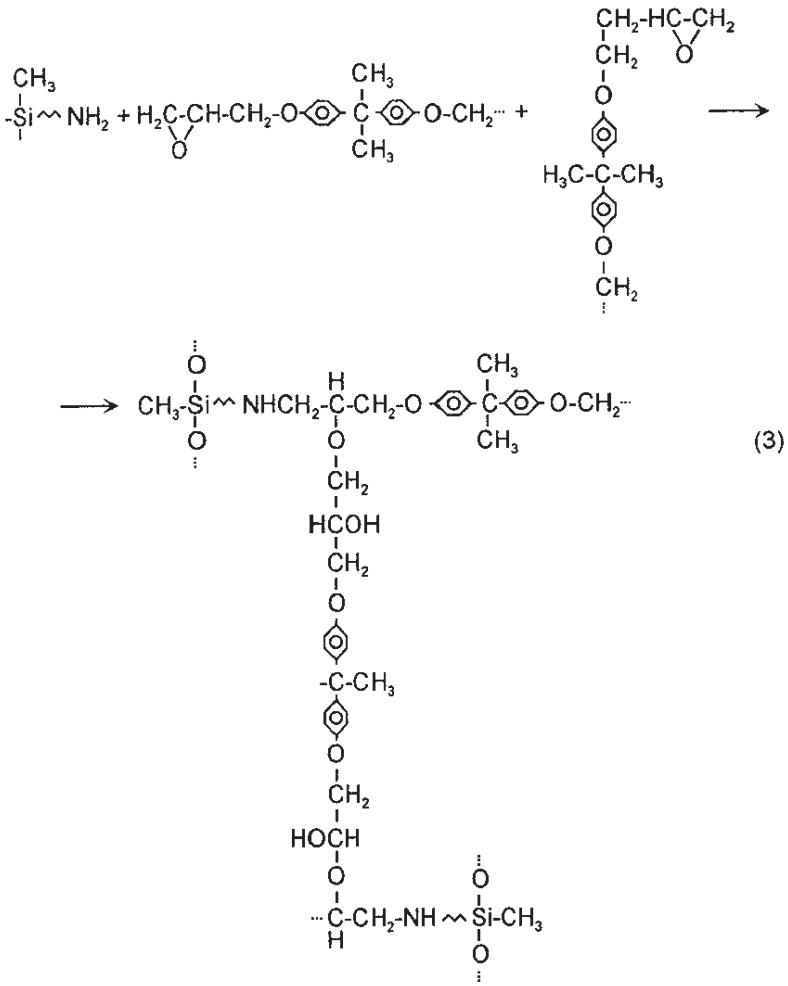
In the present investigations, in order to reduce the brittleness of the system, short organic groupings have been introduced into the basic composition using amino silanes (e.g. $H_2NCH_2CH_2CH_2(CH_3)Si(OR)_2$ crosslinked by commercially available Bisphenol/A-diepoxides (Araldit®). The experimental details have been presented elsewhere [*13*]. The objective of this investigation was to maintain the good wetting and adhesion properties as well as the thermoplastic behavior and to improve the stress dissipation power of the system by adding "elasticity". For this reason, in a sol-gel synthesis process the starting components (I, II, III, equation 2) have been hydrolysed under acidic conditions, and a condensation reaction was carried out to build up the inorganic backbone. In figure 2, the principles of the synthesis are shown. This synthesis is the result of a systematic development using different silanes and epoxides as well as an optimized reaction route. The use of amino grouping-containing silanes, for example, was found out to be a suitable means to improve the adherence to polyimide surfaces. However, the amino silane has to be bound to the inorganic -backbone during the first synthesis step (hydrolysis and condensation of the phenylsilane, the methyl vinyl silane and the TEOS) in order to be efficient.

$$(C_6H_5)_2Si(Cl_2)_2 + Si(OR)_4 + CH_2{=}CH(CH_3)SiCl_2 + H_2N(CH_2)_3Si(CH_3)(OR)_2$$



(2)

m : n : o : p = 15.4 : 1.4 : 39.3 : 14.6



(3)

The introduction of the amine after hydrolysing and condensing the starting compounds I - III to the uncured state leads to good adhesion, but low stress dissipation, since the epoxide then is not distributed uniformly within the inorganic network. The best results have been obtained by a molar ratio of amine to diepoxide of 1:1.

The process has been investigated by ^{29}Si-NMR [*12*]. In Figure 3 the ^{29}Si-NMR spectrum is shown after the polycondensation reaction before the diepoxide addition, and one can see that oligomers of a variety of types of species could be identified, based on comparison with the single components.

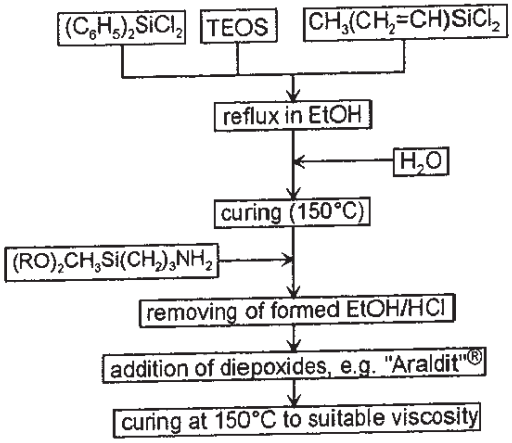


Fig. 2: Flow chart of the synthesis of the hot melt sealing agent.

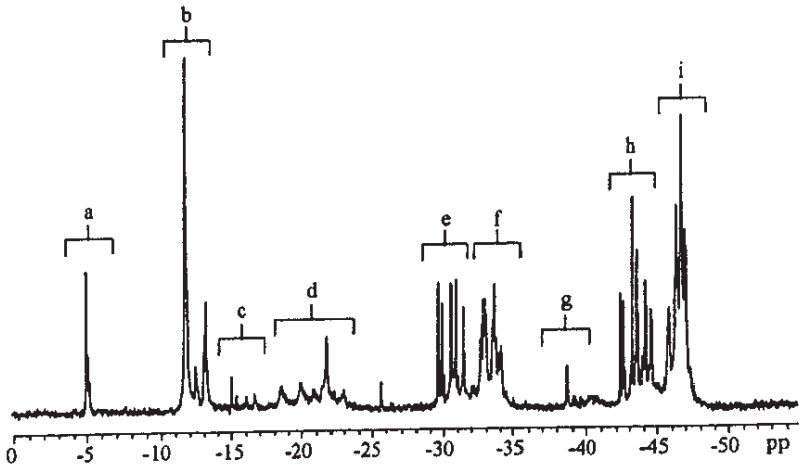


Fig. 3: ^{29}Si-NMR of the hydrolysed adhesive sol-gel systems from diphenyl silane, methylvinyl silane, amino silane and SiO_2 (four-component system without the diepoxide), a: monomeric amino silane; b: oligomeric and dimeric unit of the condensed amino silane; c: co-oligomers of the amino silane with the diphenyl silane; d: co-oligomers of the amino silane with the methylvinyl silane; e - h: oligomers and co-oligomers of the methylvinyl silane and SiO_2 with the amino silane and the diphenyl silane; i: oligomers of the phenyl silane.

In Figure 4, the solid state NMR spectrum of the system is shown after curing, which shows basically the same basic type of peaks, but monomers can no longer be detected. The system is still soluble in organic solvents.

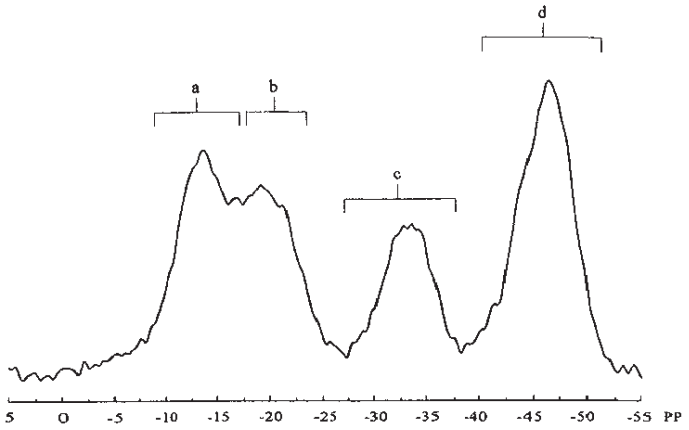


Fig. 4: ^{29}Si-NMR (solid state) of the cured four-component system. a: T_1 units of diamines; b: Si resonances of the amine with phenyl silanes (co-oligomers) and methyl vinyl silanes (co-oligomers); T_2 oligomers of the diamine; c: Si resonances of the methyl vinyl groupings with phenyl silane (co-oligomers) and with the diamine (co-oligomers); oligomeric diphenyl silanes; d: Si resonances of the phenyl silane group with the methyl silane (co-oligomers); phenyl silane oligomers.

The results show that during the condensation and curing process the monomers disappear. Similar to the epoxide-free system, after addition of the epoxide component the wettability in the uncured state with a viscosity of about 220 Pa · s (controlled by curing at 150 °C) as well as the temperature stability up to 140 °C after curing the seal at 100 °C for 5 hrs remain unchanged, but the peel strength increases substantially due to the higher deformability and stress dissipation of the seal in the peeling experiment. In Figure 5, the peel strength of compositions without amines and diepoxide are compared to the amine/diepoxide containing systems.

As one can see, the modification by organic short chains linked to the inorganic backbone leads to a strong increase of the peel strength without decrease of important properties like hot-melt processing and wetting. The peel strength values exceed the values of commercial siloxane seals (≈ 4 N/cm) used for polyimide-to-copper sealing remarkably. SEM analysis after peeling shows the typical surface patterns of a cohesion rupture, that means, both sides, the polyimide as well as the Cu surface, are covered by the sealant.

The results show clearly that by tailoring the structure of the sol-gel-derived inorganic-organic composite through organic crosslinking, the material properties can be tailored to suit the desired application. A structural model was developed, based on IR and NMR analysis. In these composites, no phase separation can be detected. The model is shown in Figure 6.

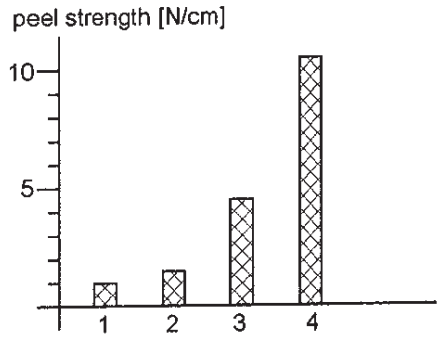


Fig. 5: Peel strength of different compositions. Methylvinyl silane (1); diphenyl silane (2); SiO_2 (3); amine (4); diepoxide (Araldit®) (5) [mole %].
1: (1) : (2) : (3) : (4) = 45 : 42.5 : 2.5 : 0
2: (1) : (2) : (3) : (4) = 60 : 37.5 : 2.5 : 0
3: (1) : (2) : (3) : (4) = 70 : 27.5 : 2.5 : 0
4: (1) : (2) : (3) : (4) : (5) = 39.3 : 15.4 : 1.4 : 14.6 : 14.6; peeling rate: 5 mm/min; sealant thickness: 28 µm.

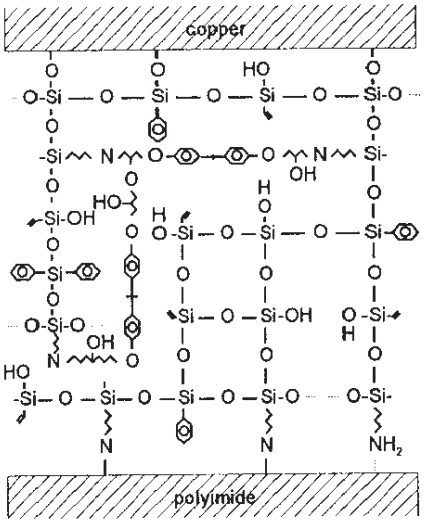


Fig. 6: Structural model of the epoxy crosslinked thermoplastic sealant.

It should be mentioned that the system is based on units crosslinked only by ≡Si-O-Si≡ bonds, additionally connected by epoxy bridging. The thermoplastic behavior again is attributed to the ≡SiOH bridging, getting weaker at elevated temperatures. The sealing agent can be applied to Cu foils by roll coating at 100 °C and then sealed to polyimide. After curing the seal is stable up to 180 °C.

Surface-Mechanical and Surface-Chemical Properties in Inorganic-Organic Nanocomposites

While hybrid sol-gel systems using SiO_2 or ≡Si-O-Si≡ bonds as inorganic network formers only seem to be preparable as molecular (or nearly molecular) types of composites, systems based on more reactive types of inorganic components with increased phase dimensions should be more difficult to be synthesized. In a molecular composite, the inorganic part looses its identity with respect to inorganic material properties, but mainly acts as a structure-modifying agent. In various cases, however, it seems to be desirable to preserve (or to use) properties related to the solid state properties of materials (ceramics or metals), e.g. passive or active optical properties, hardness or even catalytic properties. In case of optical transparency to be obtained, the particle size should be roughly less than 1/20th of the wavelength of the used light to reduce Rayleigh scattering, which means for the visible region particle sizes below 20 nm. Particle sizes in this range can be obtained by sol-gel processing very easily during the growth reaction, starting from alkoxides. For utilizing these colloids, e.g. for nanocomposite fabrication, however, it is necessary to control their surface pro-

perties with respect to particle-to-particle interaction (aggregation or agglomeration), which occurs spontaneously if the colloids are not covered by a "protecting" layer such as electric charges or non-reactive groupings. Electric charge stabilization, in general, leads to gelation with pH change or up-concentration, resulting in low-density porous gels. If nanocomposites with high optical performance have to be synthesized, gelation of the inorganic part has to be prevented at any rate, since gelation would lead to uncontrolled agglomeration with particle sizes causing undesired light scattering. As shown elsewhere [*13, 14*], transparent composites can be produced from methacrylic acid-modified Zr alkoxides reacted together with other methacrylates. An unsolved question of this reaction was related to the structure of the ZrO_2 nanoparticles synthesized from Zr alkoxide/methacrylic acid complexes [*15*]. Several investigations have been carried out for a better understanding of the process. A synthesis scheme is shown in Figure 7.

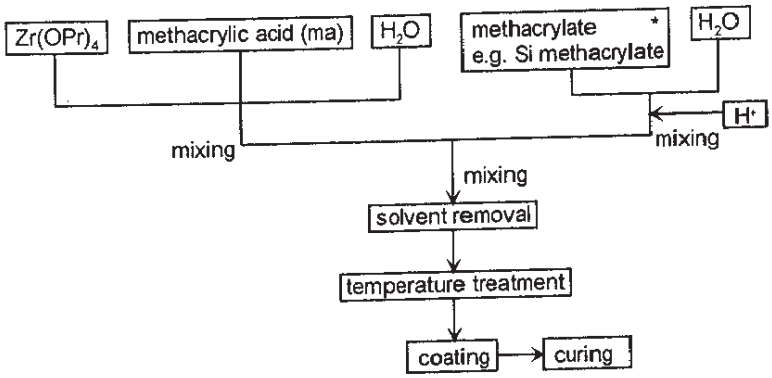


Fig. 7: Schematics of the formation of ZrO_2 (ma) composites with functional silanes. *Other functional silanes can be added to the reaction at this stage.

As shown in [*16*], coatings on glass surfaces obtained from materials fabricated according to the scheme in Figure 7, the hydrolytic stability of the ma to ZrO_2 bond is very stable in the solid material. The reaction of ma with $Zr(OPr)_4$ can be monitored by IR from the shift of the C=O frequency from 1718 to 1551 and by ^{13}C NMR. The IR as well as the NMR shift remain unchanged after hydrolysis of the $Zr(ma)(OPr)_3$. However, with excess water, precipitation takes place. The analysis of the Zr ma bond in the precipitate shows that it is still unchanged. The ZrO_2 precipitation limit, however, is rather low, and it is difficult to synthesize composites with ZrO_2 contents above 5 mole %. The reason for this can be attributed to the hydrolysis and condensation of Zr (ma) alkoxides, leading to large agglomerates and gelation before being incorporated into the inorganic-organic network as a consequence of high local H_2O concentrations, as schematically shown in Figure 8.

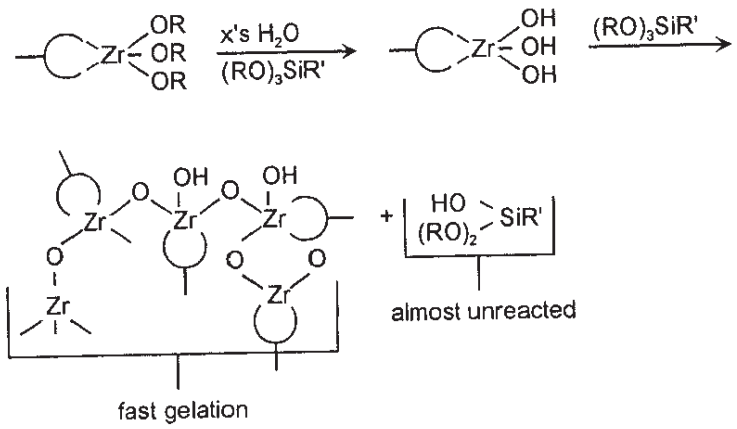


Fig. 8: Model for the precipitation of Zr (ma) alkoxides with excess water addition.

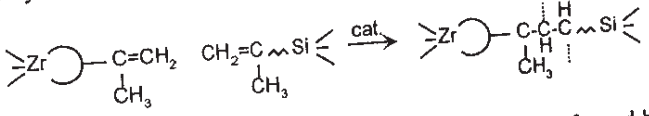
In order to avoid precipitation, the controlled chemical condensation process (CCC [*17*]) was used. The basic idea is to introduce water in form of ≡SiOH groupings using the high reactivity of the ≡ZrOR grouping.

$$\equiv SiOH + ROZr\equiv \rightarrow \equiv SiOZr\equiv + HOR \qquad (4)$$

This would require the formation of an (at least intermediate) ≡SiOZr≡ bond, as it has been proved by Babonneau [*18*] recently in similar systems. In addition to this, a catalytic effect for the condensation of silanols can be expected from ≡Zr(OR) groupings. As shown in [*19*], the prehydrolysis of $(RO)_3SiR'$ to the maximum ≡SiOH content possible for the chosen system leads to a maximum $Zr(ma)(OPr)_3$ to be added without precipitation. After refluxing the system, excess water for gelation can be added without causing phase separation.

For optimizing the silane system for $Zr(ma)(OPr)_3$ addition, H_2O content and ≡SiOH content can be monitored by Karl-Fischer titration and ^{29}Si NMR spectroscopy. In Figure 9, it is shown how the different species develop with time and how ZrOR addition affects ≡Si-O-Si≡ formation.

One can clearly see the development of the different species with time. If methacryloxy silane is used without solvent and prehydrolysed with the amount of water necessary for the complete hydrolysis of the ≡SiOR groupings with HCl as catalyst, up to 50 mole % of a $Zr(ma)(OPr)_3$ complex can be added and after refluxing and water addition, no precipitation takes place. After radical polymerization, the solid material does not show any peaks of free methacrylic acid (C=O frequency, leading to the conclusion that ma is still stably bond to Zr^{4+}. The data were confirmed by ^{13}C NMR spectroscopy. Since in the IR spectrum the C=C double bonds are reduced drastically and degrees of conversion above 90 % (95 % at 120 °C) can be obtained, one has to conclude that the ma bond to Zr^{4+} participates in the polymerization process [*20*].



(5)

The question arises, however, what type of structure is formed by the Zr(ma) complex. For this reason, a diffraction analysis was carried out with bulk materials [*20, 21*]. With X-ray, no crystalline phase could be detected, but with electron diffraction it could be shown that crystalline ZrO_2 is present, mainly in the form of the monoclinic modification with crystallite sizes below 2 nm, which is rather surprising since the preparation temperature never exceeds 120 °C (Figure 10a). One has to conclude that the crystallites are "covered" with ma bond to Zr^{4+} ions, forming a chelate type of interface to the ZrO_2 surface. From this, a structural model can be developed (Figure 10b).

The methacryloxy silane can be partially substituted by other silanes. If silanes with perfluorinated side chains are used [*19*], the fluorinated units diffuse preferentially to the surface of the wet film leading to a low surface free energy layer. This type of coatings adheres very well to polar surfaces despite of the fluorinated groupings due to the polar ≡SiOH groupings. The fluorinated groupings preferentially turn to the air interface, whereas the ZrO_2 nanoparticles remain distributed homogeneously in the layer (EDX profiling). In Figure 11, the process is shown schematically.

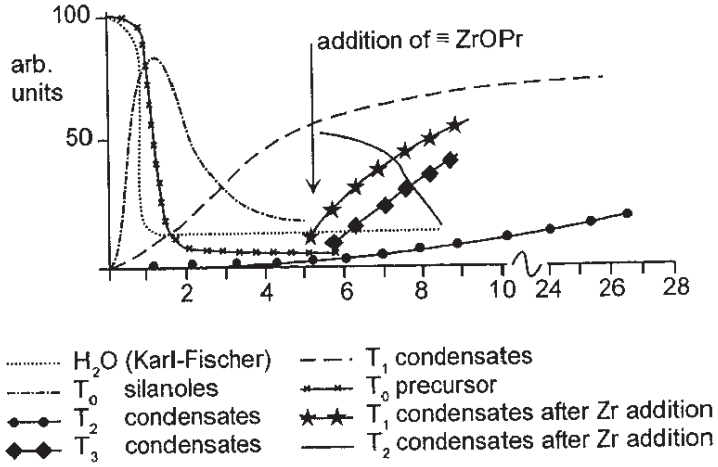


Fig. 9: Hydrolysis and condensation of methacryloxy silane monitored by ^{29}Si NMR spectroscopy and Karl-Fischer titration with and without ≡ZrOR.

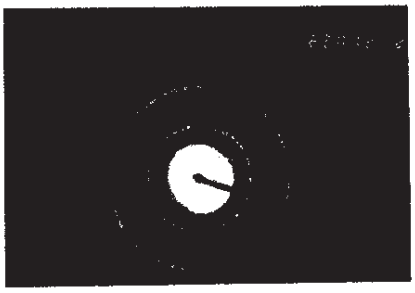


Fig. 10a: Electron diffraction pattern of the ZrO_2 containing nano-composite .

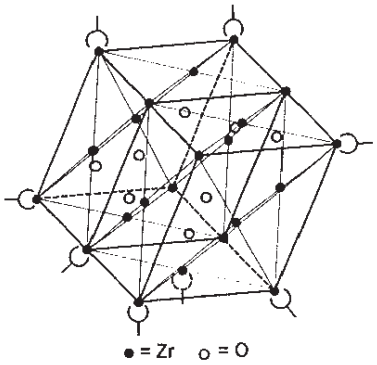


Fig. 10b: Model of the ZrO_2 ma based on the monoclinic ZrO_2 unit cell.

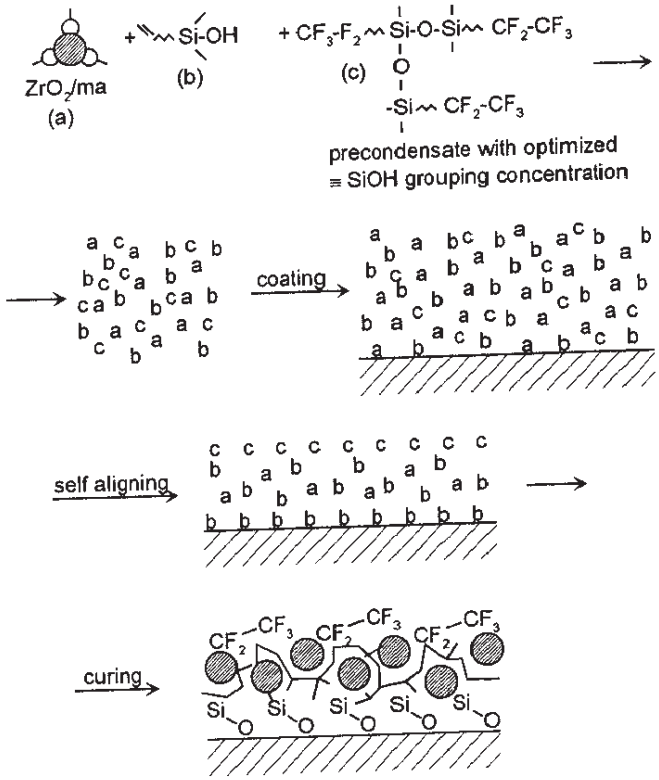


Fig. 11: Synthesis and processing of a perfluorinated grouping-containing low surface free energy nanocomposite coatings.

Due to the selfaligning effect, the concentration of silanes with a perfluorinated side chain can be kept low (only > 0.6 mole %) to obtain surface free energies of about 18 mJ/m². The coatings are highly transparent and abrasion-resistant (2 % haze after taber abrader standard test) and can be easily cured by UV. They can be applied to all types of substrates. Since the processing and properties are mainly depending on the interface of the nanoparticles (e.g. avoiding of agglomeration and gelation during processing, refractive index 1.50 to 1.55 depending on ZrO_2 content, abrasion resistance, transparency), one can speak of so-called interfacial phase determined nanocomposites. This can be considered as a new class of materials with interesting properties.

Another type of interfacial phase-determined materials has been developed based on an epoxide and boehmite or γ-Al_2O_3 with particle sizes in the range of 15

nm. Epoxy silane-based systems have been developed for plastic eye glass lens protection and have been successfully on the market for many years [*10*]. As shown in [*21*], polycondensates based on $(RO)_3Si\text{-}(CH_2)_3\text{-}O\text{-}\overbrace{CHCH_2O}$ with TEOS or Al[iprop]$_3$, in general, do not show the formation of nanoparticles to be detected by photon correlation spectroscopy and can be considered more or less as molecular types of composites after polymerization of the epoxide by methyl imidazole, for example. If boehmite powder suspended in ethanol is added to a prehydrolysed mixture of the epoxide TEOS and Al[iprop]$_3$ after having carried out a ligand exchange reaction of iprop against butoxyethanol in order to slow down the Al alkoxide reactivity according to [*22, 23*],

$$Al(iprop.)_3 + 3CH_3(CH_2)O(CH_2)_2OH \rightarrow Al(O(CH_2)_2O(CH_2)_3CH_3)_3 + 3iprop. \qquad (6)$$

it could be shown that the boehmite catalyses the epoxy polymerization to form a polyethylene oxide network, probably preferentially around the active particles. At the same time, as shown by NMR spectroscopy (Figure 12), ≡Al-O-Si≡ bonds are formed by heterocondensation between ≡AlOH and ≡SiOR.

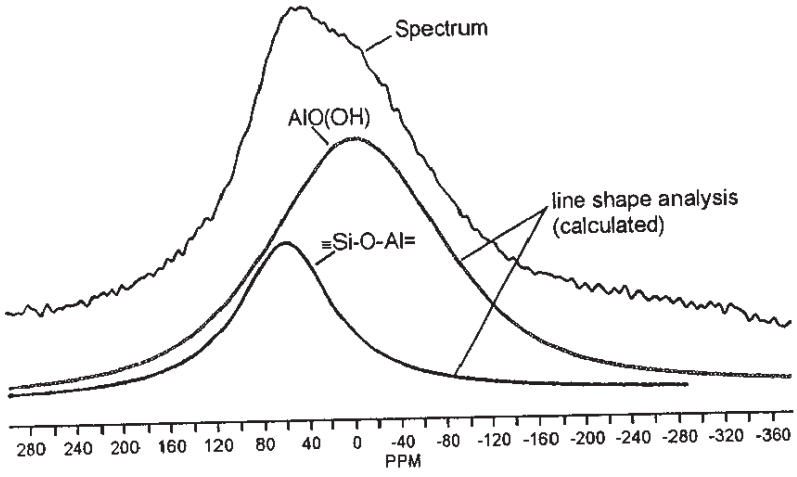


Fig. 12: NMR spectrum of the boehmite/epoxy silane reaction mixture and deconvoluted peaks [*23*].

The liquid systems can be used for coating of glass or plastics and cured between 90 and 120 °C without using any additional catalysts or addition of methyl imidazole. Due to the small particle size, they are transparent. In Figure 13, the schematics of the synthesis of the composite system is shown.

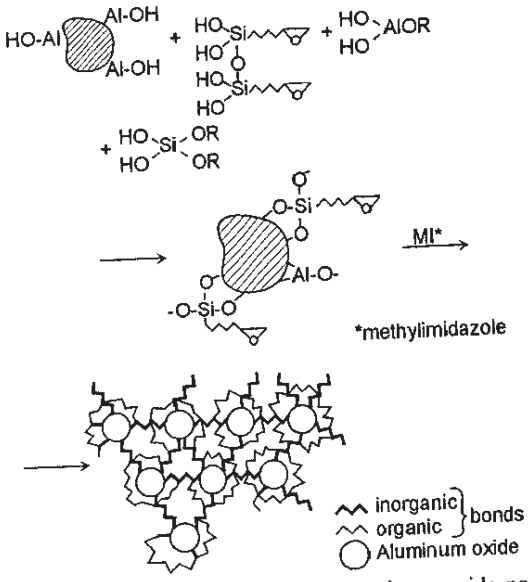


Fig. 13: Reaction scheme of the formation of a aluminum oxide particle-containing nano composite.

After curing, the scratch resistance of these systems (determined by a Vickers diamond scratched over the surface) is surprisingly high compared to polymers or ormocer coatings. In Figure 14, the load of the diamond causing the first visible scratch is shown and compared to polymers and ormocer coatings.

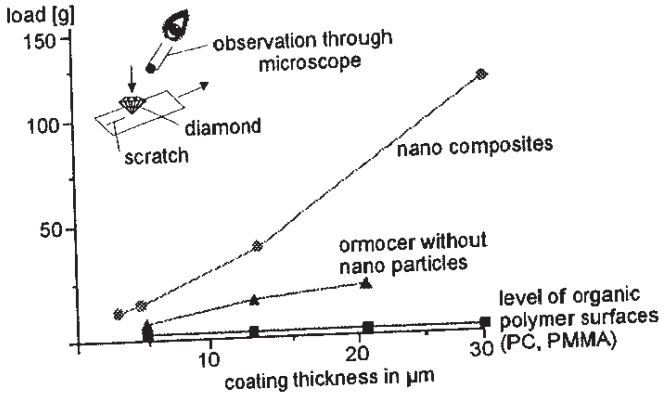


Fig. 14: Comparison of the scratch resistance of various types of coatings; ●: nano-composite; ▲: ormocers and polysiloxanes; ■:organic polymer films.

The surprisingly high scratch resistance is attributed to the change of the matrix structure at the particle's surface, probably leading to more ordered structures at the particle surface (which, for example, already have been established at polymer/metal interfaces). This could explain the surface hardness far above what has been expected from similar composition where alumina is introduced by the sol-gel process in a molecular form. The coating system has been adapted to CR39 eye glass lenses and is industrially used.

Conclusion

The three examples show that special material properties can be obtained by sol-gel based synthesis techniques and control of reaction condition and composition. For this reason, it seems to be of special interest to tailor the dimension of organic as well as of inorganic units. In the case of the hot melt composite, it was of importance to establish organic chains of well-defined length in order to obtain sufficient stress dissipation behavior to increase the overall seal strength considerably. In the case of ZrO_2-containing composites, the formation of nanoparticles with controlled sizes and well developed crystallinity can be obtained, allowing to tailor the refractive index and mechanical properties. The mechanical properties and (which is of high importance) the processing properties depend strongly on the nanoparticle surface properties and the interface to be developed during the composite synthesis. The "interfacial phase" can play an important role if its concentration is high enough. Nanocomposite systems with high surface areas open up an interesting way to new interfacial phase-determined materials.

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