

The Sol-Gel Process as a Basic Technology for Nanoparticle-Dispersed Inorganic-Organic Composites

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Abstract. Nanoparticles containing hybrid materials became of interest for many areas in the last decade. The reason for this is the fact that, in addition to the molecular inorganic-organic hybrid network, the physical, electrical, optical or catalytical properties of nanoparticles resulting from the inorganic crystalline, glassy or metallic properties also can be used for the material tailoring. For this reason, a survey is given over some interesting developments. Furthermore, in case studies, examples are given for the effect of nanoparticles on the two component Ormosil type of hybrids composed of ethyl ortho-silicate (TEOS) and methylethoxy(methoxy)triethoxy silane (MTEOS, MTMOS). It was shown that the 6 nm SiO₂-containing nanocomposite hybrid sols can be dried in form of thick films up to 14 μm after a one step dip-coating process and densified crack-free. This is attributed to the increase of relaxation ability and flexibility. This nanocomposite based on TEOS, MTEOS and particulate SiO₂ has been used to develop an industrial process for a new type of environmentally friendly glass fiber mat with a temperature resistance up to 600°C.

Keywords: sol-gel synthesis, nanocomposite review, ormosils, glass fiber binder

1. Introduction

Hybrid materials have become one of the most interesting aspects of sol-gel techniques. This is mainly due to the fact that serious drawbacks of inorganic sol-gel processing, for example crack formation in coatings [1], brittleness of sols [2] or high curing and sintering temperatures necessary for complete densification can be overcome. On the other hand, the properties of these materials are in most cases restricted through the presence of organic groupings. For example the temperature stability or the fire resistance is far higher in inorganic materials, but the diffusibility is far higher in hybrids than in inorganic materials due to the free volume caused by organic groupings.

On the other hand, due to the inorganic components in the backbone, a variety of properties superior to pure organic polymers is obtained, such as a higher modulus

of elasticity or a higher abrasion resistance. Especially the abrasion resistance has been very attractive in the beginnings of the hybrid technologies [3]. At any rate, the degrees of freedom obtained by the incorporation of organics into sol-gel materials were attractive enough to activate numerous researchers to investigate this field.

From the basic concepts, there are many possibilities to incorporate organics into sol-gel matrices, for example to bind organic groupings covalently to inorganic network formers such as the silicon-tetrahedron by using organoalkoxysilanes as sol-gel precursors. Since the functional groupings linked to the silane are manifold, a large variety of materials can be prepared using this approach. Other approaches are to link organic groupings to other types of alkoxides, e.g. by complex formation or by ionic bonds. In addition to this, organic monomers can be used to be cross-linked to the organic groupings linked to the alkoxide precursors. This type of materials have been called ormosils or ormocers. Other possibilities of preparation of hybrids are to fill

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pores of sol-gel materials by dyes or nanomers and to polymerize them eventually. Based on these possibilities, numerous materials have been developed as shown in [4], and literature cited herein. One of the interesting feature of this type of materials is their high transparency which is due to the small structural dimensions avoiding Rayleigh scattering. So, one interesting idea was to use sol-gel materials for optics as shown in [5], and literature cited herein.

One of the drawbacks of this technology is that the inorganic component acts as a network former only but does not contribute to the materials properties based on its physical solid state properties, for example of crystalline phases. For this reason, nanoparticles as components for hybrid materials are of interest since, being small enough they also can avoid Rayleigh scattering and, at the same time, they will exhibit their solid state properties or other properties attributed to their small size (for example quantum size properties). Meanwhile, a great number of investigations making use of nanoparticles as an additional component, and many fields are addressed. For this reason, in the paper, a literature summary in the field of nanocomposites is given, and in the second part, a case study about an ormocil nanocomposite and its commercial application is shown as an example.

2. Literature Review on Hybrid Nanocomposites

2.1. Colloidal Chemistry Aspects

In order to process nanoparticles within sol-gel matrices or molecular hybrid matrices, the interfaces between the particle and the matrix become of high importance due to the high specific interfaces. For example, 10 nanometer particles in general show several hundred m^2/g of surface area, and the interfacial free energy may govern the materials properties by controlling the distribution (homogenous distribution, percolation or aggregation). For this case, the concept of minimizing the interfacial free energy has been created by using appropriate surface modification of the nanoparticles [6]. If the surface modification is chemically similar to the matrix properties, one can anticipate that the interfacial free energy reaches a minimum, and homogenous dispersion can be obtained. This leads to a concept of optical nanocomposites with nanoparticles with a dimension of 10 to 20 nanometers attributed in an ormocer or polymer matrix. In this case, in addition to the ormocer matrix properties, the solid state

particle properties of the inorganic particles can be used for generating interesting new properties. The surface modification of nanoparticles is a suitable means for the tailoring of sol-gel materials, since their reactivity and the particle to particle interaction can be controlled. The reduction of the particle to particle interaction leads to a flexibilization of sols as shown by Mennig and co-workers [7], or to the change of the ζ -potential [8] or the creation of additional reactivity for subsequent chemical reactions of the particle with the matrix. The influence of the surface modification and surface reactivity of colloidal particles on sol or gel properties is an underestimated field. Pure inorganic gels are very brittle and despite this brittleness have a very low mechanical strength [9]. From the mechanical point of view, these gels in most cases are rather useless. So, the idea to investigate the mechanical and thermal properties of surface modified particulate gels as a function of their surface modification came up and how far these properties can be used for the synthesis of new sol-gel products. So, in the following, a review is given about the use of nanoparticles in hybrid and polymer matrices: From a literature research of 275 papers, a selection for different categories of materials is given, and then a practical example is shown more detailed.

2.2. Optical Materials

Optical materials with nanoparticles included are of interest due to the fact, that optical properties of nanoparticles show a variety of interesting phenomena. If the distribution and aggregation can be controlled, materials with high optical transparency can be obtained [10, 11]. In [12], ormocer types of hybrid matrices have been used as hosts for semiconductor, metal and oxide nanoparticles and photoactive nanocomposites have been prepared. Similar matrices have been used for the preparation of silver, gold, copper and platinum nanocomposites [13] or for the incorporation of semiconductors [14]. SiO_2 containing nanocomposites have been described in [15], including dyes for non-linear optical properties. A review on these types of materials is given in [16]. Inorganic-organic hybrid materials also have been used for the fabrication of photo hole burning matrices or hosts for laser dyes [17]. Zirconia containing nanocomposites have been reported for carriers for non-linear optical dyes and the optical properties have been described [18]. Active and passive optical components have been described in [19], such as dye-doped silicate gel PMMA composites, photochromic

materials, microlens arrays, as well as a new flat screen color display based on dye-doped microsphere pixels [19]. Luminescent nanocomposites based on erbium, neodymium or dysprosium have been described in [20, 21], but no fluorescence have been found in the $1.55 \mu\text{m}$ regime. Waveguiding materials based on TiO_2 nanoparticles and fluorinated polyimides have been described in [22], showing optical losses of 1.4 dB per cm at 633 nm [22]. A review about hybrid nanocomposites as an interesting basis for NLO material for optics is given in [23]. V_2O_5 nanocomposites in various hybrid and polymer matrices have been investigated in [24, 25], and optical electronic, ionic and protonic conductive properties have been investigated, and a review about the potential of inorganic-organic nanocomposites for photonic application, multiphase nanostructured composites, composite monoliths and fiber fabrication is given. In application, such as multidye solid state tunable lasers, multiphase optical power limiters, microscaled chemical sensing, biosensing fibers and solid state dye-doped fiber lasers are described [26], and in [27], second harmonic generation of dye-doped and nanoparticle-doped materials are reported. In [28], a review with 97 references about optical properties of inorganic hybrid nanocomposites is given; photoinduced polymerization of inorganic hybrid nanocomposites is discussed. Photo-densification is observed which leads to a volume compaction of the matrix and an increase of the refractive index [29]. Photo responding hybrid sol-gel materials based on methacryloxy propyle triethoxy silane for the fabrication of Bragg gratings is described in [30]. In [31], an interesting method is described for the fabrication of dye-encapsulated metal oxide particles, cadmium sulfide, copper iodide and silver iodide nanoparticles. As matrix polyvinyl-carbazol was used, and photoconductive and photorefractive property measurements have been carried out. V_2O_5 has been investigated for various purposes, for example as an electrode for lithium batteries and optical applications [32]. A synthesis for Europium²⁺-doped hybrid nanocomposite materials has been reported. The matrix consisted of dimethoxymethyl silane, methyl triethoxysilane and zirconia [33]. High non-linear optical susceptibility material of the second order with coefficient of 150 to 200 pm/V have been reported from SiO_2 hybrid nanocomposites and Red 17 [34]. In [35], the fabrication of photoconductive and photorefractive polymer nanocomposite materials have been reported using CdS and silver nanoclusters as active materials, and in [36], hybrid materials for making

photopolymerizable layer structures from organosilicate and organozirconate precursors for waveguides with optical losses of less than 0.5 dB/cm are described.

Summarizing, it is to say, that there are many reasons for the use of hybrid matrices for optical materials. The most interesting point probably are the low processing temperatures which allow processing and patterning according similar to polymers which also allow photopolymerization and the incorporation of many functions. In this interesting field, many investigations are expected in the future.

2.3. *Ferroelectric Materials*

The sol-gel process is widely used for the fabrication of purely inorganic ferroelectric materials. In various investigations, the properties of ferroelectric nanocomposites are investigated, too. In [37], the effect of lead titanate nanoparticles on the isoelectric and ferroelectric coefficients of polyvinylidene fluoride is investigated. In [38], 3 nm barium titanate particles are dispersed in styrene, and polymerized and dielectric properties have been measured and in [39], lanthanum titanate was dispersed in polyvinylidene fluoride trifluorethylene. Other work is devoted to the fabrication of spin-coating thin films of polyvinylidene fluoride trifluorethylene, doped with lead titanate nano [40–42]. The composites had high pyroelectric but very low piezoelectric activity, thereby reducing vibration induced electric noise in piezoelectric sensor applications. Polyvinylidene fluoride trifluorethylene has been used as a matrix for nanocrystalline calcium and lanthanum-modified lead titanate, and films have been fabricated [43, 44]. An interesting work has been carried out in [45], where needle-type hydrophones for the calibration of medical ultrasonic transducers have been fabricated using lead zirconate titanate in polyvinylidene fluoride trifluorethylene nanocomposites.

Summarizing it is to say, that the main work in ferroelectrics is focussed on the polyvinylidene fluoride trifluorethylene polymer as an active matrix.

2.4. *Thermal and Mechanical Properties of Polymers*

Mechanical properties of polymers containing nanoparticles have been a topic of interest since many years. In [46], a review about various nanocomposites with silica, titania or silica-titania has been given, and it has

been shown, that especially in polyamide or polyimide systems high temperature stabilities have been obtained. In [47], a review is given about metaloxide polymer nanocomposites with glassy properties and in [48], SiO₂ nanocomposites with hydroxyethylmethacrylate have been investigated. In these composites, the compressive strength and the modulus have been detected. DSC investigations have been carried out for determining the glass transition temperatures. The decomposition temperature rose from 260 to nearly 360°C with increasing SiO₂ content. Optical transparent SiO₂ nanocomposites have been prepared in polyvinylacetate matrices [49, 50]. A review with 178 references about organic-inorganic hybrid materials with emphasis on synthesis, structure property response and potential applications is given in [51]. To monitor the charge and dynamics in unfilled elastomers at their local junction environment in nanocomposites prepared by the sol-gel process, naphthalene and dansyl chromophores have been covalently attached to trifunctional cross-linked junction in polydimethylsiloxane elastomers. The transient fluorescence and isotropy measurements of the naphthalenechromophore have been carried out [52]. A styrene-maleic anhydride copolymer silicate network nanocomposite has been prepared by the sol-gel process. These composites are highly transparent and show interesting thermal and mechanical properties [53]. In [54], the preparation of a poly(trimethylhexamethylene terephthal amide)-zirconia nanocomposite is described. An increase in the tensile modulus was observed and the glass transition temperature was increased by approximately 87°C [54]. The microstructure of an acrylic polymer silicannanocomposite was characterized by scanning force microscopy [55]. In [56], polyurethane silica nanocomposites have been prepared, and it was shown that different morphologies can be generated by varying the processing conditions. SiO₂, polyethylene oxide nanocomposites have been prepared in [57], and it could be shown that the strongest influence on the hardness can be attributed to the water to alkoxide ratio during the synthesis. In [58], a review with 32 references about nanophases (carbon-rubber composites, semicrystalline polymers, silica or cellulose whiskers, dispersed in polymers as well as hybrid materials have been investigated. The reinforcing effect of possible cross-linkings of macromolecules by nanoparticles and the connectivity between reinforcing particles have been discussed. This work is mainly devoted to fundamental phenomena with only a few perspectives for

applications. Clay mineral based structures will be cited in 2.6.

2.5. Proton Conductors

Within the scope of the development of nanoparticulate polymer or hybrid matrices, ionic or protonic conductors seems to be an interesting area of research and development. In most cases, silica particles are used in order to increase temperature stability or conductivity. The use of nafion as polymer was investigated in most cases. In [59], nafion matrices with SiO₂ particles were investigated, and it was found that gradient films could be prepared with the highest concentration of silicon near the surface. In [60], core-shell titanate silicate particles were prepared in-situ by a sequential alkoxide procedure in nafion membrane, and structural analysis of the nanocomposite was carried out. In [61], similar systems with SiO₂ and Al₂O₃ phases have been prepared. From SAXS analysis, structural phases in the range of 5 μm have been found, and in [62], the use of drying controlling chemical additives has been investigated [62]. Another preparation route has been used in [63], where nafion was infiltrated in a porous silica network to form a clear glass hard material. In [64], bilayer systems from SiO₂ or through the sol-gel process and perfluoro-carboxylate/sulfonate have been investigated. An SiO₂ polyethyleneoxide nanocomposite was described in [65], which leads to the good protonic conductivities at temperatures above 100°C. The authors claim that the high thermostability is due to the inorganic-organic framework. Similar systems have been prepared from SiO₂-polyethyleneglycol and SiO₂-polypropyleneglycol. As silicon oxide precursors, isocyanatopropyletriethoxysilane and O, O'-bis((2-aminopropyl)poly(ethyleneglycol)) and similar compounds were used. The authors claim that a maximum conductivity is obtained if the oxygen to lithium ratio is 15 [66]. In [67], a process for tailoring of perfluorosulfonated ionomer-entrapped sol-gel derived silica nanocomposites for electro-chemical sensing of RE (DMPE) 3⁺ was described. The fabrication of membranes with silica nanoparticles based on polyvinylidene flouride supported silicone composite membranes based on a PDMS and TEOS hybrids for the separation of methane from butane was described in [68]. Poly(amide, imide)/TiO₂ nanocomposite gas membranes separation were synthesized and the permeation behavior of oxigene, hydrogen,

carbondioxide, hydrogen and methane was described [69]. Only carbondioxide and hydrogen were found to have low activation energies for permeation.

2.6. *Self-Assembling and Layered Structure Nanocomposites*

Self-assembling systems and layered structures either fabricated from clay minerals or by in situ processes in connection with nanocomposites have been investigated in various publications. In [70], a review with 55 references is given about intercalating oxides or nanoclusters between 0.4 and 2.0 nm with approximately 1 nm layers of smectite clays. The properties with respect to catalytic molecular sieving, dehumidifying and adsorption of these materials are referred. Other members of the smectite family like beidellite, nontronite, saponite or hectorite are listed. In [71], a general review from Toyota is given about the chemistry of polymer clay hybrids with polymers such as nylon 6, nitrile rubber and others. The mechanism of reinforcement is also discussed with results of CP-MAS, NMR and pulsed NMR studies. Self-assembling systems are investigated, using amphiphilic monomers and organic crosslinkers together with silica precursor solution. A water solution photoacid generator was used to dissolve the hydrophilic gels in order to photoinitiate an acid-catalysed silica condensation for the in situ formation of the ordered nanocomposite [72]. In [73], a review with about 95 references is given on nanostructured pillared layered metal(IV) phosphates. In [74], the self-assembly of layered aluminum silsesquioxanes as clay-like organic-inorganic nanocomposites is described. The Si/Al ratio was varied where the organic functionality is introduced by a Si-C bond. An interesting approach was carried out in [75], where a template synthesis of layered alumina and magnesia-silsesquioxane was investigated, and a series of layered inorganic-organic nanocomposites where the organic functionality again was introduced by silicon-carbon bond was used. The fabrication and characterization of concentric tubular composite micro- and nanostructures using a template synthesis method is described in [76]. This method has been used to prepare micro- and nanostructures composed of metals, carbons, semiconductors, polymers and lithium-intercalation materials. These composites consist of an outer tubule of one material surrounding inner tubules of different materials. These tubules are used for example for the electropolymerization of conducting and insulating polymers to

prepare inorganic-organic nanocomposites. In [77], ultrahard zirconia polymer thin film coatings have been described on single-crystal silicon and quartz substrates using the ionically self-assembled monolayer (ISAM) process. In [78], a review with 38 references is given on the opportunities to produce patterned and porous nanocomposite materials of films, fibers or powders by the evaporation-induced self-assembly process.

Summarizing it is to say, that the fabrication of a self-assembly and layered structures seems to become of high interest, but examples for applications only are existing in the area of clay-based polymer nanocomposites. This topic is presently investigated in the majority of the chemical laboratories of polymer industry.

2.7. *Nanocomposites with Biological Components or for Biological Purposes*

Increasing interest can be observed for the combination of biological components with nanoparticles. For example in [79], biopolymers like gelatin or chitosan are used in microemulsion process for the formation of organogels together with silica-alkoxides to form percolating inorganic-organic networks. The formation of biodegradable nanocomposites based on poly(ϵ -caprolactone) and SiO₂ in form of inorganic-organic nanocomposites is reported, and in vitro cell culture and biodegradation tests have been performed. Recently, flexible transparent films have been prepared from γ -amino propyletriethoxysilane and chitosan [80]. X-ray diffractions indicate that a nanocomposite structure has been obtained similar to that of the form 1 of the pristine chitosan [81]. Transparent monolithic silica materials doped with 5 to 20% of dibenzoyl-L-tartaric acid and D-glucose have been prepared and the optical rotation measurements have been investigated. It was found that the doped silica nanocomposite systems show similar angles of rotation like the pure organic compounds [82]. Nanocomposites have become of interest also for dental application as shown in [83], low shrinkage UV-curable nanocomposites have been prepared from vinylcyclopropyl silanes, isocyanatopropyl silanes and various organic compounds. The synthesis leads to solvent-free liquid resins to be cured by UV-light-induced radical polymerization. In [84], the use of polyhydroxy compounds, such as starch, glucose, maltose together with polyvinylalcohol or polyacrylic acid were used together with TiO₂ to form layers. Onto these layers, alkoxides are absorbed to form various types of layered nanocomposites [84]. In [85], the effect of

TEOS on tetraethyleneglycoldimethacrylates were investigated. The abrasion and wear resistance of these components and the paste formation were investigated. An exotic system was investigated in [86]: the tobacco mosaic virus has been used as a template in reactions such as the co-crystallization of cadmium or lead sulfide or the oxidative hydrolysis of iron oxides. Moreover, SiO₂ was examined for the synthesis of inorganic-organic nanotubes. These nanotubes were investigated by TEM electron diffraction. It was concluded, that the virus proved to be a suitable biological template for the synthesis of nanotubes. Summarizing it is to say, that the state of the art using biological components or the application for biological purposes using nanoparticle systems with organic matrices is at its infancy, but maybe of high interest for the future.

2.8. General Problems in Inorganic-Organic Nanocomposite Materials

Fundamental investigations for inorganic-organic nanocomposite materials become more and more of interest in the area of hybrid materials. As already indicated, this has several reasons especially with the effect of interfaces and new degrees of freedoms for material property tailoring. Meanwhile, many previews are existing which allow to receive overviews in various fields. In [87], a review with 34 references is given in the field of dye-incorporated sol-gel glasses for nonlinear optics, tunable lasers, luminescent solar concentrators, insulating electroconductive fibers and high-temperature superconductors. In [88], a review with 330 references is given about synergistic enhancement of inorganic functional materials. The most extensive studies of synergistic enhancement come from the field of heterogeneous catalysis, interaction or reaction of solid particles under applied stress, for example in the preparation of composites, mechanical blending, microencapsulation, surface treatment. Moreover, phenomena related to particle or film size, nonlinear optical properties, magnetic properties are reported. In [89], a review with 47 references is given using different matrices and describing for example nonlinear optical properties in nanocomposites and gradient index lenses. In [90], a review with 81 references is given on the preparation of sol-gel nanocomposite materials incorporating covalent bonds between organic and inorganic phases and discussing also nonshrinking composite formulations. In [91], a review with 52

references is given on nanocomposites with retrospective and prospective considerations. This pointed out that in the last few years, nanocomposite materials have become a major part of new material synthesis all over the world for mechanical, optical, magnetic and dielectric applications. Hybrid siloxane-oxide systems were prepared in form of nanocomposites with polysiloxane chains crosslinked with the oxide particles [92]. An article with about 45 references is devoted to dye-doped silicate matrices based on Ormosils and nanocomposite materials [93]. In [94], various methods such as low melting fluxes, hydrothermal processes, hydrothermal processes with superimposed electric fields, hydrothermal processes with mechanic forces and mechanochemical effects including uniaxial pressure and shear, acoustic wave stimulation and others are reported in the field of various nanocompositions [94]. In [95], the application of hybrid nanocomposite materials as corrosion protection, coatings on copper, especially below pH 7 is reported. In [96], hybrid particulate nanocomposites from different types has been synthesized by use of porous oxide impregnation with organics and dyes [96]. In [97], a method is reported using titanium isopropoxide in polyvinylacetate in THF solvent. Dynamical mechanical spectroscopy reveals the existence of two relaxations which might account for an interphase between PVA and TiO₂ clusters. In [98], the synthesis of inorganic-organic nanocomposite materials with perfluorocarboxylate and perfluorosulfonate-carboxylate compounds for the fabrication of bilayer materials is reported, and the structure is investigated by electron microscope and X-ray methods. An asymmetric distribution of the silica phase is observed. In [99], an educational article is published on the history and concepts of nanocomposites, and the prognosis is given that this new class of materials will dominate new synthesis for the next period. In [100], the synthesis of a new nanocomposite toner liquid by radical polymerization of organic acids in presence of inorganic particles is described in this patent. In [101], a polyoxypropylene or epoxide polymer matrix together with Bisphenol A and SiO₂ nanoparticles derived from TEOS is described. In [102] butadiene-styrene latex matrix nanocomposites with SiO₂, Na₂O, ZnO systems are synthesized. In [103], in a SiO₂ polysiloxane nanocomposite system process-structure-property relationships are evaluated. In [104], a review with 64 references about the sol-gel processing of inorganic-organic nanocomposites is described, and the author concludes that this technique opens new possibilities

in the field of material science. In [105], also a review with 31 references about the last 20 years of the sol-gel process is given. The author concludes that a turning point was reached with the emergence of Ormosils and inorganic-organic nanocomposites. He states that this will open a gateway to a whole class of new materials. In [106], a review with 69 references is given about inorganic-organic nanocomposites, and emphasis is given to the formation of inorganic nano building blocks. In [107], a review is given about the sol-gel inorganic-organic hybrids with specific respect to nanocomposites and the use of nanoparticles. [108] describes a process for making vanadiumoxide containing nanocomposites in functionalized polyethyleneglycol polymers. DSC, TGA and TMA methods are used to characterize the system. It is shown that by doping with lithium sols, significant electrical conductivity can be obtained. Versatile routes to inorganic hybrid nanocomposite materials is described in [109], where organically modified silicon halides and alkoxides are reacted together in a solvent-free non-hydrolytic sol-gel process. A review with 81 references on inorganic-organic hybrid materials is given in [110], for example in systems like hydropropyl cellulose, polyvinylalcohol and polyvinylidene fluoride. These systems are modified with TEOS to form SiO₂ nanoparticles. A review with 69 references is given in [111], referring to the fabrication of hybrid nanocomposites and presence of polymers, biocomposites and biomimetics. The fabrication of forsterite-PMMA nanocomposites was prepared by a modified sol-gel method [112]. The monolithic composites are optically transparent and are machinable. Polyamide SiO₂ nanocomposites are reported in [113] and in [114], a PVC titania nanocomposite has been fabricated and characterized. A review with 73 references is given on hybrid materials for electrical and optical applications, basically using polysilsequioxanes [115]. In [116], SiO₂ nanocomposites with low density and a rapid fabrication, a process based on tetrafluoroalkoxysilanes is described. [117] is a review with 101 references and summarizes the recent developments of new sol-gel derived materials like nanocomposites for optics, like 2nd-order nonlinear and photochromic properties. Summarizing it is to say that many new synthesis routes using the nanoparticle or nanocomposite approach are currently developed, and all these authors are very optimistic on the interesting properties of new materials.

2.9. Photosensitive and Photochromic Materials

Photosensitivity such as resist or photopolymerization behavior have been used to fabricate micro fresnel lenses by a two-wave mixing process [118]. Photochromic organic dyes like 2,3-di-phenol indenone have been used to dope transparent silica gel-PMMA nanocomposites. Their behavior under UV-light exposure and the coloring and fading rates have been investigated [119]. In [120], a review with 29 references is given about vinyl polymer-modified hybrid materials and photocatalysed sol-gel reactions. For nanoparticulate materials, alkoxides of silicon, titanium and aluminum are investigated, and monolithic materials have been prepared. Photochemical synthesis of vinyl polymer-inorganic hybrid materials is discussed [120]. Photochromic component containing systems such as spiropyrans, spirooxazines and tetraarylporphyrins have been investigated in [121]. The hybrid matrix is consisting of dimethyldiethoxysilane and zirconium nanoparticles. The type of chemical bonds reaction behaviors and optical response has been discussed. Nanocomposite materials also have been used for the fabrication of gradient index materials by electrophoretic movement of charged nanoparticles in polymerizable matrices [122]. In [123], the reaction of methacrylates and TEOS together with SiO₂ nanoparticles under UV-light influence has been investigated, and the polymerization processes have been studied. Materials with a light transmittance of over 80% have been obtained. The photoinduced structural relaxation and densification of sol-gel derived nanocomposite thin films has been investigated in [124]. The material based on methacryloxypropyl trimethoxysilane, methacrylic acid, and zirconium dioxide show a refractive index increase through UV-radiation. Sol-gel derived hybrid nanocomposites based on zirconia, spirooxazines, diarylethene derivatives and furylfulgides have been investigated and doped with Eu²⁺. A fast kinetics of coloration and thermal fading was obtained [125]. In [126], photochromic properties of sulfonated spiropyran components trapped in a silica matrix has been investigated, and it was stated that the half life time of photochromic dyes could be increased by up to 2.7 times. Summarizing it is to say that by the use of nanocomposite matrices interesting effects with respect to photochromism, graded index formation and photopolymerization could be found, and this seems to be an interesting field for future developments.

3. Case Study on the Effect of Nanoparticles on Hybrid Materials with Thick Film Sol-Gel and Binder Fabrication as an Example

This case study is presented as an example to demonstrate how nanoparticles are able to affect many properties of a given matrix system in an unexpected way.

3.1. Experimental

80 g of TEOS were mixed in a glass flask with 20 g of MTEOS and 25 g of H₂O or alternatively with 83 g of SiO₂ sol (Levasit 300/30, Bayer, with 30 wt.-% of SiO₂), upconcentrated to a 50 wt.-% solution and were added to the alkoxide mixture under heavy stirring. Concentrated HCl was added to adjust the pH value to about 1–5. After 5 minutes, the sol was cooled on ice to 0°C and filtered. For batches up to 50 kg, the content of water or silica sol is reduced to half of the content compared to the corresponding laboratory scale batches. By this measure, the pot life of the sol is prolonged to at least 3 months at room temperature. Before further processing, the sol has to be activated by the addition of 52 g of water per kg sol.

For the preparation of xerogels, the sol was heated up to 80°C for 12 hours. White powders were obtained. As critical film thickness, the maximum thickness was defined, which could be obtained by a one step dip coating and firing to 500°C without crack formation (withdrawal speed 1 mm/s, drying for 1 hour at 80°C, heating rate 1 to 5 K/min, SiO₂ slides as substrates).

3.2. Results

As shown elsewhere [127], an experimental route has been developed to modify SiO₂ sols with TEOS and methyltriethoxysilane (MTEOS). In Fig. 1, the flow chart of the sol fabrication is shown. Using this method,

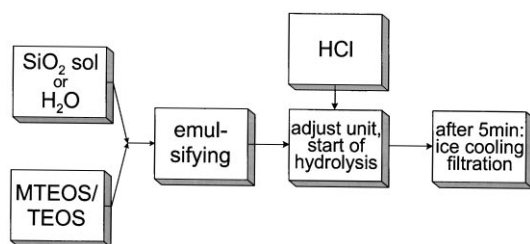


Figure 1. Flow chart of the fabrication of the modified SiO₂ sols.

no additional solvent has to be used. It is necessary to use ice cooling, because otherwise turbid sols are obtained, having aggregates up to 100 nanometers, as investigated by photon correlation spectroscopy. It was of interest to investigate how far the reaction of MTEOS/TEOS with SiO₂ changes the basic properties of the particle-free hybrid gels. As indicators, the film formation ability, ²⁹Si-NMR spectroscopy and the thermal stability of the CH₃-groupings were taken into account. Especially the last one is of high interest, since the question arises, how far the flexibilized sols lead to higher film thicknesses without cracking. For this reason, the critical thickness has been measured, in the way that the highest obtainable thickness of a 500°C densified films has been taken where no crack formation takes place. As coating method, a single step dip coating was used. Due to the upconcentration of the SiO₂ sol (see exp.) and since no additional solvent is used, highly concentrated sols (50–60 wt.-%) have been obtained. In the ²⁹Si-NMR analysis, a clear difference occurs in the Q and T development with time compared to SiO₂-free sols. Addition of SiO₂ in all cases show a clearly enhanced Q⁴ and T³ formation. In order to investigate the influence of the composition on the critical coating thickness, the SiO₂ particle content was varied in a wide range. In Fig. 2, the results are shown. In addition to the ethoxy silanes, methoxy silanes also have been included in the experiments for comparison. As one can see clearly, the maximum critical thickness up to 14 micrometers is obtained with about 40 wt.-% of SiO₂ particles. This shows that the addition of SiO₂ sol to the silane composition leads to a structure which is favorable for a good densification

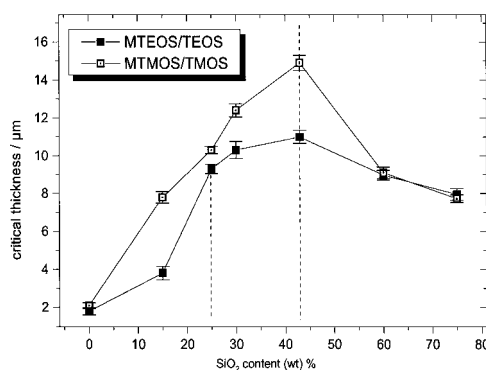


Figure 2. Critical thickness of MTEOS/TEOS (MTMOS/TMOS respectively) composition as a function of the SiO₂ particle content: MTEOS : TEOS ratio: 80 : 20; one step dip coating; firing conditions 500°C/hr; dip coating 30 minutes after sol preparation.

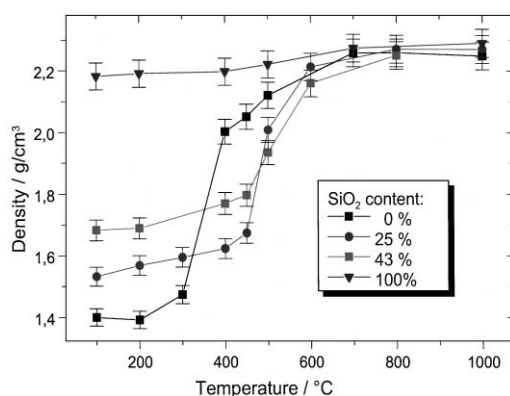


Figure 3. Density of the gels as a function of SiO_2 content and T .

behavior and which is much more suitable for relaxation than pure MTEOS/TEOS or MTMOS/TMOS mixture. Since with higher SiO_2 particle content, it became more and more difficult to obtain clear solutions, all further experiments had been carried out with 25 wt.-% of SiO_2 particles.

Investigation of the elastomechanical behavior [127] show that the SiO_2 containing systems do not differ much from the SiO_2 -free systems but are distinctively more elastic than SiO_2 gels. Other influences of the SiO_2 particle in TEOS sols are related to the skeletal density. As shown in Fig. 3, the density is a function of the SiO_2 content, and it clearly shows that with increasing SiO_2 content the powder density increases also. Whereas the powder density of the 80°C dried SiO_2 is almost very high (2.18 g/cm^2), the SiO_2 -free composition has a density of about 1.4. It is surprising that the SiO_2 content leads to a retarded densification behavior, which cannot explain the increase of critical thickness. At 650°C, all powders reach density close to theory. The most significant difference between SiO_2 containing and SiO_2 -free sols is the 350–450°C regime. In order to explain these findings, DTA/MS measurements have been carried out, as shown in Fig. 4. It clearly can be seen, that the most important fact is the shift of the oxidation of the CH_3 groupings to higher temperatures from 450°C (SiO_2 -nanoparticle free) in the SiO_2 -free to 600°C in the 60 wt.-% SiO_2 nanoparticle containing system. This now may explain the better densification behavior, to since for example in the 25% SiO_2 system, at 500°C, the density at 500°C is almost 91% of the theory, but the methyl groupings still are almost completely present (oxydation maximum at 530°C). This should lead to an increased relaxation behavior even at higher temperatures. For this reason, as

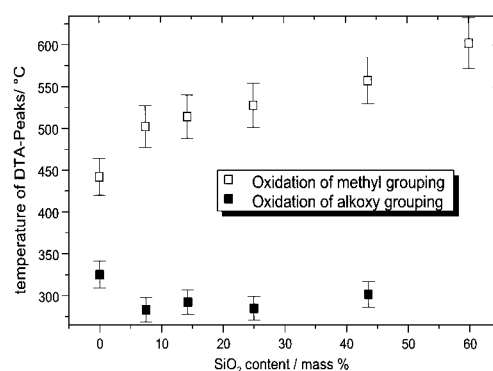


Figure 4. Oxidation behavior of methyl and alkoxy groupings as a function of T . The peak maximum of the DTA peaks of the different compositions are displayed.

a model, core-shell sol structure having SiO_2 particles as cores and “flexible” shell seems to be a advantageous structure for introducing flexibility by reducing the particle to particle interaction.

Based on these results, it seemed to be of interest to investigate the applicability of the hybrid nanocomposite systems as a high inorganic content binder for glass fibers. It was anticipated that especially for the linkage of fiber interactions, thick crack-free connections have to be obtained by the binder. For this reason, commercially available glass fiber mats were used, and the phenolic resin binder was extracted from these mats. After dipping of the glass fibers in the new binder, these glass fiber mats had sufficient elasticity to be of interest for insulating purposes. As one can see in Fig. 5, the elasticity of the glass fiber mat is surprisingly high. In comparison, unmodified SiO_2 sols have been used, leading to extremely brittle products which can be crushed very easily. Based on these investigations, a process has been built up for the fabrication of 50 kg batches of the new binder. The binder has been tested in a glass fiber mat fabricating company (Pfleiderer Dämmstoffe, Germany), and the technology has been developed for the fabrication of glass fiber mats as shown in Fig. 6. The results of these investigations led to the development of an industrial process for the batch and continuous flow production of the binder. Due to the pH control and H_2O content, a shelf life of the binder of more than three months could be obtained with respect to sufficient binding properties. The viscosity could be adjusted to a level, that the production process was possible without any change of technology compared to phenolic resin binder. In Fig. 6, industrially fabricated glass fiber mats are shown. The glass

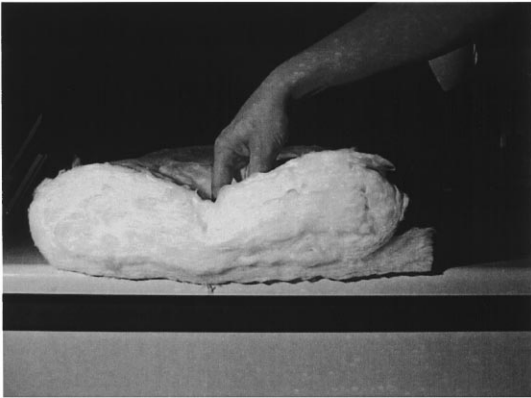


Figure 5. Demonstration of the elasticity of the new glass fiber binders.



Figure 6. Glass fiber insulation mats fabricated on an industrial scale with the new binder.

fiber mats are containing 1–2% of organics in form of CH₃ groupings and are stable up to 600°C. After heating up to 500°C, 40% of the pristine mechanical strength is maintained, which is far sufficient for high temperature insulation applications.

4. Conclusions

Based on the investigation of the thermomechanical properties of modified SiO₂ sols, a hybrid binder system for inorganic fibers has been developed, substituting phenolic resins. This binder system should be suitable for many other applications, and first interesting results already have been obtained on natural fibers, core sands and others. It shows that the hybrid sol-gel technique combined with nanotechnologies leads to materials with interesting application potentials.

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