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Coatings for mechanical and chemical protection based on organic-inorganic sol-gel nanocomposites

R. KASEMANN and H. SCHMIDT

Institut für Neue Materialien gem. GmbH, Im Stadtwald, Geb. 43, D-66123 Saarbrücken, Germany.

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Abstract. – The sol-gel process opens the possibility of combining inorganic and organic units on a molecular or nanosized level. The flexible chemical approach of tailoring inorganic structures as well as organic polymeric structures in combination with the new concept of incorporation of nanoscaled metal oxide particles opens the possibility of achieving new multifunctional materials like extremely high scratch resistance, antisoiling properties, antifogging properties and corrosion-inhibitant coatings on metals.

Résumé. – Nano-composites sol-gel organiques et organométalliques utilisés dans l'élaboration de revêtements assurant une protection mécanique et chimique. Le procédé sol-gel offre la possibilité de combiner des unités organiques et inorganiques à l'échelle moléculaire ou nanométrique. La souplesse de la chimie pour façonner des structures inorganiques et des polymères organiques, associée au nouveau concept d'incorporation de nano-particules d'oxyde, rendent possible l'élaboration de nouveaux matériaux multifonctionnels tels que des revêtements extrêmement résistants à l'abrasion, anti-boue, anti-buée et inhibiteurs de corrosion.

Introduction

Sol-Gel processing of inorganic-organic molecular or nanocomposites has gained increased interest in the last decade. A key factor is the incorporation of organic groupings linked to the inorganic backbone, formed by hydrolysis and condensation, e.g. starting from alkoxides. The organic groupings can play the role of network modifiers (alkyl, aryl...) as well the role of a second type of network formers (vinyl, methacryl, epoxy...). Due to the increased relaxation properties by the network modifiers the densification temperatures are drastically decreased in comparison to pure inorganic sol-gel materials. For example, this principle is shown by modification of SiO_2 networks by methyl groups for spin-on glasses [1]. The achievable densification temperatures lower than the decomposition temperature of organics, the possibility of preparing multicomponent materials, the possible incorporation of organically polymerizable groups to form interpenetrating networks and the controllable phase dimensions of the inorganic-organic components (molecular to nanoscaled, ≤ 5 nm) are the reasons for the high interest in this type of materials for a broad variety of applications [2-17]. In these papers a variety of synthesized materials are shown including a type of hard coatings for soft surface protection. These coatings mean while have been sucessfully applied in industry. The present paper is focused on the development of "third" functions into this type of coatings, for example the homogeneous incorporation of metal oxide particles with particles sizes ≤ 50 nm into more or less molecular inorganic-organic composite matrices (Ormocers) for drastically improved abrasion resistence, the incorporation of perfluorinated groupings to achieve low energy surfaces (antisoiling effects), or other components to obtain antifogging behavior or corrosion inhibitation on metals. The material development strategies are summarized in Figure 1.

The first step of the materials synthesis is the classical approach of the synthesis of Ormocer sols by controlled hydrolysis and condensation of metal alkoxides, organically modified metal alkoxides with the known link principles between the inorganic backbone and organics (see Fig. 2) as well as organically functionalized alkoxides to achieve organic polymer structures. In the second step different "third" type of modifiers can be added or special chemical structures can be synthesized to obtain additional functions.

These synthesis routes are described in detail elsewhere [18-25]. The homogeneous incorporation of nanosized metal oxides (≥ 50 nm, e.g. Al_2O_3, ZrO_2, TiO_2)

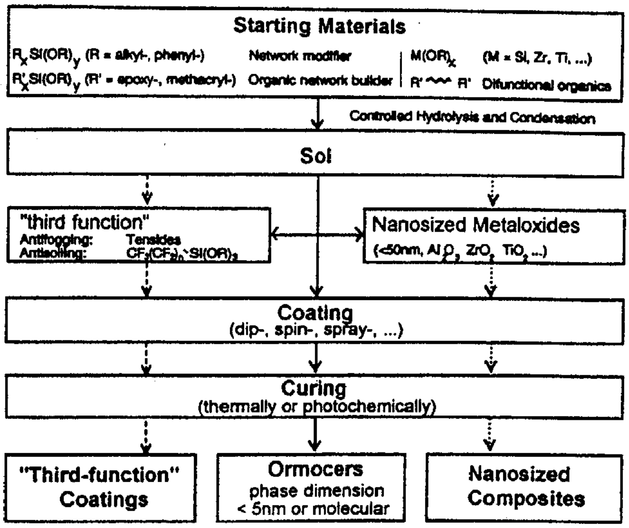

Figure 1. – Basic features of the synthesis strategies.

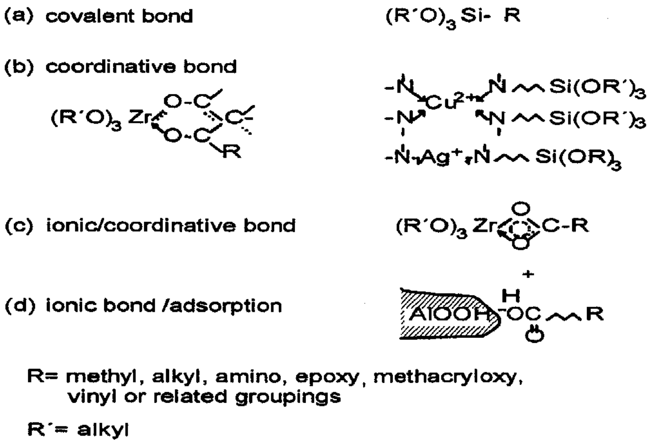

Figure 2. – Link principles between organic and inorganic units.

leads to nanosized composites with drastically improved mechanical properties [18]. The use of side chain fluorinated alkoxy silanes opens the way to achieve low energy surfaces (antisoiling properties) on several substrates [19-21]. The incorporation of tensides in suitable inorganic-organic composites leads to antifogging behavior [22, 23]. Corrosion inhibitant properties are achieved by tailoring the interface between metal surface and coating materials [24-26].

Transparent hard coatings for polymers

Transparent polymers are widely used in industrial applications. They have a lower weight in comparison to glass, can be colored more easily by diffusion of dispersive dyes and have an increased impact resistance. Main disadvantage for all application of transparent polymers is the soft surface and thus the low scratch and abrasion resistance leading to light scattering and decreased transmission. To overcome these problems, transparent "hard coatings" based on polyorganosiloxanes [27] and Ormocer materials (molecular type [13, 28] have been known for a long time as so called "molecular" composites. The increased scratch resistance can be attributed to the "inorganic" backbone, whereas the three-dimensionally linked network of the Ormocer coating shows advantages in comparison to the two-dimensionally cross-linked polysiloxane network.

However, for heavy duty conditions with high abraive stress, these coatings are not sufficient. For this reason the conception of increasing the inorganic phase dimension into a range, where Rayleigh scattering still can be neglected, but the "mechanical properties" of the inorganic phase become obvious. Depending on the difference of the refractive index between particle and matrix, the dimension should be capt below 50 or better below 20 nm. As matrix, a cocondensate of an epoxysilane with TEOS was used. For proper incorporation of the nanoparticels (boehmite sol with 50 nm average partical diameter according to photocorrelation spectroscopy was used), it is of importance to establish a maximum SiOH group concentration. This was controlled by ^{29}Si NMR spectroscopy (monitored during synthesis) Figure 3 shows the synthesis scheme.

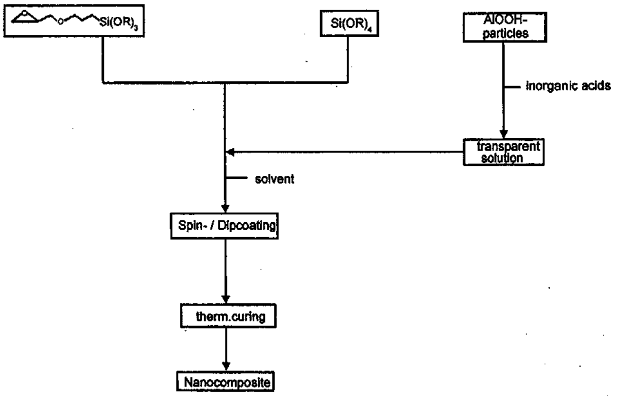

Figure 3. – Synthesis scheme of the inorganic-organic nanocomposite.

The synthesized transparent sols are applied by usual coating techniques (spin coating, dip coating) on polycarbonate surfaces and are cured thermally at 100°C. The coatings with 11 wt. % boehmite particles show perfect optical transparency due to the controlled phase dimensions, very good adhesion proved by cross cut/tape test and remarkable mechanical properties. The scratch resistance, proved by modified Erichson test, strongly depends on the coating thickness, reaches 120 g at a

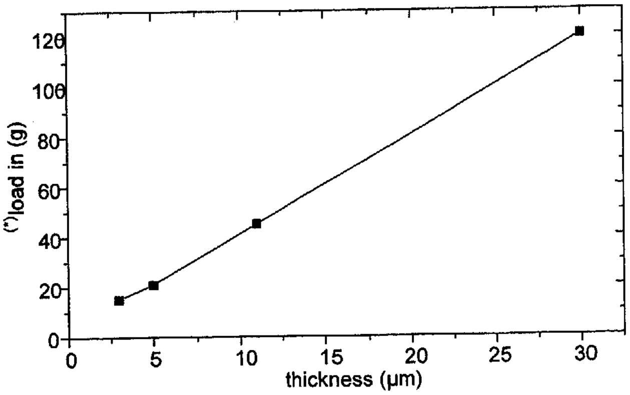

Figure 4. – Scratch resistance depending on the thickness of the coating (diamond load of the first visible scratch by microscope).

thickness of 30 μm (Fig. 4) and exceeds conventional Ormocere hard coatings by the factor 10.

The Δ% haze value after 100 cycles of taber abrader test is the same as measured on float glass (1%). These results can not be explained by simple "addition" of the properties of the inorganic particles and the inorganic-organic matrix. We propose a string covalent bond formation of the particle surface OH groups with sol components by condensation, as shown in Figure 5.

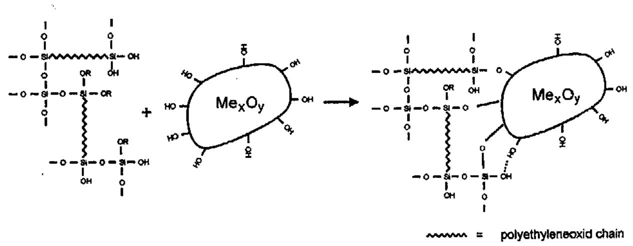

Figure 5. – Scheme of the incorporation of metal oxides into an inorganic-organic sol.

The high interfacial area (particle/matrix) determined the shown, so far unknown material properties, which is still under investigation. Boehmite particles can be substituted e.g. by ZrO_2, TiO_2, γ-Al_2O_3 in the above mentioned manner with similar material properties. The novel concept for the synthesis of inorganic-organic nanocomposites opens the possibility for the manufactoring of transparent materials with new material properties and, thereby, a wide range of applications, which are not restricted to scratch resistant coatings for transparent polymers.

Antifogging coating materials

Fogging (droplet condensation of water) is a common appearance especially on glass surfaces and leads to a loss of transmission. Pristine glass surfaces show contact angles for water in the range of 10° [29], but under environmental conditions, hydrophobic components are strongly absorbed to the surface due to the ionic character of the SiOH groups leading to the increase of the contact angle of glass surfaces up to 70°. With increasing contact angles, water vapor condensates not as a film (antifogging behavior), but (with increased contact angles) as droplets. For this reason, a permanent wettability is desired for a variety of applications. Many attempts have been made to establish permanent wettability, mainly by application of coatings with hydrophilic matrices. These "static" modifications show, in general, low long-term stability because of the adsorption of hydrophobic components. For this reason a synthesis route has been developed for an inorganic-organic composite system with high concentrations of non-ionic hydrophilic C–OH groupings to decrease the strength of adsorbed hydrophobic components and the incorporation of hydrophilic components (non-ionic tensides) to achieve controlled release of the tensides to the surface [22, 23]. The released tensides can decrease the interfacial tension of condensed water and leads to film condensation. The concept of controlled release of tensides already has been demonstrated in polyurethane matrices [30]. These coatings show long-term antifogging effects. Disadvantage for several applications is the soft polymer surface. For this reason an inorganic-organic nanocomposite starting from epoxy-functionalized silanes where a tailored amount of the epoxy groups is ring-opened to dioles is developed. The synthesis scheme is shown in Figure 6.

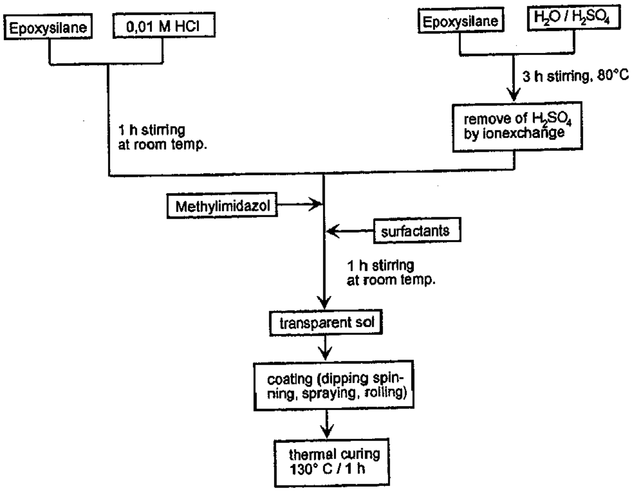

Figure 6. – Synthesis scheme of the hydrophilic coating materials.

The ring-opening reaction of the epoxide forming the glycole is proved by ^{13}C NMR, shown in Figure 7.

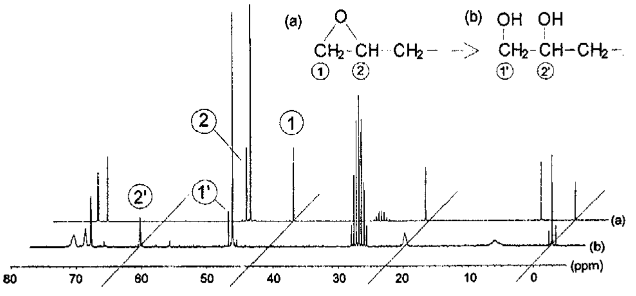

Figure 7. – Hydrolytic ring-opening shown by ^{13}C NMR. Signals for the epoxy group at 43.3 ppm and 51.4 ppm (① and ②) disappear during synthesis and the diole (50.7 and 64.8, ①' and ②') is formed.

The coated glass surfaces show high scratch and abrasion resistance due to the inorganic-organic nanocomposite structure. The coatings show long-term stable antifogging effects, tested for a period of one year til now. Figure 8 shows a fogging experiment of a coated mirror in comparison to an uncoated one.

Because of the shown properties, a variety of applications (architectural glazing, automotive industry) are possible.

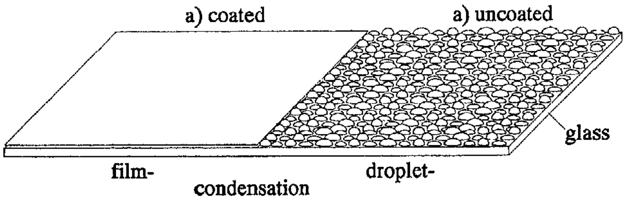

Figure 8. – Scheme of film condensation (antifogging) on the coated surface in comparison to droplet condensation (fogging) on glass surfaces.

Low energy coating materials with antisoiling properties

Low surfaces free energy surfaces are mainly known from fluorinated polymers. However, these polymers are soft, not very transparent, and, due to the bulk property of antiadhesion, often adhesion problems occur. It is well known from grafting processes or Langmuir-Blodget films, that molecular interactions can be used to generate well defined interfacial structures. The driving force in all these cases are thermodynamics, which tend to decrease the ΔG value of the system. For this reason, it should be possible to generate a self organising system containing polar components and perfluorinated systems linked by relatively long spacers providing mobility. By the use of the polar substrates (glass, activated polymers) liquid coating films should arrange in a way facing the polar groupings to the substrate and the perfluorinated to the (dry) air interface. The chosen experimental approach was the homogeneous incorporation of side-chain fluorinated alkoxysilanes in a molecular inorganic-organic nanocomposite based on methacryloxypropyltrimethoxysilane and a zirconia alkoxide complexed with methacrylic acid, described in detail elsewhere [19, 20]. The developed synthesis strategy is shown in Figure 9.

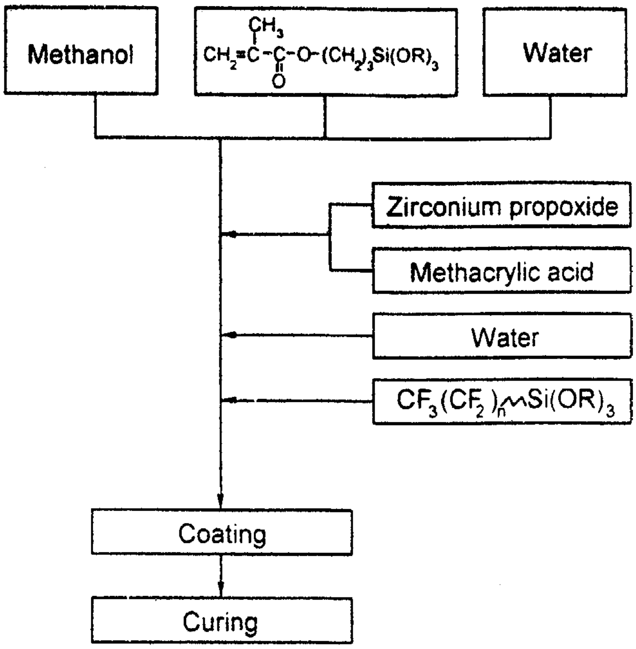

Figure 9. – Synthesis scheme of the low energy coating material.

The sols can be applied by usual coating techniques on polymer substrates (PC, SAN). The coatings can be cured by UV-exposure and/or thermally. The transparent coatings show very good adhesion, scratch resistance of 12 g and after 100 cycles taber abrader test a $\Delta\%$ haze value of 1.5% (uncoated polycarbonate >30%). The wetting behavior of the coatings, investigated by contact angle measurements is shown in Figure 10.

The set of contact angles reach a plateau at the addition only 1% of the side-chain fluorinated alkoxides. This is due to an enrichment of fluorinated chains at the air interface, proved by ESCA-measurements [19]. The decreased concentration of fluorinated chains at the substrate/coating interface leads to the shown good adhesion. The increase of fluorinated chains can be explained by thermodynamics, that means that the interfacial energy is minimized. The calculated surface free energies of the coating, starting from the set of contact angles is in range of 17-19 mJ/m^2 (polytetrafluorethylene: 20 mJ/m^2). The antisoiling properties of the coatings are shown in Figure 11.

Using the same principle of enrichment of fluorinated chains in a sol-gel system based on methyltrialkoxysilane, tetraalkoxysilan, silica-sol and side chain fluorinated

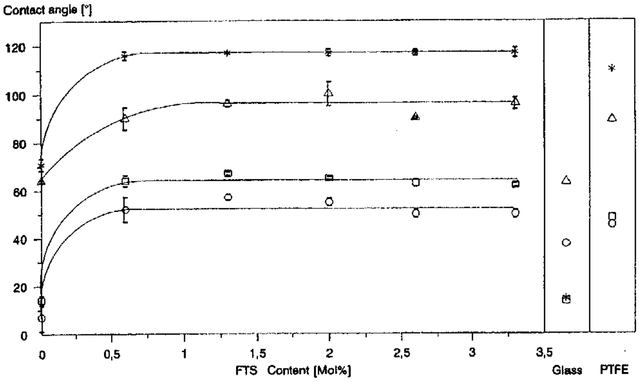

Figure 10. – Contact angle measurements depending on the concentration of sidechain fluorinated trialkoxy silane (FTS) for water (*), glycerol (Δ), l-octanol (O) and hexadecane (□) in comparison to glass and PTFE.

alkoxysilanes coating materials for glass surfaces are synthesized [21]. These coatings are cured at 350°C, are transparent and show similar wetting behavior and thereby low surface free energies as shown above. The mechanical properties of these coatings are similar to glass surfaces. The thermodynamically driven enrichment of perfluorinated chains, linked to the inorganic backbone of an inorganic organic composite, is a new general principle to obtain low energy contings for a wide field of applications.

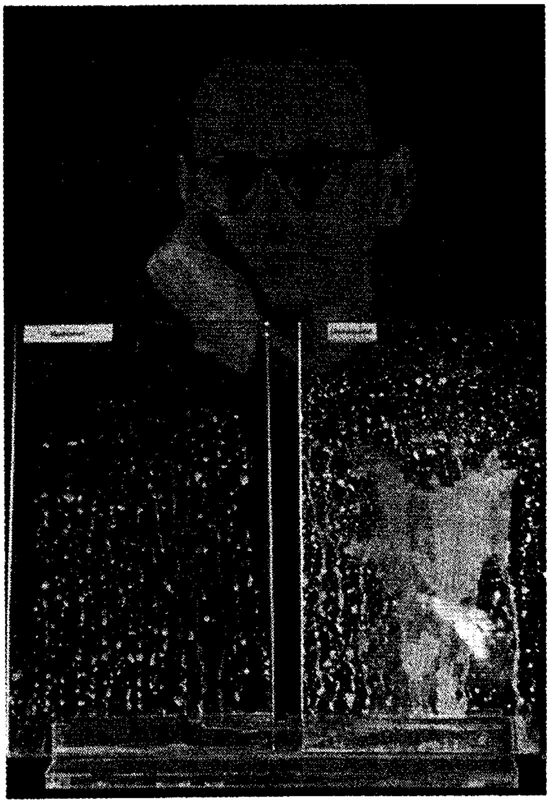

Figure 11. – Uncoated (right) and low energy coated surface soiled with a suspension of aerosil, motor oil and water.

Corrosion inhibitant coatings for metal surfaces

As shown in the previous examples, the systems consist of several components with special functionalities. The possibility of using one of the components to create special interfaces by establishing high SiOH contents was already shown with the first example (ultra hard coatings). The question arises whether this principle can be used for tailing of the interfaces for metal protection, for example aluminum. Aluminum surfaces are covered by Al_2O_3 and in wet atmosphere with H_2O Al hydroxides are formed on the surfaces. For permanent protection of Al surfaces, a passivation layer using a chromation process (Cr–VI treatment) has to be generated followed by a polymer protective coating. It was assumed that SiOH and SiOR group containing coatings should form a stable bound to AlOH containing surfaces according to eg. 1 or 2:

$$\equiv \mathrm{SiOH{+}HOAl} = \rightarrow \mathrm{Si\text{-}O\text{-}Al} = \mathrm{H_2O} \qquad (1)$$

$$\equiv \mathrm{SiOR{+}HOAl} = \rightarrow \mathrm{Si\text{-}O\text{-}Al} = \mathrm{HOR} \qquad (2)$$

Coatings prepared from epoxysilanes and propyltrimethoxy silane (PTMS) using F^- as a catalyst show an excellent corrosion protection [24], but are very brittle and form cracks by bending. For this reason, an organic chain was introduced to connect the epoxy group. Diols were chosen for this purpose (Fig. 12).

The epoxy functions can be reacted to polyethylenoxide chains or can be connected by polyaddition reaction with

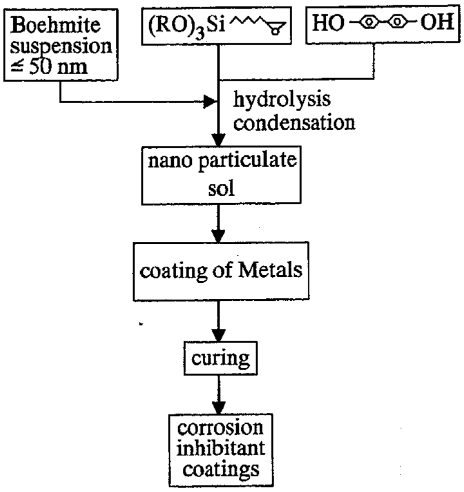

Figure 12. – Synthesis scheme of preparation of the corrosion inhibitant nanocomposite system for metals.

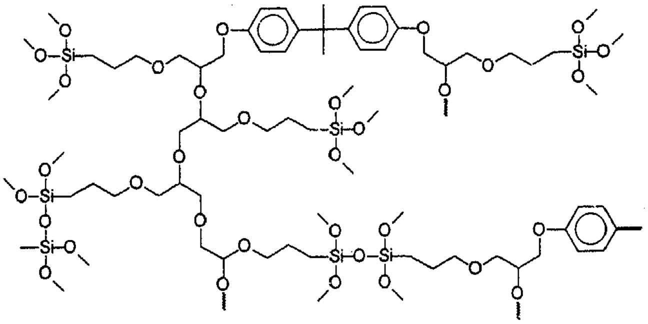

Figure 13. – Structure model of the synthesized epoxy silane/bisphenol A matrix.

the aromatic diol (e.g. bisphenol A) in the presence of a basic catalyst (1-Methylimidazol) (see Fig. 13) [25, 26]. The coatings can be applied without any pretreatment by simple coating techniques (spray, dip, spin coating) and are cured thermally at 130°C for 1 hour. The coatings are transparent, show excellent adhesion on untreated aluminum, magnesium and silver. The high scratch and abrasion resistance is due to the nanosized structure of the material.

Figure 14 shows the corrosion behavior after 1 month of salt spay test in comparison to an uncoated substrate.

The results for coated magnesium surfaces are similar to the coated aluminum substrates. The coatings are also stable against filiform corrosion (1 hour conc. HCl, 2 weeks saturated water vapor atmosphere at 40°C). Only by the use of the short-chain organic crosslinking by diols it has been possible to obtain scratch resistance, corrosion inhibition as well as sufficient flexibility (bending after coating does not effect the protection). It is assumed that the interface is formed by heterocondensation of silanols with surface Al–OH–groups. This interface then is stabilized by the Ormocer nanocomposite matrix and the corrosion process can not proceed. This hypothesis is supported by the effect that no corrosion takes place during salt spray- or filiform test along the interface on cross-cuts made to the coating.

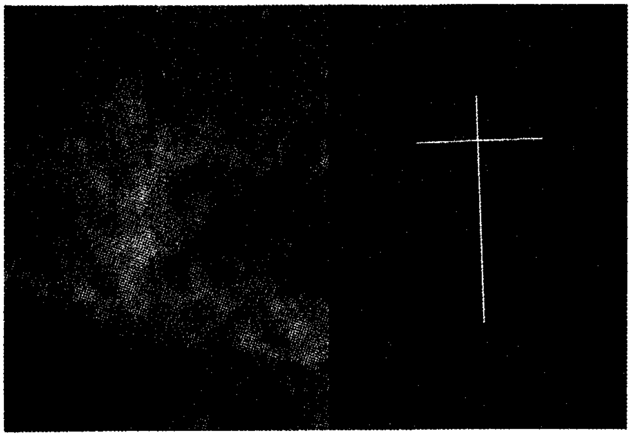

Figure 14. – Coated and uncoated aluminum samples after 4 weeks of salt spray test.

Interface tailoring is an interesting way to achieve transparent, scratch and abrasion resistant inorganic-organic nanocomposite coatings for metals with high corrosion protection as a "third" function.

Conclusion

The sol-gel process for the preparation of molecular or nanoscaled inorganic-organic composites is a flexible tool for tailoring material properties for a variety of applications. The described new concept of incorporation of nanoscaled metaloxide particles is a tool to achieve so far unknown mechanical properties. The possibility of introducing "third-function" is one of the most interesting fields in sol-gel inorganic-organic composites science, that is in its infancy.

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