Hybrid Sol−Gel-Derived Polymers: Applications of Multifunctional Materials

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Received February 12, 2001

The homogeneous combination of inorganic and organic moieties in a single-phase material provides unique possibilities to tailor the mechanical, electrical, and optical properties with respect to numerous applications. The synthetic pathway follows the well-known sol−gel procedure. Nevertheless, the establishment of defined hybrid products necessitates a basic understanding of the underlying chemistry as well as of the parameters influencing the processing techniques. Modern spectroscopy provides versatile tools, e.g., multinuclear NMR experiments and Raman scattering to investigate the sol−gel processing of organo(alkoxy)-silanes in their co-condensation reactions with main group or transition metal alkoxides as well as in their copolymerization reactions with each other or with organic molecules. This almost infinite modular design concept has led to the industrial application of coatings for transparent plastics, glasses, and metals to prevent these substrates from mechanical abrasion, permeation, or corrosion or to achieve decorative functions. Further passive optical properties can be realized by generating submicrometer surface patterns. By the integration of organic or inorganic dopants, like dyes or nanoparticles, highly sophisticated multifunctional hybrid polymers or nanocomposites are accessible and have become important to achieve active optical functions, e.g. switching, light harvesting, or storage media. Recently developed porous and dense bulk hybrid polymers have shown that the range of possible applications is not limited to surface refinement by coatings. This contribution reviews the present status as well as the perspectives of these types of advanced materials.

1. Introduction and Classification of Hybrid Polymers

Nanotechnology is one of the key technologies of the 21st century.[1] The unique properties of nanostructured materials have now been elucidated for several years.[2,3] A wet chemical method creating nanocrystalline or nanoscaled amorphous materials is the sol−gel process.[4,5] With this well-established synthetical technique inorganic materials (glassy or ceramic) and inorganic−organic (hybrid) polymers or nanocomposites can be processed to form (nano)particles, coatings, fibers, or bulk materials (Figure 1).

Inorganic sol−gel-derived materials had been investigated and commercialized a few decades ago[6,7] and due to the profound understanding of the underlying chemical and technical processes[4,5] are still present as important examples of large-scale applications of the sol−gel technology.

In the meantime, all products illustrated in Figure 1 are also available on the basis of inorganic−organic (hybrid) materials (ORMOSILs,[8−10] ceramers,[11,12] ORMOCERs,[13] nanomers[14]). To a certain extent, these hybrid materials combine the most important properties of their constituents, like high transparency (glasslike), low processing temperatures (polymer-like), sufficient thermal stability (silicone-like), and are easily accessible because of an unique availability of the respective precursors (commercially available metal alkoxides and organo(alkoxy)silanes as well as nanoparticles). A limited selection of these precursors is shown in Figure 2.

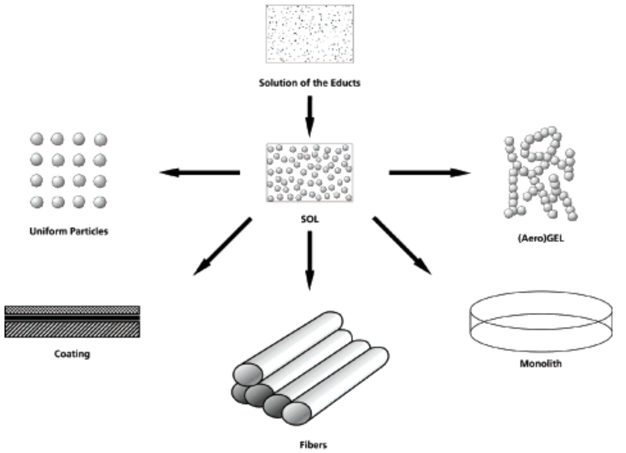

Figure 1. Shape of different products available through processing by sol−gel technology (drawn in accordance with ref 4).

Besides the simple metal or silicon alkoxides that—after hydrolysis—lead to the formation of an inorganic oxidic network, organo(alkoxy)silanes can be used to incorporate polymerizable organic substituents (epoxy, vinyl, or methacryloxy groups) into the final product, because the Si−C bonds in these molecules are stable under the mild conditions of sol−gel processing. The polymerization reactions of the functional organic groups can be induced by thermal or photochemical means,

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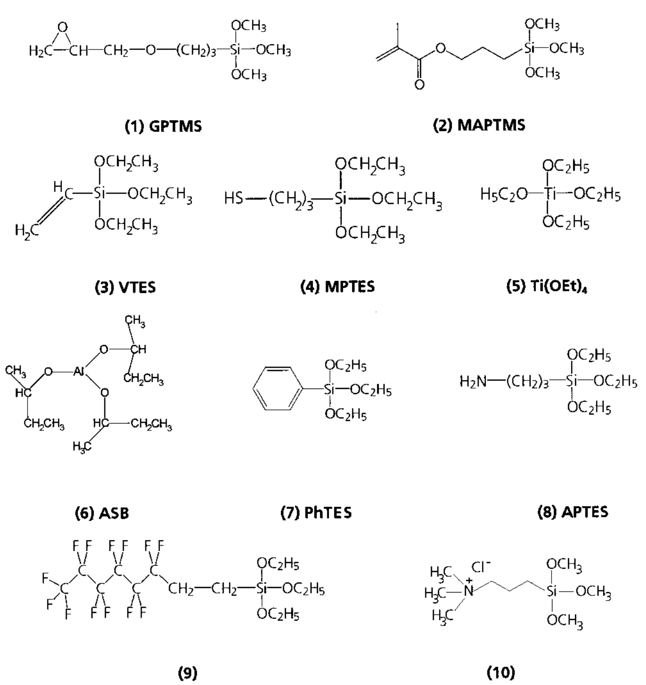


Figure 2. Organo(alkoxy)silanes and metal alkoxides serving as precursors for sol–gel-derived (hybrid) materials.

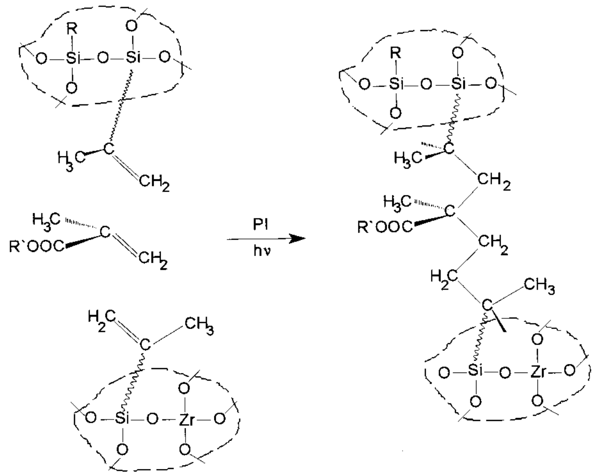


Figure 3. Cross-linking of inorganic clusters or nanoparticles via photochemically induced polymerization of (meth)acrylic functional groups.

thereby cross-linking the preformed nanosized inorganic moieties as schematically illustrated in Figure 3.

This simplified picture shows the principal possibilities to vary the composition, micro- or nanostructure, and, correspondingly, the properties of hybrid sol–gel-derived materials. The inorganic skeleton can be modified by starting from many different silicon, main group, or transition metal alkoxides that predominantly influence the mechanical, optical, and thermal properties, whereas the organic part is modified by selecting certain types out of an immense number of available organo(alkoxy)silanes as well as organic monomers or prepolymers, which are responsible for the resulting flexibility and processability. The inorganic part can either be more or less molecularly dispersed (clusterlike) or consists of nanosized, comparatively hard particles.

This procedure is just one of a series of comparatively simple wet chemical methods to produce nanophase materials via sol–gel techniques. Many similar synthetic pathways have been investigated throughout the past decade and were extensively reviewed elsewhere.[15–19] The huge number of possible compositions, synthetic routes, and potential applications is one of the most attractive features of this research field. However, while offering versatile methods to synthesize novel and advanced multifunctional materials and tailor their properties to different requirements, there has been severe criticism concerning the still insufficient number of effectively realized industrial applications.[20,21]

Consequently, most reviews have a strong focus on the chemical background of the material synthesis or intend to elaborate on common structural principles and just mention potential or claimed applications. Therefore, this contribution was more or less written from the point of view of applied research. This seems to be justified, because on one hand the results of the basic research work performed throughout the world, and which are of utmost importance for any successful technology, have already been excellently presented to the public. On the other hand there seems to be a strong need to increase the public knowledge about the applied research field of sol–gel technology and its achievements.

Inorganic–organic materials can be grossly divided into two major classes:[15,17]

Class I. Organic molecules, prepolymers or even polymers are embedded in an inorganic matrix. These materials are synthesized by carrying out the hydrolysis and condensation of the inorganic compound, i.e., the formation of the inorganic network, in the presence of the organic compound or by polymerizing organic monomers in porous inorganic hosts. Only weak bonds exist beween both phases.

Class II. The inorganic and organic components are connected by covalent bonds. This approach requires molecular precursors that contain a hydrolytically stable chemical bond between the element that will form the inorganic network during sol–gel processing and the organic moieties.

The most prominent examples representing class I are organic dyes or biomolecules incorporated in porous sol–gel matrixes.[22–24] The guest molecules are physically dissolved together with the precursors of the inorganic host (e.g., tetraethoxysilane, TEOS, or tetramethoxysilane, TMOS) or introduced to the sol state and become entrapped in the gel or xerogel resulting from condensation and drying of the mixture, eventually after the shaping process (see Figure 2). In these cases, sol–gel-based low temperature processing is an elegant way to combine the unique optical or catalytic properties of organic constituents with the inertness and transparency of a widely inorganic environment. Sol–gel biosensors[25] and active laser devices[26] have been developed by this approach. A lot of further examples may be found in the above-mentioned review papers.

Alternatively, the organic components can be chemically modified to covalently attach them to the inorganic network. A few examples of the chemical reactions used to synthesize silylated dyes are displayed in Figure 4.

The chromophores after silylation are accessible to common hydrolysis and polycondensation reactions together with the more simple precursors shown in

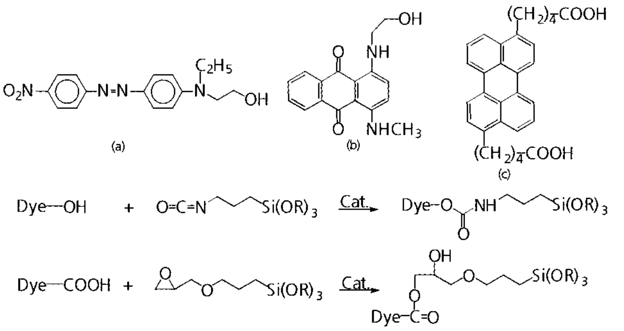


Figure 4. Structure and chemical modification of selected organic dyes for sol–gel processing.

Figure 2, thereby giving rise to an even broader range of class II materials. The covalent attachment together with the higher network density in hybrid polymeric materials enables one to enlarge the incorporated amount of the organic ingredients, reduces dye leaching problems, and, in special cases, leads to stabilizing effects, possibly by isolating the dye molecules from each other or from their degradation products as well as reducing the oxygen permeation rates inside the matrix.[22,25,27–29]

These first examples illustrate the complexity and the almost infinite range of possible combinations of silicon alkoxide precursors to synthesize hybrid sol–gel-derived materials. Structural features and properties are further extended by the additional use of transition metal alkoxides[30] and organic monomers or prepolymers.[31] Under these circumstances, a detailed knowledge about the chemical reactions taking place during the hydrolysis and condensation steps between the organo(alkoxy)-silanes and the respective metal alkoxides as well as other possible components is necessary to design defined hybrid polymers or nanocomposites.

2. Chemical Reactivity and Characterization of Hybrid Sol–Gel Materials

If the hybrid system is not built up from nanocrystalline components, the intricate mixture of inorganic and organic phases in most cases leads to amorphous materials. Therefore, X-ray or neutron scattering methods, which are of major importance to study the size and short-range order of the inorganic moieties present, e.g., in transition metal oxide sol–gels[32] are less applicable. Other techniques, like multinuclear NMR– or FTIR-spectroscopy and Raman scattering have become important tools to investigate the chemical and structural background of sol–gel-based hybrid materials.

The principal chemical reactions involved in the initial steps of sol–gel processing of inorganic and hybrid sol–gel materials are given below (Scheme 1).

Practically any chemical element (**E**) can be transformed into its alkoxide and thereby used in sol–gel processes.[33,34] Meanwhile a lot of mixed alkoxides are also available, which can be favorably used to control the stoichiometry of ceramic sol–gel materials.[35] The hydrolysis and condensation reactions of these simple alkoxides have already been studied in detail.[4,5] The most important aspect for the synthesis of hybrid polymers is the fact that Si–C bonds are hydrolytically stable, thus enabling the integration of organic substituents (**R**) into the preformed inorganic network.

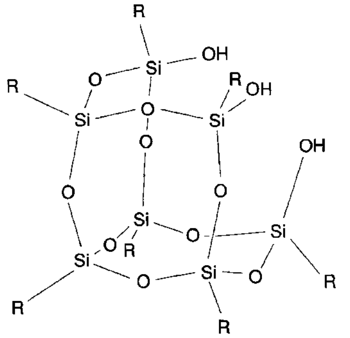


Figure 5. Silicon oxide cluster probably present in sols derived from organo(alkoxy)silanes (drawn in accordance with ref 19).

Scheme 1. Hydrolysis (1, 3) and Initial Condensation Reactions (2a,b, 3a,b) of Main Group or Transition Metal Alkoxides (E(OR)$_n$) and Organo(alkoxy)silanes (R–Si(OR)$_3$)

$$\mathbf{E}(OR)_n + m\,H_2O \longrightarrow \mathbf{E}(OH)_m(OR)_{n-m} + m\,ROH \qquad (1)$$

$$2\,\mathbf{E}(OH)_m(OR)_{n-m} \longrightarrow (RO)_{n-m}(HO)_{m-1}\mathbf{E}\text{-O-}\mathbf{E}(OH)_m(OR)_{n-m-1} + ROH \qquad (2a)$$

$$2\,\mathbf{E}(OH)_m(OR)_{n-m} \longrightarrow (RO)_{n-m}(HO)_{m-1}\mathbf{E}\text{-O-}\mathbf{E}(OH)_{m-1}(OR)_{n-m} + H_2O \qquad (2b)$$

$$\mathbf{R}\text{-Si}(OR)_3 + m\,H_2O \longrightarrow \mathbf{R}\text{-Si}(OH)_m(OR)_{3-m} + m\,ROH \qquad (3)$$

$$2\,\mathbf{R}\text{-Si}(OH)_m(OR)_{3-m} \longrightarrow \mathbf{R}(HO)_{m-1}(RO)_{3-m}\text{Si-O-Si}(OR)_{3-m-1}(OH)_m + ROH \qquad (3a)$$

$$2\,\mathbf{R}\text{-Si}(OH)_m(OR)_{3-m} \longrightarrow \mathbf{R}(HO)_{m-1}(RO)_{3-m}\text{Si-O-Si}(OR)_{3-m}(OH)_{m-1} + H_2O \qquad (3b)$$

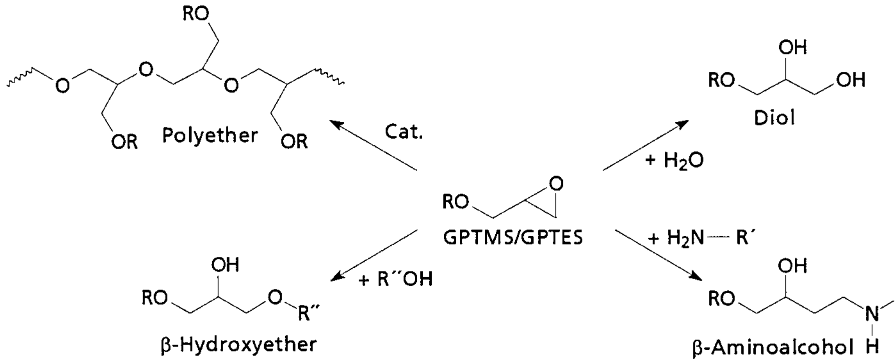
In recent years, the widespread use of highly sophisticated NMR facilities—even for investigating the solid state of matter—has contributed to a wealth of knowledge about the structural features present in the amorphous networks of hybrid sol–gel materials. The connectivity of the inorganic network has been studied by ^{29}Si, ^{27}Al, and ^{17}O NMR techniques.[36–39] The latter nuclei have been useful to study the existence of Si–O–Ti and Si–O–Zr-bonds in liquid sols[37] and to verify the homogeneous distribution of T and Q sites within hybrid model systems.[38] The results demonstrate that more or less highly condensed oxidic networks are formed resembling silsesquioxane moieties, which can be regarded as model compounds for sol–gel processes.[40] In this context the targeted synthesis of organically sustituted polyhedral silsesquioxanes (POSS) has become an important branch of hybrid sol–gel chemistry,[41] and well characterized new nanosized building blocks are now commercially available.

Figure 5 shows one simplified model of an incompletely condensed, substituted silicon oxide cluster probably present in the colloidal solutions evolving from the hydrolysis of organo(alkoxy)silanes.

It is important to note that similar clusters have been isolated from sols derived from transition metal alkoxides, which have been modified by chelating ligands, like acetic acid, (meth)acrylic acid, acetylacetone, etc.[42–44] The stability of these complexes might lead to a new family of metal alkoxide based hybrid nanocomposites.[45–47]

Because of the complexity of the possible chemical reactions (cf. Scheme 1) and the numerous parameters influencing the hydrolysis and condensation of organo-(alkoxy)silanes (pH, temperature, catalyst, water/silane ratio[48]) a more or less broad distribution of dimers, oligomers, and higher condensation products can be

Scheme 2. Possible Reaction Pathways of Epoxy Groups Present in GPTMS or 3-Glycidoxypropyltri(ethoxy)silane (GPTES)



expected and has been confirmed by chromatographic experiments. Size exclusion chromatography (SEC) was used to investigate the molar mass distribution in sols obtained from vinyltrimethoxysilane,[49] (3-glycidoxypropyl)trimethoxysilane,[50] and (3-methacryloxypropyl)trimethoxysilane.[51]

The results can be interpreted in the sense of initial formation of small clusters or oligomers, which grow to larger polycondensates presumably by a cluster−cluster aggregation mechanism. The peripheral positions of the organic substituents as illustrated in Figure 5 are important to allow subsequent polymerization reactions to cross-link the individual inorganic condensates and embedding them into an organic matrix. The high transparency of the resulting hybrid polymers is a further hint to their submicrometer or nanostructural phase size. Thus, hybrid polymers can be regarded as nanocomposites with a “transparent filler”. As the high reactivity of metal alkoxides toward hydrolysis seems to generate metal−oxo−hydroxo clusters even in the presence of less reactive silicon alkoxides[36] there is no sharp borderline between molecularly dispersed hybrid polymers and nanocomposites derived from alkoxides and nanoparticles.

The synthesis of precisely defined submicrometer structures can be difficult, especially if heteroelements (mostly Al, Ti, Zr, Sn) and reactive organic substituents R are present. This situation has triggered activities to start with predetermined inorganic nanobuilding blocks and cross-link them via well-known organic polymerization reactions[52,53] or vice versa.[54]

Still more work has to be performed regarding the reactions of organo(alkoxy)silanes, if polymerizable functional groups are involved. The epoxy group present in one of the very important precursors, (3-glycidoxypropyl)trimethoxysilane (GPTMS, Figure 2, **1**) or its ethoxy derivative (GPTES) can either undergo hydrolysis or alcoholysis to form the corresponding diol or β-hydroxy ethers or polyaddition reactions to form polyether linkages (Scheme 2).

In this case, ^{13}C NMR techniques—especially in the solid state—seem to reach their limitations due to very similar chemical shifts of the carbon atoms adjescent to the different types of oxygen atoms.

Vibrational spectroscopies, especially Raman scattering techniques, have become a versatile tool to conveniently monitor the hydrolysis reactions of organo(alkoxy)silanes[55−58] and to continuously observe the presence of their functional groups throughout the sol−gel process as well as their polymerization reactions. As an example, the Raman spectrum derived from a sol of a hybrid material useful for coating glasses is displayed in Figure 6.

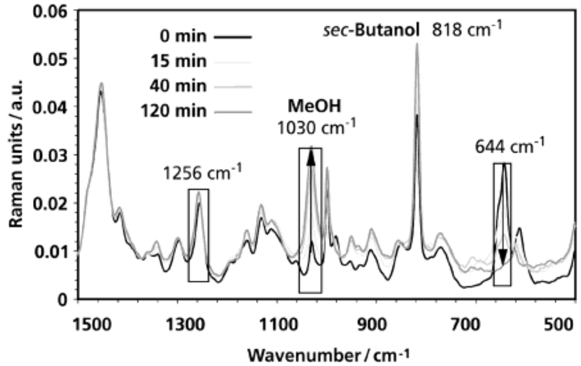


Figure 6. Sequence of Raman spectra demonstrating the spectral changes during hydrolysis of a mixture of GPTMS, ASB, PhTMS, and APTES (for abbreviations, see Figure 2).

The constituents forming the sol were GPTMS, aluminum-tris(2-butylate) (ASB, Figure 2, **6**) and phenyltrimethoxysilane (PhTMS, Figure 2, **7**), respectively. The removal of the alkoxy groups during hydrolysis can be quantitatively followed by the vanishing Raman emission at 644 cm^{-1}, which is due to the symmetric stretching vibration of the trimethoxysilyl moieties of GPTMS, and the evolution of methanol and butanol is indicated by the increasing Raman emissions around 1030 and 818 cm^{-1}, respectively, which result from the C−O stretching and C−C−O-bending vibration of the solvent molecules. The ring breathing mode of the epoxy moieties located at 1256 cm^{-1} concurrently demonstrates the stability of these groups under the chosen hydrolysis conditions, i.e., stoichiometric amounts of water and stirring for 2 h at about 10 °C. All these features can be advantageously observed by a single experiment within short acquisition time intervals and by investigating just one spectrum.

The subsequent polyaddition reaction of the epoxy groups in the thermal curing step of a coating formed from the above sol can be detected either via Raman measurements, which are also possible in the gel or xerogel state, or by measurements in the NIR spectral range.[29] Figure 7 depicts the series of spectra obtained during heating of films of the above-described composition.

The combination bands due to the oxirane ring decline and combination bands of alcohols do not appear,

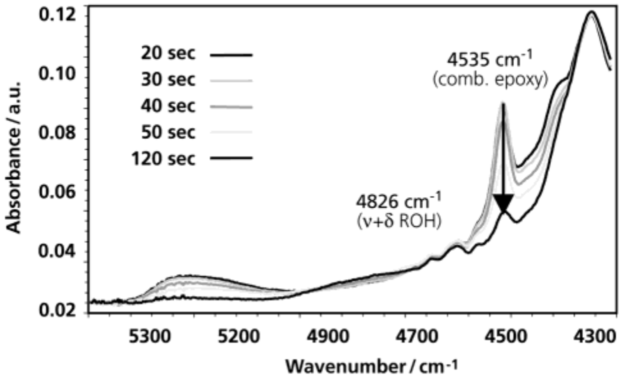


Figure 7. Sequence of NIR-spectra demonstrating the spectral changes during heating of a coating derived from a hydrolyzate of GPTMS, ASB, PhTMS, and APTES at 160 °C.

verifying that practically no diols or β-hydroxyethers are formed from the epoxy moieties during the solidification of the film (cf. Scheme 2). Water and alcohols still present in the gel state are removed very fast (within seconds) from the thin layers. These results are a strong indirect proof of the predominant homopolymerization of the epoxy functions in the curing process leading to the hybrid inorganic−organic network.

Similar experiments have been performed on hybrid polymers derived from (3-methacryloxy)propyltrimethoxysilane (Figure 2, **2**), and it was shown that a high degree of polymerization of the organic groups can be achieved.[59] However, in accordance with Flory's theory, neither the inorganic condensation nor the organic polymerization will go to completion in the hybrid polymeric materials and a certain degree of internal stresses, intrinsic defects, "grain boundaries", or interfacial incompatibilities will result from this aspect. These deficiencies will limit the ultimately achievable figures of merit of properties and, consequently, the range of actual applications. One important example are residual Si−OH groups contributing to the luminescence quenching of rare-earth-metal ions incorporated in hybrids and to the optical loss phenomena observed in optical waveguide applications (cf. section 3.5).

Nevertheless, the advantages of sol−gel-derived hybrid materials and the steady improvement of knowledge with respect to their mechanical, electrical, and optical properties have already been demonstrated by several well-established industrial applications and numerous application oriented research activities all over the world. Meanwhile an increasing number of industrial research groups and startup companies dealing with hybrid materials seem to indicate a major breakthrough of the technology.

3. Industrial Applications and Actual Developments of Hybrid Polymers

3.1. Exploiting Mechanical Properties: Abrasion Resistant Coatings for Plastics. Hard poly(methylsiloxane)s and related colloidal silica containing coating formulations have been developed several decades ago and still find industrial application in improving the wear and abrasion resistance of engineering plastics, e.g. on top of headlights of cars made from polycarbonate (PC) or side windows in busses made from poly(methyl methacrylate) (PMMA). The respective formulations or coated products are well-known (e.g. AS 4000, General Electric Co., Lucite, Dupont Co.) and are sold in large amounts worldwide. Their properties and standard test procedures to evaluate the performance of these parts have been described very often, even before the advent of hybrid sol−gel technology. These coatings are easily available and now can be redefined as an early application of nanosized materials.

As already mentioned the nanostructural character of many sol−gel-derived hybrids can be described by the term nanocomposite, whereby the "filler" is transparent (<100 nm). The latter constituents are either formed in situ by cohydrolysis of slowly reacting organo(alkoxy)-silanes in the presence of main group or transition metal alkoxides as described above[36] or incorporated during sol−gel processing.[60] Due to their highly cross-linked nature, these components are hard and, therefore, improve the scratch and abrasion resistance of hybrid coatings to a level well above the typical values of purely organic materials. These outstanding mechanical properties together with the high transparency of these hybrids and their processability at low temperatures are the background for their industrial use in protecting soft materials like transparent plastics.

Most of the industrial companies involved in the ophthalmic lens business worldwide nowadays are used to produce thermosetting films on top of polymeric lenses (CR 39, polycarbonate, poly(methyl methacrylate) etc.) by wet chemical techniques.[61,62] The lenses are coated via spin- or dip-coating in large quantities. In 1997 the US market was dominated by plastic lenses that hold a market share of 90%, i.e., 84 million pairs of lenses, which are repurchased every 25−27 months. 64% of the plastic lenses are made from CR 39 monomer (diethylene glycol bis(allyl carbonate)); 47% of these lenses were hard coated.[63]

One of the first hybrid sol−gel systems developed for CR 39 ($n_D = 1.498$) was developed by sol−gel processing of GPTMS, TMOS, and titanium tetraethylate ($Ti(OEt)_4$, Figure 2, **5**). The incorporation of the titanium alkoxide precursor (20 mol %) resulted in a higher refractive index ($n_D = 1.533$) of the coating and in a fast curing behavior even for polymeric lenses of low thermal stability.[64−66] In the meantime, nanocomposites based on the incorporation of boehmite nanoparticles have been commercialized showing similar properties,[67] but a lower refractive index.

The improved mechanical stability of the hybrid coatings vs the noncoated hard resin lens can be visualized by semiquantitative, application-oriented standard test procedures. Figure 8 shows a comparison of the abrasion resistance of the noncoated CR 39 base material and its behavior when coated with thin layers (ca. 3 μm) of the two coatings described above. The increase of haze is determined in accordance with ISO/CD 15258 (tumble test). In this test, the lenses are abraded by sand and other abrasive materials in a drum; afterward, the increase of haze caused by the scratched surface in dependence on the time in the drum is determined via commercial hazemeters.

The increase of haze of the lens is less when the hybrid coatings have been applied by spin coating and cured for several hours at elevated temperatures (100−110 °C).

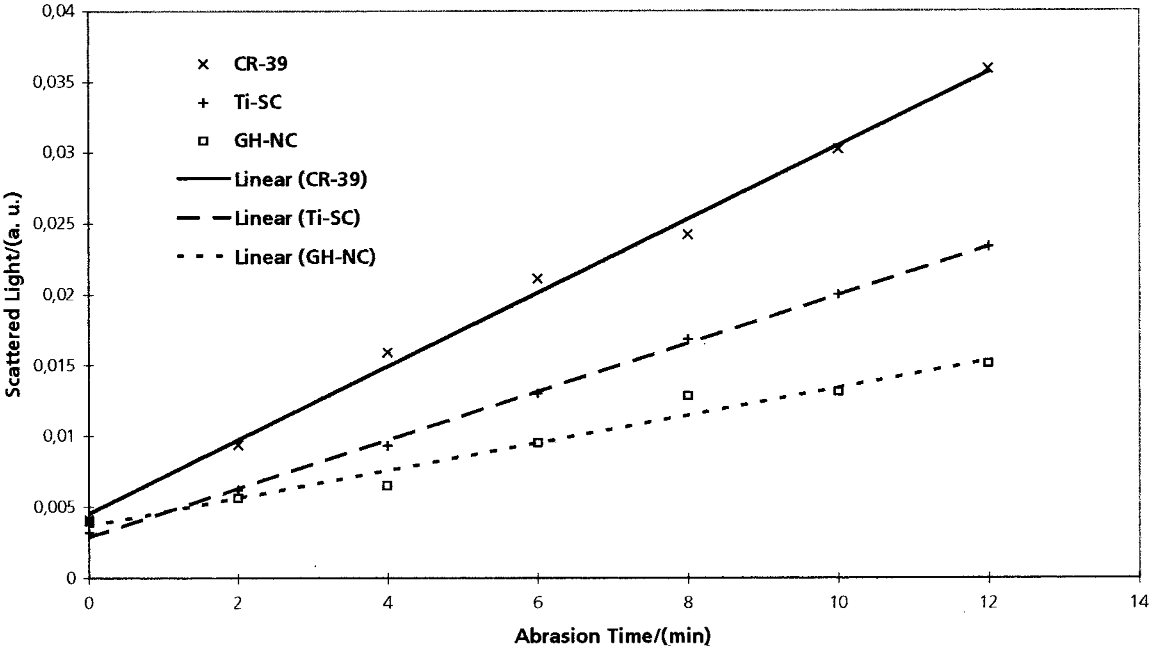
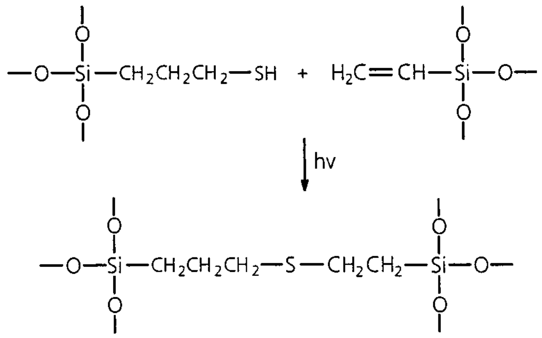


Figure 8. Increase of haze of hybrid sol−gel coatings on top of CR39 polymeric lenses during abrasive treatment (Tumble Test according to ISO/CD 15258, Appendix C: (×) noncoated substrate; (+) coating containing Ti−alkoxide; (□) coating containing AlOOH nanoparticles).

Scheme 3. Cross-Linking of Inorganic Moieties via UV-Induced Thiol/Ene Addition



Similar results have been achieved on polycarbonate (PC) substrates equipped with UV-curable hybrid coatings and were correlated with indentation methods.[68] The transparent PC showed microhardness values of 125 (±3) MPa, whereas the coatings demonstrated microhardnesses up to 220 (±10) MPa. Slightly higher values have been measured for the thermally cured Ti-containing system described above (∼260 (±10) MPa) and the boehmite nanoparticles containing system (∼306 MPa[67]). The correlation of these data with composition and microstructural features of the hybrid nanocomposites presents one major task for further optimization and application of such coatings on plastics.[69]

The ophthalmic lens market is innovative and highly competitive. In recent years polymer lenses showing high refractive indices ($n_D = 1.56, 1,60, 1.67$) have been commercialized, and therefore, high index coatings are necessary to avoid interference strings appearing with thin coatings and insufficient index matching between coating and substrate. Here, the hybrid sol−gel coatings based on transition metals offer good prospects to develop adhesive, abrasion resistant, transparent, and index-matched materials.[70]

A limiting factor in the application of thermally curing hybrids or poly(methylsiloxanes) is the long curing time (several hours) necessary to fully exploit their mechanical properties. Highly promising activities are, therefore, concerned with UV-curable systems and have led to the successful development of a hard coating for plastic substrates made from poly(methyl methacrylate) (PMMA). The hybrid coating material in this case has been derived from vinyltriethoxysilane (VTES, Figure 2, **3**) and (3-mercaptopropyl)triethoxysilane (MPTES, Figure 2, **4**) by cohydrolysis and cocondensation.[71] The UV-induced curing reaction involves a thiol/ene addition as illustrated in Scheme 3.

Highly condensed, nanosized inorganic moieties are cross-linked by fairly short organic chains and on top of PMMA display high abrasion resistance and good adhesion as well as perfect index matching to the substrate. The coating is applied by dip coating and has been commercialized to protect PMMA-based polymeric magnifying lenses.[72] An example of the respective products is shown in Figure 9.

Other developments on polymer lenses concern antireflective and hydrophobic or “easy-to-clean” coatings also derived from hybrid sol−gel type polymers. Products have been announced (Kelar) and seem to be close to commercial application.[73]

If the new concepts for hybrid polymers or nanocomposites as described above are to be successful to impart sufficient scratch and abrasion resistance to polycarbonate and other thermoforming polymers for substituting glass in automotive glazing applications, a better understanding of the structure−property relationships seems to be of utmost currrent importance.[74−76]

The prospects of hybrid sol−gel technology with respect to improved abrasion resistant coatings have already led to the foundation of a company named Exatec,[74,75] a joint venture of General Electric Plastics and Bayer AG, aiming at the ambitious goal of

Figure 9. Commercial magnifying lens euipped with an abrasion resistant, UV cured hybrid coating (Ceratec, Eschenbach Co., Nürnberg, Germany).

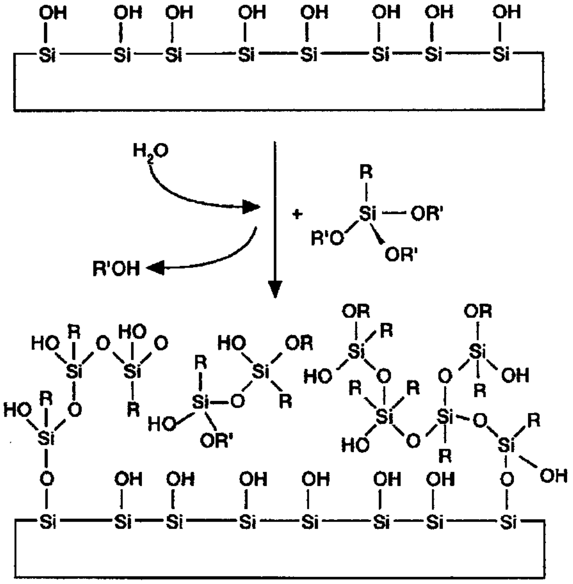


Figure 10. Schematic drawing visualizing the adhesion mechanism of hybrid sol−gel coatings on glass surfaces (drawn in accordance with ref 77).

replacing glass in automotive vehicles by coated polycarbonate.

3.2. Exploiting Passive Optical Properties: Decorative and Functional Coatings for Glasses. The glasslike transparency of many sol−gel-based inorganic or hybrid materials has rendered them candidates to modify glasses by applying thin coatings. The proper adhesion of the above-described molecular hybrids or nanocomposites to plastic substrates is a critical aspect. Sometimes, especially on nonpolar substrates like polycarbonate or polyolefins, a primer layer or physical pretreatment is required. On glass surfaces the situation is completely different due to the presence of SiOH groups,[77] which can react with their counterparts in the sol−gel-based materials. Figure 10 visualizes the idealized model of modifying a silicate-based inorganic material with a hybrid sol−gel coating.

This situation, in most cases, precludes adhesion problems and has stimulated intense research and development efforts to modify glasses by transparent, functional inorganic or hybrid sol−gel coatings.[78,79] The large scale dip coating process to prepare reflective and antireflective layers based on Pd containing TiO_2 or SiO_2/TiO_2 systems has become a well-established technology (Irox, Amiran, Calorex, Schott Co.).[7]

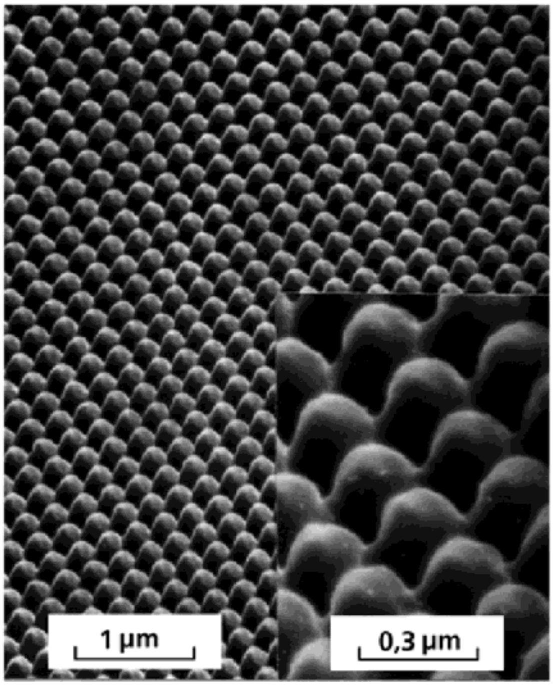


Figure 11. Antireflective, nanostructural pattern generated in the surface of a hybrid polymeric matrix by a two-step embossing/UV-curing technique.[83]

One more recent development has exploited the porous nature of silica-based sol−gel thin films to also impart antireflective properties to architectural glasses. In this case organic additives present in the coating solution serve the purpose to attain a gradient in porosity after thermal treatment at around 600 °C. The porosity gradient leads to a corresponding gradient of the refractive index, thereby increasing the visible light transmissivity of the glass substrate to very high values (>99%).[80] This system is highly suitable for solar applications as cover sheets for PV cells and collectors. It might soon be commercially available.[81]

Similar index gradients can be achieved by generating submicrometer structures on glass surfaces via patterning of appropriate coatings. The nanostructural pattern is visualized by the SE micrograph resulting from an embossed hybrid polymeric layer as displayed in Figure 11.

These so-called "moth-eye" patterns[82] can be inscribed into hybrid sol−gel-derived polymers of the type shown in Scheme 4. The linear polysiloxanes prepared by acid-catalyzed hydrolysis of novel multifunctional acrylic precursors can be isolated from the reaction mixture and form resins that can be processed almost solventless to produce thick layers on plane glass.

After embossing of the resinous layers, the polysiloxane chains can be cross-linked by UV exposure—eventually through the substrate—to become tack free. The imprinted submicrometer structure is fixed, and the resulting thermosetting matrix demonstrates sufficient abrasion resistance to be used for coating various optical parts. As UV curing is possible, this procedure is also

Scheme 4. Molecular Structures of Hybrid Polymeric Resins Used To Prepare Submicrometer Patterns by Embossing Techniques[71]

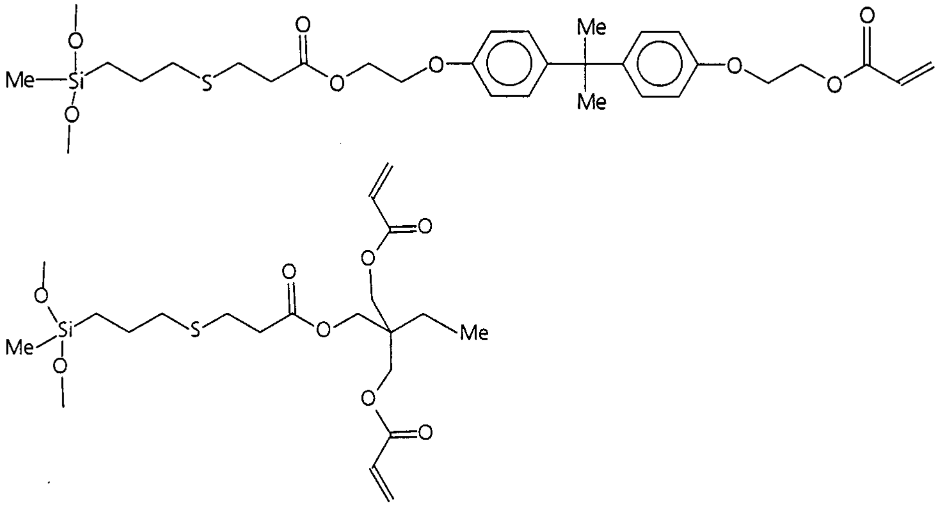


Table 1. Typical Properties of Hybrid Sols and Coatings Synthesized and Applied on Glass Surfaces To Achieve Decorative Effects

property		method/standard
viscosity	10.5−12.0 mm^2/s (clear-coat)	capillary viscometer
solids content	42−45% (clear-coat)	DIN 52316-A
density	1.002 kg/m^3 (clear-coat)	pycnometer
flash point	301 K	DIN−ISO 3676
spraying conditions	spray nozzle diameter 0.2−1.4 mm; pressure 1.5−3 bar	
curing conditions	433 K/2 h to 473 K/600 s	
layer thickness	8−12 μm	profilometer
adhesion	B 5−4	ASTM D 3359
microhardness	ca. 220−280 MPa	Fischerscope H 100
abrasion resistance	1.3−2.3% (clear-coat, depending on epoxide content)	ASTM D 1044 (100 rev.)
refractive index	1.503−1.534 (clear-coat, depending on epoxide content)	Abbé refractometer

valid to be applied on polymeric substrates of low thermal stability.

Thereby, the mechanical (good adhesion to glass and plastics, abrasion resistance), optical (high transparency), and processing advantages (stepwise transformation of a thermoforming resinous matrix to a thermoset, fairly hard matrix) of sol−gel-derived hybrid polymeric resins have been combined with a topographical modification to create novel optical features (refractive index gradient, antireflective surface).

One more traditional aspect is the coloration of glasses via hybrid coatings. On glass surfaces a coating derived from GPTMS, ASB, and PhTMS has shown excellent adhesion, abrasion resistance, and chemical stability.[84] Commercially available organic dyes can be dissolved in the respective sols, and colored coatings are obtained by spraying the sol onto the glass.[85] The incorporation of hydrophobic organic epoxy resins copolymerizing with the functional groups present as substituents in the GPTMS improves the chemical stability of the cured coating against alkaline media, thereby imposing on the coating sufficient stability in dishwashing machines. Table 1 summarizes the typical properties of the respective sols and coatings.

The low viscosity of the sol requires special practical means to prevent the wet film from developing a nonuniform layer thickness during spraying. Therefore, the glass pieces (crystal glass goblets) are mounted horizontally on a rotating disk and the gelation of the sol, i.e., the viscosity increase occurs while rotating the parts. Afterward, the goblets are placed on a conveyor belt and cured below 200 °C in a furnace. By means of the aromatic epoxy prepolymers, the refractive index can be adjusted to the substrate and the optical appearance of the thin coatings as well as their abrasion resistance have contributed to a further successful product, now on the market since 1995. Figure 12 gives an impression of the high optical quality of coated glassware.

The method is highly flexible, either enabling the partial coating of objects or complete coloration. The broad color range of organic dyes is now available to achieve fashionable and new articles, which cannot be manufactured by traditional means. The procedure is environmentally friendly and also cost-effective in comparison to the laborious traditional coloration techniques via molten glass batches containing toxic transition metal oxides.

Dye-doped transparent hybrid sol−gel coatings containing organic dyes, in particular their silylated derivatives, are also in use on container glasses[86] as well as on cathode ray tubes (CRTs) to improve color TV image resolution.[87,88] In the latter application, the respective dyes, e.g., methylene blue, have been stabilized by the addition of singlet oxygen quenchers, e.g., bis(*O*,*O*′-diethylphosphorodithiolato)nickel (DPD). Other coloration methods comprised the silylation of phenoxazinium or phenazinium dyes to covalently attach them to the silicate matrix or pigmentation with nanosized organic pigments, e.g., copper phthalocyanine.[89] Different types of organic pigments incorporated in tetraethoxysilane-based coatings have been investigated, too.[90] The lightfastness and the scratch resistance of

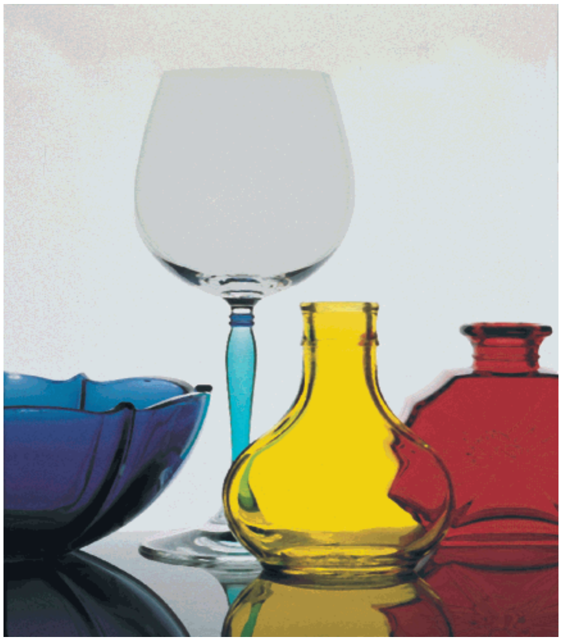


Figure 12. Glassware demonstrating the high quality optical appearance of crystal glass and other types of glasses after being spray coated with colored, sol−gel-derived hybrids.

these coatings seem to be sufficient for spin-coating of large TV screens.

Colored glass bottles have been commercially available in Japan since 1999.[86] They are coated via a combined dipping and rotating process by sols consisting of co-condensates of TMOS, titanium tetraisopropylate, VTES, and MAPTMS. Intense coloration is achieved by entrapping of nanosized organic pigments. A two-step UV and thermal curing process is performed in a special coating plant.[86] One major advantage of the coloration by organic dyes or pigments is the recyclability of the glass containers due to complete degradation of the organic constituents at high temperatures.

Superfine organic pigments are also used to coat large sheets of glass for architectural purposes.[91] A dip-coating facility has been built up and the practical durability of the colored thin films investigated by several abrasion and weathering tests. It was concluded that there is potential for interior use. The light and chemical stability, however, is insufficient for outdoor application. Nevertheless, the pigmentation of hybrid coatings to produce opaque coatings for decorative applications has not yet been fully exploited and might result in future products.[92]

3.3. Exploiting Barrier Properties: Corrosion Protection of Metals and Reduction of Permeability of Polymeric Sheets. The development of hybrid, colored coatings for lead crystal glasses has also shown that the leaching of lead ions out of the glass surface is drastically reduced due to the highly cross-linked nature of the coating material. This results both in a low solubility and a slow diffusion coefficient for the mobile lead ions with respect to the hybrid layer.[85] It is obvious from these experimental results that hybrid sol−gel coatings might be able to protect metals from corrosive stresses, especially if the corrosion is initiated by chemical reagents, e.g., chlorine ions in salt spray test facilities. Comparatively few reports have appeared describing the application of sol−gel-derived inorganic and hybrid coatings on top of metals, such as stainless steel,[93] aluminum alloys,[94] bronze,[95] and brass.[96]

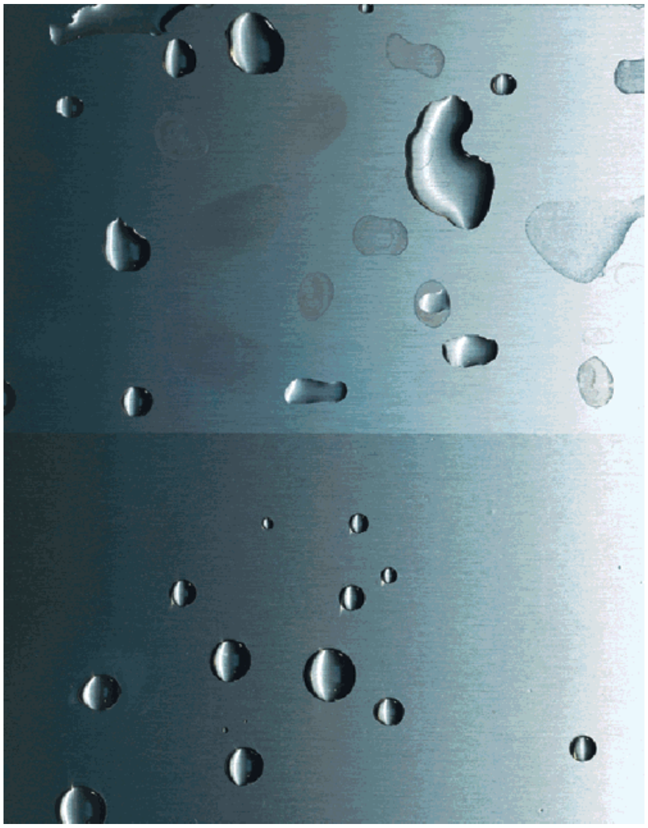


Figure 13. Stainless steel substrate coated by spraying of an abrasion resistant, fluorinated hybrid coating (lower part), demonstrating the “easy-to-clean” aspect (One2Steel, Kuhfuss Sanitär Co., Herford, Germany).

There have been preliminary results concerning structure−property relationships in the anticorrosive behavior of the coatings,[94] but the research field of sol−gel coatings on metals seems to be still in its infancy, despite the fact that the application on brass has already been commercialized.[96] The perspectives for industrial use might be higher, if thin hybrid sol−gel coatings are used as an interlayer between the metal surface and conventional protective coatings resulting in higher layer thicknesses and less corrosive stress implied directly onto the hybrid sol−gel film. One very important route to application will be to replace toxic chromate(VI)-based conversion coatings by well developed environmentally friendly sol−gel hybrids.[97]

For reasons of cost, the hybrid film has to combine several functions that cannot be achieved with conventional organic or inorganic coatings alone. Figure 13 shows a fully transparent, abrasion resistant and oleophobic hybrid sol−gel coating on top of stainless steel that is equipped with a fluorinated silane (Figure 2, **9**) to achieve water repellent and “easy-to-clean” properties on this mechanically and chemically very sensitive metal surface.

The low-temperature processing conditions of the sol−gel hybrids and their fast curing behavior enables one to perform coil coating processes and to apply thin films on metal sheets or polymeric foils. These properties are necessary prerequisites to commercialize hybrid barrier coatings.[98] The barrier effect of thin (5−10 μm) hybrid layers with respect to the permeation of hydrocarbons through high-density polyethylene (HDPE) substrates has been described long ago.[99] Very low permeability values have been recognized and were attributed to the synergistic cooperation of the inorganic and organic moieties present in the coatings derived from GPTMS or MAPTMS and ASB. Obviously, the nonpolar hydrocarbon molecules do not readily dissolve in or migrate through the rigid, glasslike hybrid matrix.

Meanwhile, as can be expected, a similar barrier effect has been found concerning the permeation rates of flavors, e.g. linalyl acetate, isoamyl acetate, menthol, and others, which are also large, mainly hydrophobic substances.[100] Their permeation rates through biaxially oriented polypropylene (BOPP) samples (30 μm) decreased from 43, 29, and 47 μg/m^2 d for the uncoated substrate, respectively, to below the detection limit of a new gas chromatographic test method.[101] The coating was UV curable and composed of (3-mercaptopropyl)-triethoxysilane (Figure 2, **4**) and 1,1,1-tris(hydroxymethyl)propanetriacrylate, which were both subjected to a base-catalyzed nucleophilic addition of the mercapto group to the triacrylate before hydrolysis to form a new molecular precursor.[102]

Thin hybrid sol–gel coatings in combination with SiO_x layers produced by vacuum coating techniques on polymeric packaging materials, such as poly(ethylene terephthalate) (PET), have been successfully developed to reduce the permeation rate of oxygen to very low values ($<$0.05 cm^3/m^2 d bar[102]). The structural requirements for low permeation rates of oxygen are a high condensation degree of the inorganic part of the hybrid material and also a high degree of polymerization of the epoxy moieties of the GPTMS present in the coating material.[98] Despite the fact that several—sometimes conflicting—parameters have to be controlled to achieve high barrier effects against oxygen and water, the hybrid polymers offer a very good chance to realize transparent, abrasion resistant, fast curing, and impermeable coatings for food packaging applications.

3.4. Exploiting Electrical Properties: Antistatic Films and Ionic Conductors. Most hybrids are highly isolating materials due to the nonionic nature of the individual precursors and the neutral reaction conditions of the sol–gel process. Typically, specific bulk electrical resistivities of 10^{13}–10^{16} $\Omega\cdot$cm can be achieved. This insulating behavior, together with the high adhesion to various surfaces via Si–OH groups and the possibility to use conventional photoresist technologies to form microstructural patterns, is the basis for their use as passivation and dielectric layers in microelectronic applications.[103,104]

Nevertheless, the selection of appropriate organo(alkoxy)silane precursors also allows to reduce the high bulk or surface resistivities to about 10^8 Ω.[105] Coatings exhibiting surface resistivities in this range are useful to reduce electrostatic charging of transparent plastics, e.g., on windows or touch panels integrated in heavy duty industrial machinery. The easy removal of electrostatic charges prevents the plastic sheets from soiling and consequently reduces cleaning and maintenance intervals, thereby increasing the lifetime of the soft plastic sheets. One precursor used in coatings for this application is depicted in Figure 2 (**10**). The coatings have to meet the additional requirements of scratch and abrasion resistance as well as perfect transparency, functions that can hardly be achieved with organic materials.

A further increase in the conductivity of hybrids can be realized by reducing the glass transition temperature of the material to values far below room temperature. Hybrids derived from TMOS and poly(ethylene glycol)s (PEG) of low molecular weight (200–600) have been used as constituents for hosting Li^+ ions, which were introduced by addition of $LiClO_4$ during sol–gel processing.[106] The T_g values ranged from −74 (PEG_{200}) to −50 °C (PEG_{600}); i.e., they increased with higher molecular weight of the organic polymer. Concurrently, the ionic conductivity decreased from 5.3×10^{-5} to 1.8×10^{-5} S/cm at room temperature, thus demonstrating the influence of the mobility of the polymeric chains, which are bonded to an inorganic backbone and with their freely dangling ends serve to solubilize and transport the metal cations.

There have been extensive studies concerning further structure/property relationships, e.g., the $[Li^+]/[O]$ ratio, and the dynamic behavior of the polymeric chains in the presence of rigid inorganic clusters.[107] These inorganic–organic solid ionic conductors (organically modified electrolytes, ORMOLYTES) seem to be very well characterized and might find applications in high power supplies,[106] electrochromic devices,[108] and fuel cells.

Similar concepts were realized by incorporating Li^+–salts in hybrid inorganic–organic polymers based on GPTMS and MAPTMS copolymerized with epoxy-functional polyethers.[109,110] Solid-state protonic conductors have been generated by incorporating sulfonic acid groups in hybrid polymers.[111]

3.5. Exploiting Active Optical Properties: Development of Photoactive Coatings and Systems. There is widespread agreement within the sol–gel scientific community that active optical applications of hybrid polymers or nanocomposites might present one of the most attractive fields to realize applications for the 21st century.[20,21] Due to the huge number of recent literature concerning these applications, just a few directions and achievements can be mentioned in this short review. An overview has also been given concerning optical applications of nanocomposites throughout the past decade.[112] No products have been discussed, but there has been substantial progress toward possible application in the following key research areas:

- The first is nonlinear optically active materials and their dynamical behavior;[113] meanwhile, high second-order NLO coefficients have been realized.[114]
- An interesting cheap, new photoelectrochemical cell based on a chelating metal–complex dye and doped TiO_2 nanoparticles has been developed for solar energy conversion.[115]
- Luminescing hybrids doped with rare earth metal ions or quantum dots have been intensively studied and the structural properties of the host matrix adjusted to achieve large fluorescence quantum yields.[116–118]
- Hybrid optical switching and data storage devices have been described based on photochromic dyes or photochemical hole burning.[116,117,119]
- Sol–gel-based hybrid coatings have been used to detect various species via fiber-optic sensors.[120–123]

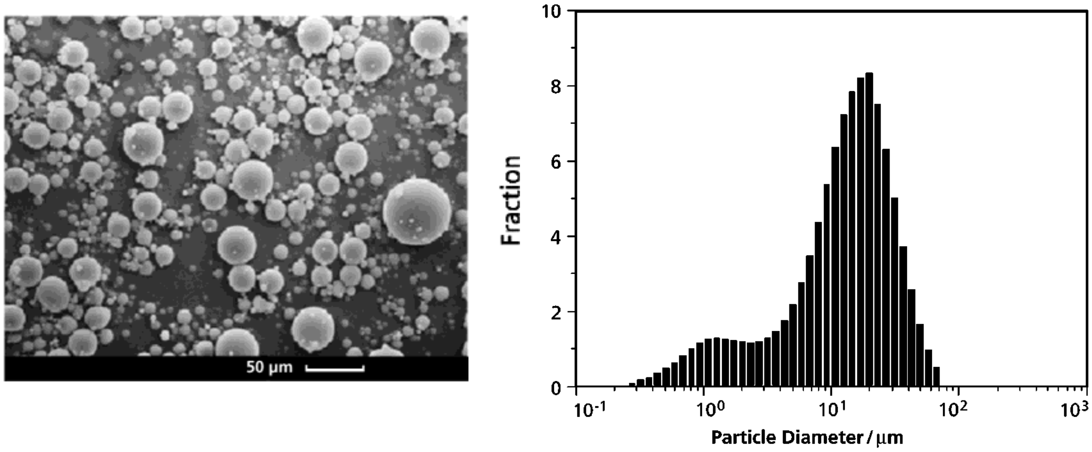


Figure 14. SE micrograph and histogram (DLS) showing the shape and size distribution of a dye-doped hybrid pigment (1 mol % silylated Disperse Red 1 (cf. Figure 4a) in GPTMS/ASB 79:20).

Further information may be found in several recent reviews.[116,124−126] It is obvious that these fields are very promising. Several disadvantages, e.g., the intrinsic defects of the hybrid polymer or nanocomposite discussed above, the insufficient photochemical stability of organic dyes, and the reduced crystallinity of low-temperature processed nanoparticles as well as temperature and time-dependent matrix−dopant interactions, have to be overcome by further basic studies to achieve long-term stable and reliable devices.

3.6. Structural Hybrid Materials: Hybrid (Nano)-particles, Aerogels, Bulk Nanocomposites and Fibers. Despite the fact that the sol−gel process has strong advantages for producing thin films of inorganic or hybrid materials, it has also been extensively used to manufacture powders, in the beginning mainly with the goal to synthesize better ceramics through chemistry. Spray drying procedures were used to separate the inorganic condensates from their solvents.

Other sol−gel-based methods, e.g. the Stöber process, used to generate fine particles by controlled precipitation, have been known for many years.[5,127] Nanosized silica and other metal oxide particles can be obtained exhibiting spherical shape and a very narrow size distribution. A lot of them meanwhile are commercially available as stable colloidal solutions. There have been many activities to modify these nanoparticles with organic dyes to achieve, e.g., fluorescent labels for analytical purposes.[128,129] The dyes may be bonded to the particle surface[130] or physically entrapped,[131] and applications in biomedical or diagnostic test kits are to be expected due to the fact that polymer latex particles or gold colloids are extensively used in this respect. The surface modification and self-organization of these and similar colloidal particles into 2D and 3D arrays have been described recently.[132,133]

Small hybrid nanoparticles were synthesized by a Stöber process in the presence of (3-aminopropyl)-triethoxysilane (APTES, Figure 2, **8**).[134] The synthesis of larger colored spheres—even from non-silica-based materials—have been described,[135] but irregular shapes resulted from the room-temperature aerosol based process.

Hybrid pigments based on dyes covalently attached to the inorganic matrix were obtained by spray drying of sols derived from GPTMS and ASB.[136] A high degree of condensation was found by ^{29}Si CP−MAS NMR measurements. Figure 14 shows the SE micrograph of the powder resulting from a sol containing 1 mol % of silylated Disperse Red 1 (cf. Figure 4a) and the respective particle size distribution measured by dynamic light scattering (DLS).

The particle size distribution was bimodal between 0.5 and 70 μm with maxima at 1 and 20 μm. Similar results were achieved with anthrachinone and perylene dyes (s. Figure 4, parts b and c). The photostability of the azo dye proved to be higher in the hybrid matrix than in pure inorganic or organic matrixes.[29] Hybrid pigments might find applications in fields where conventional organic pigments fail due to their higher solubility or lower thermal stability. The current research work concentrates on chemical and technical means to reduce the broad particle size distribution and to avoid the formation of large hollow spheres.

The production of bulk materials from sols or gels is very difficult due to the high content of liquid phase leading to large volume shrinkage and strong capillary forces evolving in the gel state during drying. This mostly results in crack formation.[4] One way out of this drawback is supercritical drying, thereby avoiding phase separation and the related stresses. By this technique, highly porous materials (aerogels[137,138]) can be obtained, which show a low coefficient of thermal conductivity and are further investigated as almost transparent heat insulation materials.

The main disadvantages are their brittleness due to the high porosity of up to more than 90% and their moisture sensitivity due to a large number of inner surface Si−OH groups. The latter problem has been addressed by investigating hybrid aerogels,[45] which are formed by co-condensation of silicon alkoxides (TMOS) and organo(alkoxy)silanes ($R{-}Si(OCH_3)_3$ with $R = -CH_3, -(CH_2)_n{-}Cl, -(CH_2)_n{-}CN, -(CH_2)_n{-}NR_2$, etc.) at various ratios.[139] Due to the different hydrolysis rates of both silanes, the organic substituents R are located at the surface of the initially formed silica clusters and, therefore, lead to organically modified aerogels. If the appropriate substituents (alkyl, aryl) are used these hybrid aerogels are permanently hydrophobic and are not destroyed by moisture. These new porous hybrids might also be useful for catalytic or separation processes.

The second possibility to avoid crack formation in sol−gel-derived materials is by reducing the cross-linking capabilities of the precursors, e.g. by replacing tetraalkoxysilanes (TMOS, TEOS) successively by trialkoxysilanes ($R-Si(OR')_3$) and dialkoxysilanes ($R_2Si(OR')_2$), thereby increasing the mechanical stress relaxation possibilites during drying and curing. The crack formation probability can be further reduced by organic polymerization reactions through incorporation of organo(alkoxy)silanes with several polymerizable functional groups R as discussed before.

By these means, e.g., fast curing resins can be obtained that are derived from new precursors as displayed in Scheme 4.[140,141] Their hybrid network can be modified by varying the number of alkoxy groups and the type and number of (meth)acrylic substituents, through different spacer units and by copolymerizing different precursors.[142,143]

The resulting materials mainly based on multi(acrylate)alkoxysilanes show very low volume shrinkage (2−8%) and have been developed to replace organic polymers and amalgam as dental filling materials.[144] In the meantime, the combination of the resins with nanoparticulate fillers[145] and the use of spiroortho ester silanes[146] with a volume change during the polymerization step of below 0.5% have contributed to develop a broad range of hybrid polymers showing thermal expansion coefficients from 184 to 67 $\times 10^{-6}$ K^{-1} and Young's moduli from around 1 up to 4000 MPa. The biocompatibility of these hybrids has been demonstrated,[147] and two products are already commercially available (Definite, Degussa-Dental Co., Frankfurt, Germany; Admira, Voco Co., Cuxhaven, Germany).

The picture of hybrid sol−gel-based products (see Figure 1) can be accomplished by remarking that new types of hollow fibers can be drawn from sols containing the above-discussed resins and adjusted to the rheological properties of the spinning procedure.[142] Their properties cover the whole range from highly flexible to glasslike brittle in dependence on the composition and processing parameters and their oxygen permeabilities vary alike. They are also useful to produce micro- or nanoporous hollow silica fibers by controlled pyrolysis of the highly variable organic network. Applications of these fibers in separation processes can be expected.

4. Conclusion

Hybrid polymers or nanocomposites derived from organo(alkoxy)silanes, main group or transition metal alkoxides, and various other constituents via sol−gel processing have become versatile—in many cases even commercially available—materials for the protection or modification of transparent plastics, metals, and glasses via coating procedures. The background for this successful industrial implementation of hybrids has been the tremendous range of available precursors and the steadily increasing knowledge about their reactivity during sol−gel processing.

Further long-term developments concerning the incorporation of organic dyes or inorganic nanoparticles might result in fascinating properties of the derived materials and seem to be promising to achieve highly sophisticated applications in the field of microsystems technology as well as of optically active devices. The introduction of micro- or nanosized topographical features (porosity and micro- or nanopatterns) further increases the potential by creating novel multifunctional hybrids with properties not only based on the underlying chemistry.

Coatings have been the first commercial products due to the ease of fabrication of thin layers by sol−gel techniques. In the meantime, new hybrid nanoparticles, porous hybrids, and even bulk materials have been realized and seem to exhibit the same market potential as the "traditional" sol−gel films. There is no doubt that due to the fruitful global activities in this research field, this potential will become real, if the basic understanding of hybrid materials grows as fast as the synthetical knowledge.

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CM011060M