

Considerations about the sol-gel process: From the classical sol-gel route to advanced chemical nanotechnologies

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Abstract This paper was given on occasion of receiving the first Life Time Award by the International Society on Sol-Gel Science and Technology. Its intention is to provide an insight on the development of this field, its driving forces and especially on its impact on application and industrial technologies. The motivation of the work carried out in the last decades is that in the early days of the sol-gel technologies, where this route started to interest industry as well as scientists, the author got interested in a field which was clearly application-driven and strongly anchored in the material scientist community rather than in fundamental chemistry. If one is talking about application-oriented technologies, of course, markets and industrial needs have to be taken into consideration, because the restrictions or bottle-necks, but also chances provided by economical needs strongly may govern the field. In opposition to these fields, only driven by science, may not have these restrictions as far as it is possible to raise funds for the scientific work. For this reason, the attempt is made to point out the connections between application and science in the sol-gel field. Since I am working in the sol-gel field since 1975, strongly focused on industrial applications, it should be understandable that many of my own development examples are used to demonstrate this way.

Another problem, of course, is connected to the sol-gel field: This is a question of appropriate definitions as well as to draw a clear borderline of the field. Especially in the last decade, the connection of sol-gel materials to nanostructured materials has become closer, so that it is difficult to

clearly divide these fields. On the other hand, the fabrication of nanoparticles by hydrolysis and condensation processes or controlled precipitation processes can be defined as a sol-gel technology, but in many cases is just not done. This leads to the fact that in many areas, sol-gel types of processes are used, but called different. Due to the fact that the properties of small particles either in solution or dispersed in an appropriate matrix show highly interesting material properties, it would be desirable that the sol-gel community would try to interact stronger with these developments (e.g. the “particle” community). This also might include a focus of the sol-gel area a little bit more back to the routes, to material science development and engineering. According to my opinion, this would be a very interesting supplement for the field as it is represented today.

Keywords Sol-gel · Nanostructured materials · Nanoparticles · Industrial applications

1. Introduction

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2. General considerations

2.1. The fascination of the sol-gel process

The sol-gel process got its first fascination by the idea to produce inorganic materials, in general only accessible by high temperature processes, such as glass melting or ceramic firing, at modest temperatures, for example in case of glass close to the transformation or softening point (T_g). Looking into the literature, the first example for a sol-gel reaction always is attributed to Ebelman [1], who by accident left tetraethylorthosilicate alone and when he came back a couple of months later, he found something which almost looked like a glass. The density was over 1.8 and the hardness was suitable to scratch glass. At this point, the chemical knowledge wasn't well enough proceeded in order to reconstruct the appropriate formula for the “silica”, which obviously was a gel, but already very highly condensed. If sufficient time is available, the condensation will further proceed and lead to compact glasses as demonstrated in the Libyan desert glasses which are fully densified silica, a pro-

cess which took a couple of million years. In the meantime, there were a lot of investigations on silicon, as a homologous element to carbon and people discovered silanes, their fabrication, their chemical reactivity and especially the condensation ability to form polymerized structures. It was tried to fabricate analogous compounds to hydrocarbons, but in this case, the extension of the electronic system of the silicon leads to distinctly different behaviour compared to carbon. The preferred “polycondensation principle” is the formation of the silicon-oxygen-silicon bond rather than the silicon-silicon bond. Silicon analogous compounds (compared to hydrocarbons), in general, are not stable at ambient conditions. Until the development of silicones many authors investigated monomolecular or oligomeric silanes, in most cases partly substituted by organic ligands (organo alkoxy silanes). These investigations are dating back to the beginning of the last century, but the consequent investigation for the fabrication of new materials never was carried out. By the patents of Geffcken and Berger in 1939 [2], a method was presented to fabricate thin films produced from alkoxides, not only based on silica, but on alumina and titania as well as others. This work already presented an interesting aspect, since, as known from the chemistry of the alkoxides outside of silica, they rapidly hydrolyse and form crystals, some of them even at room temperatures (alumina, for example, in form of boehmite, or titania in form of anatase). Solid particles like crystals, however, scatter light, and if one wants to have them transparent, the crystal size has to be kept distinctly below the scattering limits according to Rayleigh's equation. This means, the films prepared by Geffcken and Berger were crystalline, but optical highly transparent, so that the films have to be nanostructured. This simple consideration never has been published in this way because nobody took care about nanostructured materials at this time. When Schott Glaswerke at Mainz after the Second World War took these basics and under the guidance of Dislich [3, 4] developed an industrial process for depositing functional coatings on flat glass, the glass community got aware of the process, and a lot of scientific investigations for coatings on glass were started: The sol-gel community was born. Meanwhile, the ceramic community also got interest in the systems (for example, the works of Roy [5–8] or Mazdiyany [9], because one saw a high potential to produce high performance ultra-fine ceramic powders. In this connection, the problem of processing of extremely fine powders became very obvious: The problem of agglomeration either by (mostly weak) chemical forces, polar interaction or van-der-Waals-forces. Ceramists started many discussions about the question, why obviously in summary the bulk ceramic sol-gel processing does not lead to any advantages despite the fact it should. Agglomeration only seemed to be avoidable by suspending the particles in diluted systems, for example, as shown by Matijevec [10, 11]. As a consequence of these processing problems, the

Table 1 Variety of compositions and routes for sol-gel-processing

Alkoxide routes	CCC route [SM. . .]
Inorganic	Non-aqueous condensation
Organically modified alkoxides	Building blocks
Additional monomers, oligomers or polymers	
Complex alkoxides	Coatings
Aqueous systems	Bulk
Colloidal routes	Glasses
Nanocomposites	Ceramics
	Composites

sol-gel process never really has gained significant importance in ceramic powder fabrication. Based on the work of a great number of scientific investigations, many routes have been investigated.

In Table 1, a few variations about the different sol-gel routes are given. The most investigated route is the alkoxide route, especially for inorganic systems. Inorganic means that after firing no organics are available. The organically modified alkoxides or organo alkoxy silanes are characterized by having a Si-C bond which survives, in general, hydrolysis and condensation processes (which, by the way, is something unique) and if not fired too high, the organics are kept within the system; many hybrid systems have been synthesized, for example Ormosils, Ormocers, Ceramers or Polycerams (names given by various authors to these technologies). The addition of organic monomers or oligomers may lead to a so-called hybrid network either by being linked to the inorganic backbone or independently of it (interpenetrating network). The introduction of any type of functional groups can be achieved by linking complex organic structures to the alkoxides. Whereas most of the investigations were carried out in organic solution due to the solubility of alkoxides in these solvents, aqueous routes also were investigated, especially if one moves to the sol phase, because inorganic sols (stabilized colloids) were known since a long time, especially in the case of silica. So the colloidal route and the polymerized route were defined. Most of these topics have been laid down in the book of Brinker and Scherer [12] which for a long time was considered something like a bible for the sol-gel community.

The most investigated system which still has a lot of interest, are tetraorthosilicates. One of the reasons is that their hydrolysis rate is rather slow, so that many mechanistic investigations can be made and second, condensation products almost independent of their structure do not tend to precipitate easily, because dispersed silica particles even in aqueous solutions “disguise” themselves with an aqueous surface-layer which prevents aggregation and precipitation or gel formation even at the point of zero charge. Other systems like titania, alumina or zirconia show an extremely high hy-

drolysis and condensation rate and precipitation cannot be avoided. This led to investigations in order to look for the control of addition of water to the alkoxides: If it is possible to produce water very slowly and homogeneously within a reaction mixture, this might be a way of controlling the reaction rate. So the principle of the chemical controlled condensation was developed [13–15] which led to the formation of almost molecular distribution of heteroatoms together with silica. Based on this, homogeneous and optical highly transparent contact lens materials with co-condensates of titania and alkoxy silanes could be achieved [16].

Due to the fact that it is possible to prefabricate complex chemical structures based on alkoxides, the idea came up to build so-called building blocks which could survive the processing and could lead to new materials with ultra homogeneous distribution of the different components. This fascinating idea has become a big issue, but only in a few cases, reached early practical significance [17, 18].

Summarizing it is to say that starting from the 50s and the 60s, the sol-gel field became diversified in a lot of different branches and this was a function of the variability of the chemistry behind.

In the 80s the commercialization of the process started, especially in Japanese companies [19–22], which clearly reflects the academic and especially the state of industrial structures (e. g. the foundation of the Japanese “New Glass Forum”. The interest of the glass community in commercialisation was documented by the foundation of “Technical Committee 16 (Sol-gel Process in 1981, chairman: H. Schmidt, until 1990), but now the above mentioned rules coming from industrialization and market became very important. This will be discussed in more detail in the next chapter.

3. The sol-gel technologies and markets

If it goes to market, costs play an important role. Materials fabricated from alkoxides in most cases are expensive compared to technical mass commodity materials like glass, ceramic raw materials or polymers. Coatings, in general, since the employed amount per part is comparable low compared to the bulk may permit higher prices as far as it doesn't have to compete with commodity coatings like paints and lacquers or sometimes with gas phase or vacuum deposition for large-scale applications. A great effort also was made to produce parts or bulk materials through the sol-gel process. But not only the processing problems, but also the price was restrictive. From Geltech inc. ltd. in California, for a while, sol-gel derived silica lenses have been produced with high performance for military applications, but there never has been a breakthrough from

Fig. 1 Materials on their way to the market

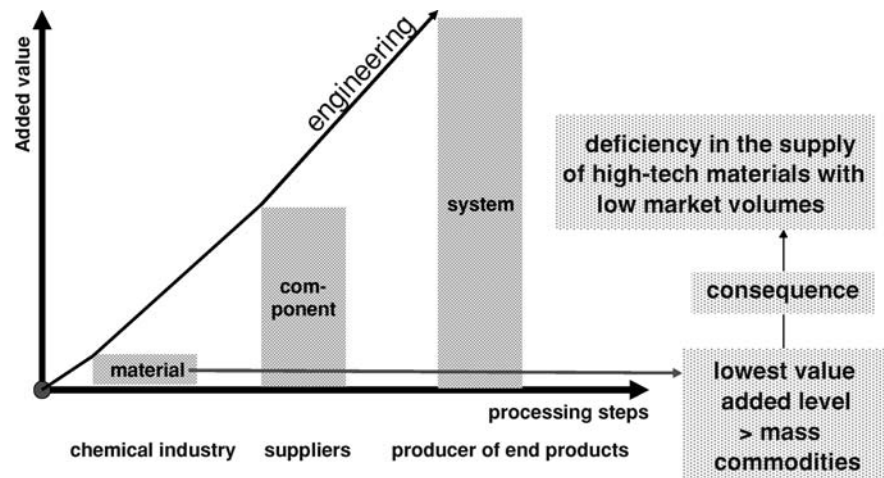
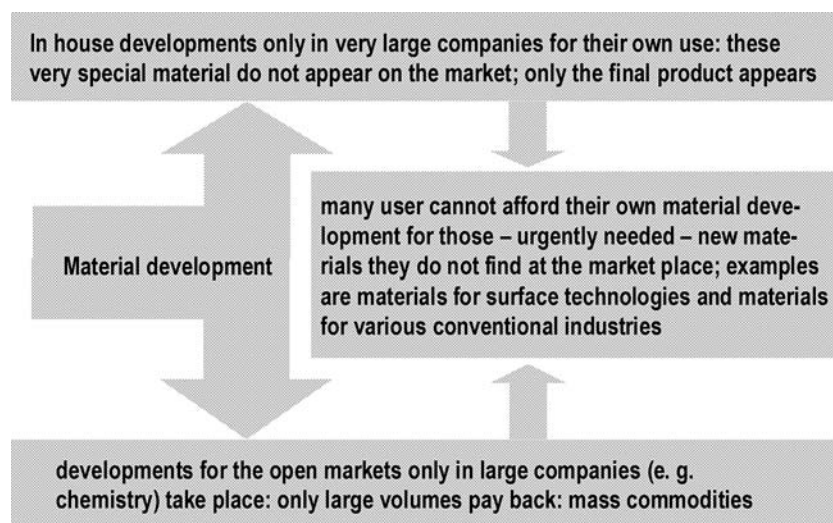


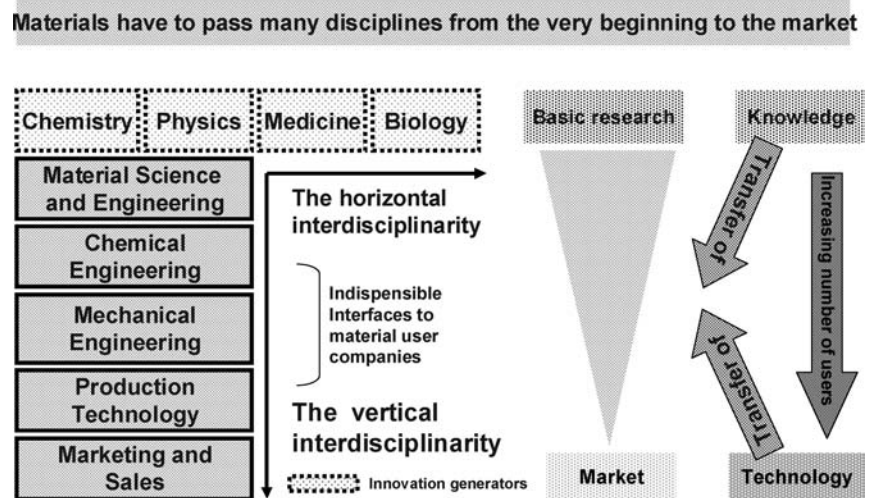
Fig. 2 Two materials development fronts



these products. Olympus company propagated to fabricate graded index lenses made by diffusion of high-refractive ions into gel rod [23–25] and then, after densification and fixing the refractive index gradient cut into disks and polished. These are a few examples where inorganic bulk materials have been fabricated by sol-gel techniques, but price and processing costs always were extremely limiting. This also refers to ceramic raw materials which with a few exceptions (for example barium titanate) never gained high significance for technical applications. An exception is silica sols which are produced by precipitation from water glass. These methods have become mass production processes utilized by chemical industry and products are sold in tens of thousands of tons, but hardly for coatings but for many other purposes like fillers. The reason why other sol-gel materials for specific coatings are, with a few exceptions, not offered on the market is very simple: The typical material producers (for example, chemical industry for polymers, ceramic materials and others) are operating on the first

step (and lowest level) of a value added chain (Fig. 1). The component system and device maker using these materials generate much higher value added fractions than the material sellers. For this reason and due to the long time to market and in connection with this, very often expensive production, chemical industry has to focus on market segments with large volumes which is, in general, not the case for specific coatings. On the other hand, the majority materials users companies are medium size and, even if they would be interested in using these coatings, in general, do not have the skills of chemical processing routes. Only in a limited number of very large companies, for example in the electronic industry own material development pays back do “harvesting” the added value in the own final products. In general, this does not take place in small and medium sized enterprises or in companies where the sol-gel coating technology is not a core technology or a key issue of their productions. So, the world seems to be “divided” into two material development fronts as it is indicated in Fig. 2. In the

Fig. 3 The "vertical Interdisciplinarity"



case of sufficient need for proprietary material and the necessity for maintaining the proprietary material IP secret, large companies, in general, develop their own materials which never appear on the market. In-house developments are typical for large electronic or optical companies. According to the overview given by Sakka [19, 21] about the industrial utilization of sol-gel techniques, Japanese companies are by far the main user of these technologies, which fits into the high number of electronic optical and display companies in this country. Development and sales of sol-gel materials exists mainly for coating purposes or additives (e. g. SiO₂ for rheological control of lacquers or wash coats for catalysts). Special inorganic sol-gel coating materials are hardly offered on the market, only in small quantities for tests maybe from special labs. The situation changes if one considers so-called hybrid materials where organics are included as described above. In these cases, the field of application is larger and increasing. Hard coatings based on these technologies for plastics, of polycarbonate or PMMA for eye glass lenses made from CR 39 are offered on the markets and used in various industrial applications. But, of course, these coating materials do not reach the level of classical mass commodity polymer lacquer based systems. This means there is something like a supply gap between research which clearly has demonstrated manifold the nice and interesting properties and the use in industry. The limitation is a result of the material sales market and the value added situation and could only be overcome if research in academia would find a structure in order to provide turn-key solutions for industrial surface technological applications. For these reasons, the so-called vertical interdisciplinarity has been proposed as shown in Fig. 3. A well managed collaboration, starting from the basics and ending with the production line would open many opportunities for SMEs to participate in new material innovation potential, as it is valid for sol-gel materials.

4. Principles of sol preparation and the significance of surface modification

4.1. Bottom up

Basically for the preparation of sols different routes are imaginable. The so-called bottom-up route, that means starting from molecular precursors like alkoxides, is the by far most common route. According to the definition given in the book of Brinker and Scherer different types of sols may be distinguished (sols here are defined as a homogeneous dispersion of nm-sized entities in a liquid). The colloid size, in general, is below the so-called scattering limit according to Rayleigh’s equation, which means, roughly spoken, around $\frac{1}{20}$ below the wavelength of the incident light. In general, the nucleation and nucleation and growth process according to Eq. (1) leads to colloidal particles, if one operates outside the point of zero charge: surface charge prevent the agglomeration through repulsing forces:

$$I = A \cdot e^{-\frac{(\Delta G_n + \Delta G_D)}{k \cdot T}} \tag{1}$$

$$A = 2 \cdot n_v \cdot v^{1/3} \frac{k \cdot T}{h} \sqrt{\frac{\sigma}{k \cdot T}}$$

where ΔG_n is the Gibbs free energy for nucleation, ΔG_D is the Gibbs free energy for diffusion, n_v is the number of nucleating or crystallizing species per unit volume of the liquid, v is the volume per formula unit of the nucleating species, σ is the interfacial free energy.

The important parameter to interfere with the nucleation and growth process, since σ represents the interfacial free energy between a growing nucleus and its chemical environment. σ can be controlled by molecules interacting with the surface of the nucleus or growing particle. If we have crystal size depending significant differences in σ , the crystal direction with the highest σ value grows the fastest. In this case,

non-spherical shapes, like plate-like or rod-like crystals may be obtained as there are many examples in crystallizing systems (e.g., needles of calcium sulfate in aqueous solution or plate-like boehmite particles, also derived from alkoxides). In case of silica, due to the differences in hydrolysis rates of the different OR-group in tetra orthosilicates under acid conditions, the fraction of chain-like oligomers is rather high, so that polymer type of sol particles have been formed (polymerized gels). If one goes to very high pH values, spherical shaped particles are formed which also is the case under alkaline conditions [26–29]. The formation of polymer type of sols also can be enforced by side-blocking of reactive sites, in alkoxides, for example, by β -diketone complex formation. This was demonstrated on alumina [30, 31]. This means that the addition of additives to the sol-forming sys-

tem may change the structure of sols considerably, but not only the structure of sols, but also the particle size can be influenced.

A so-called “stabilization” of sols is indispensable for their colloidal stability. Due to the extremely high surface energy, the overall surface-free energy of a system is very high. The overall van-der-Waals energy also increases exponentially with decreasing particle size. This means that without stabilization, aggregation would be unavoidable. Inorganic sol particles, in most cases organically modified systems, too, show sufficient reactive groupings, for example, OH-groupings on their surfaces in order to form hydrogen bridges or covalent bonds by condensation to produce hard agglomerates which, in general, are difficult to redisperse. The simplest way to avoid agglomeration is the generation

Fig. 4. Colloidal chemistry as basis for sol processing

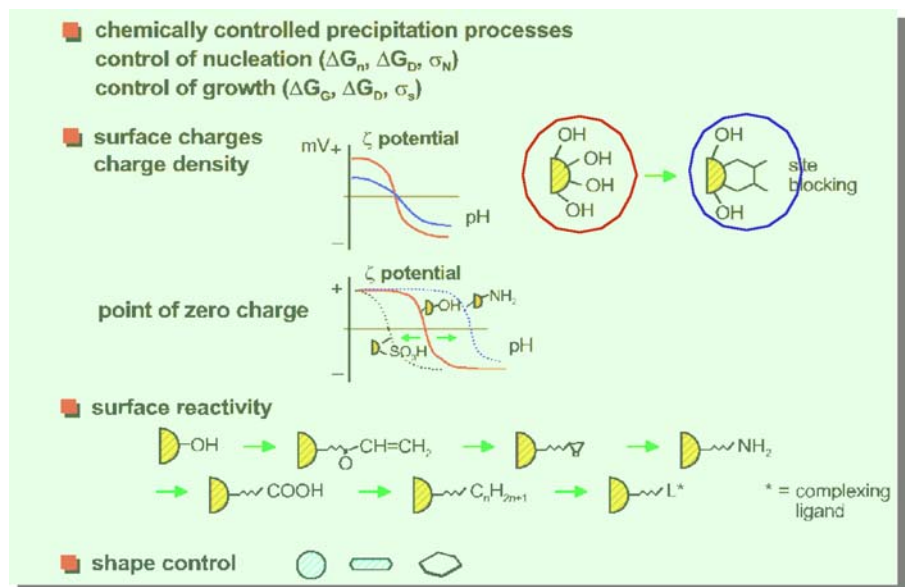
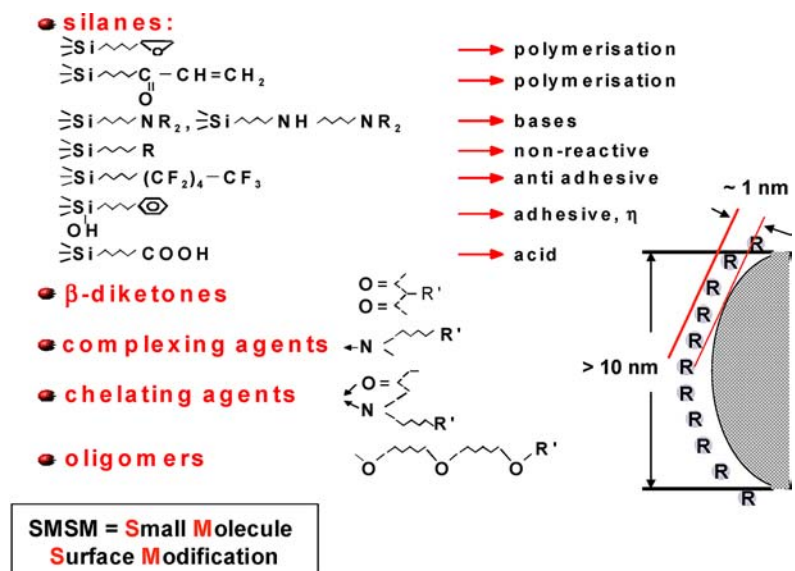


Fig. 5 Role of surface modification and examples



of surface charges on the particle surface by the appropriate pH value which can be easily determined by the measurement of the ζ -potential; pH values outside of the point of zero charge according to the DVLO theory produce positive or negative charge on the surface with repulsing forces. By up-concentration (undergoing the critical distance), the repulsive forces are converted into attractive forces and gelation occurs. The same happens if a system is shifted close to the point of zero charge. In Fig. 4 the basic principles are summarized [32]. It is demonstrated how the ζ -potential can be either shifted in its absolute value by side-blocking, for example, complex formation, or by functionalizing the surface with ionic groupings. The functionalizing also leads to the fact that the electrostatic stabilization (by charges only) may be converted into an electrostatic stabilization where the sol stabilization also is guaranteed by ionic forces, but, in opposition to the electrostatic stabilization by appropriate choice of the functional groupings, a high degree of reversibility can be achieved since the groups are chosen in a way that they cannot undergo chemical reaction by the formation of chemical bonds. This leads to so-called soft agglomerates (in some respect also flocculation) which can be used for further processing (dispersion into matrices, film formation and so on).

If one intends to process such sols to materials, these topics have to be taken into consideration. An uncontrolled agglomeration, in general, leads to gels with a high porosity. To process gels to dense materials or coatings, in most cases is difficult. This means, the typical gel phases should be avoided, if possible. As mentioned above, due to the fact that strong forces or bonds become active between particles, it becomes very difficult to end up with a dense packing.

Especially the interfacial free energy term σ provides an interesting tool to interfere with the process by using surface interacting components during nucleation and growth (“surface modification”). Another important effect of surface functionalization is to build up controlled chemical reactivities on top of the particles as also demonstrated in Fig. 5. Shape control may be achieved by the use of surfactants with crystal size specific affinities. In Fig. 5, some possibilities of surface modification are shown. In case of providing specific chemical reactivities on the colloidal particle surface, the modifying components should be relatively small compared to the particle’s diameter in order not to change the overall chemical system too much. In order to keep the modifying agents on top of the surface, strong chemical bonds have to be established. This principle may be called Small Molecule Surface Modification (SMSM). Shown in Fig. 6 is the reaction of zirconia nanoparticles (about 9 nm in diameter) with a carboxylic acid. A shift of the carbonyl frequency from around 1700 cm^{-1} to 1600 cm^{-1} regime indicates that the particle surface reacts exactly the same

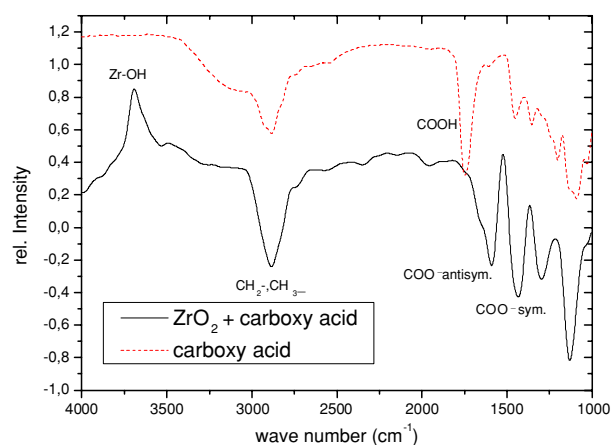


Fig. 6 Reaction of zirconia nanoparticles with a carboxylic acid

way as Zr^{4+} ions do. Similar observations have been made with β -diketones, but also on other nanoscaled particles like boehmite. This may be taken as an indication that surface atoms or ions in nanoparticles show similar chemical behaviour as the corresponding ions in solution. This, however, allows the utilization of a great deal of ionic chemistry on nanoparticle surfaces and opens up an interesting type of new chemistry, building up complex hybrid particles by combining a sol-gel process for the fabrication of colloid particles with ionic chemistry to build up complex chemical structures. Molecular reactivities during the sol-gel processing, especially using mixed systems, always have been interesting. By the introduction of NMR spectroscopy, especially with ^{17}O [33–35], many interesting results have been obtained. Summarizing it is to say that sol-gel processing has been investigated in many details over the last three or four decades. Especially, the potential of surface modification has come into the focus of many scientists during the last ten years [36].

4.2. Top down

Whereas the bottom up approaches are the mostly used technologies if chemical routes are considered, the top down approach (milling) only recently has been investigated. As described in detail in [37], milling has become possible by employing the above mentioned SMSM principle. As known from the milling literature, if one intends to achieve small particle sizes, so-called milling additives have to be used in order to slow down the recombination process by blocking active surfaces generated by the mechanical impact. Due to the fact that nanoparticles increase their diffusion rate by decreasing size, conventional additives which, in general, are oligomeric, organic, compounds, very often with ionic groupings, have to be substituted by small molecules to improve the diffusion rate of the surface blockers, too. If molecules are used which, at the same time, act as the

Table 2 Ball milling: effect of surface modification

	Surface modifiers	d_{10} (nm)	d_{50} (nm)	d_{90} (nm)
Alkylcarboxylic acids	Cornic acid	12	17	46
	Acetic acid	10	13	27
Ethercarboxylic acids	3-oxabutanic acid	9	12	33
	3,6-dioxahexanoic acid	9	13	24
	Trioxadecanoic acid	9	11	23
Unsaturated acids	Acrylic acid		–	
	Methacrylic acid		–	
	Sorbic acid		–	
Amino acids	N-(2-hydroxyethyl) ethylenediamine N,N,N', triacetic acid	10	13	32
	N-(2-hydroxyethyl) iminodiacetic acid	9	11,4	13,5
	Bicin	8	10	19
	6-amino hexanoic acid	11	15	33

desired surface modifiers, it is possible to grind material down to nano size and obtain within one and the same step the desired surface modification. As described in [37], a process has been developed by Tabellion et al. which leads to surface modified particles in the nano-range. In Table 2, a survey of some of the used surface modifying agents and their effect on milling zirconia is given. As milling device, a rotating ball mill was used rotating up to 4000 rpm including an ultrasonic device for avoiding re-agglomeration.

This technology has been adopted by Bühler PARTEC Company, which now has started marketing of the technology on a large scale.

In the last thirty years, the interest in nanostructured material strongly has grown since the discovery of very interesting properties in metals by Gleiter [38]. Colloidal sol-gel processing leads to nanoparticles which has become more and more significant. In order to process nanoparticles to materials (ceramics or nanocomposites), the surface modification seems indispensable either for avoiding of agglomeration or for adopting the desired chemical reactivity. For this reason, in the following chapters, the utilization of the sol-gel process for nanoparticle processing is described and as mentioned in the introduction, a few product developments and commercialization examples are given.

5. Examples for materials and applications based on sol-gel nanoparticle technologies

5.1. Surface modification for generating specific reactivities for polyurethane nanocomposites

One of the most attractive features of surface modification is to provide specific reactivities for further reaction, for example to incorporate nanoparticles into polymers or to use

them as a structure-controlling tool for obtaining specific material properties. Polyurethanes are well-known and widely used class of polymers which are obtained by the reaction of isocyanates with diols as a rule. Many attempts have been made in order to improve the scratch resistance of this type of polymer, especially while maintaining their transparency, for example as top coats in automotive coating. The dispersion of SiO₂ nanoparticles in polyurethanes was widely used in order to obtain these properties [39]. Problems arise from appropriate dispersion. This means the surface of the SiO₂ has to be compatibilized in order not to aggregate in the matrix. In addition to this, the simple dispersion of nanoparticles in matrices very often does not lead to the desired result. The fact is that nanoparticles, in opposition to very often expressed opinions, do not represent a “ceramic” phase within the polymer. For this reason, a new route was investigated by Kluge which is described in detail elsewhere [40, 41]. In this case, silica surfaces are surface modified by epoxy silanes which

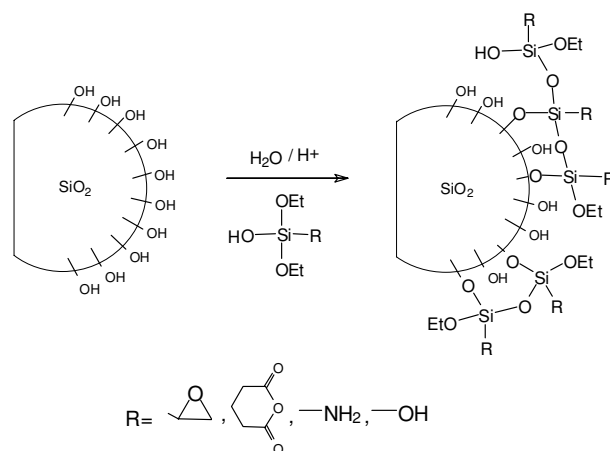


Fig. 7 Surface modification of nanoparticles with reactive polymerizable or polycondensable groupings

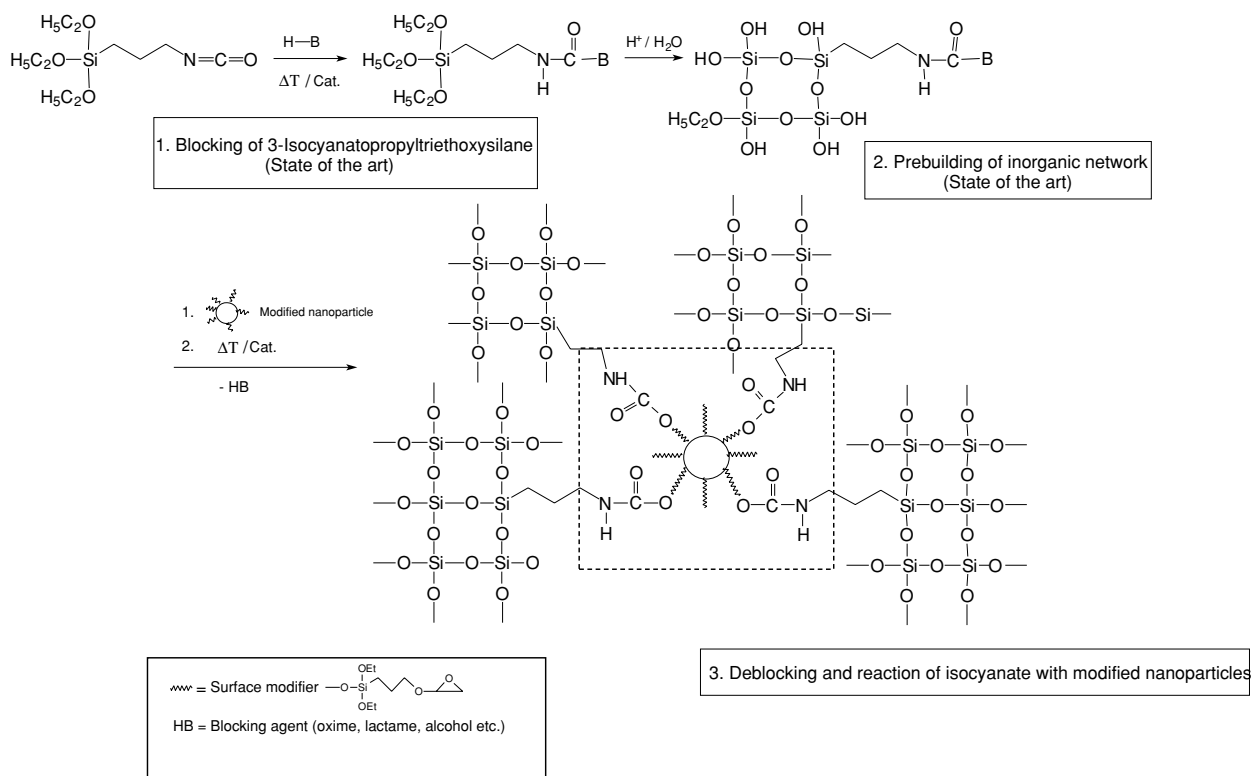


Fig. 8 Synthesis principles of PU "star" nanocomposites

form diols by epoxy ring opening. The reaction with isocyanates, in this case isocyanates blocked by state of the art blockers, will react under the described reaction conditions and form a polyurethane network where the nanoparticles act as inorganic "stars". In Fig. 7, the basics of the surface modification are shown which is not only restricted to epoxy silanes. In Fig. 8, the basic principles of the formation of the "star" polyurethanes are shown. The resulting two component systems can be spin-coated on any type of substrate and in Fig. 9, coatings on aluminium plates tested with a Taber Abrader test, are shown. The coatings were cured for 10 minutes at 100°C and then, the Taber Abrader was used for 1000 cycles which is a very high value for polymers (standard is 100 cycles). Compared to state of the art conventional polyurethanes, there is a dramatic effect, first by the use of silanes even without nanoparticles which shows a reduction from about 40 mg weight loss to around 3–4 mg which is attributed to the fact that within the polyurethane network, an additional inorganic backbone is built up. By the introduction of 6 nm SiO₂ nanoparticles (IPAST from Nishin Chemicals), the surface modification with epoxy silanes and subsequent formation of polyurethane structures, the weight loss can be reduced to about 1 mg which is an improvement of the factor of 40 compared to the state of the art. As shown in Fig. 9, the best results are obtained around 10 wt.% of SiO₂.

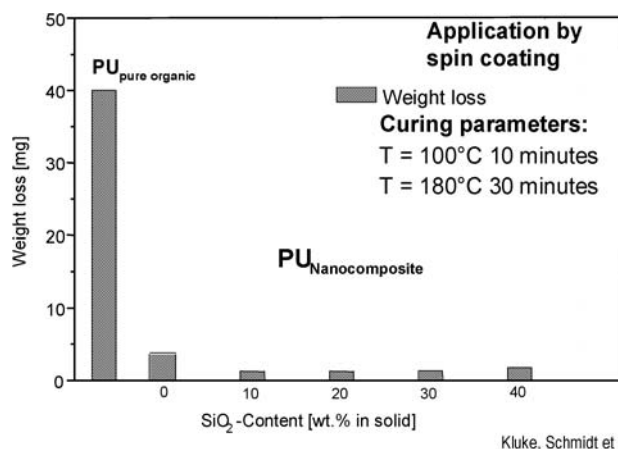
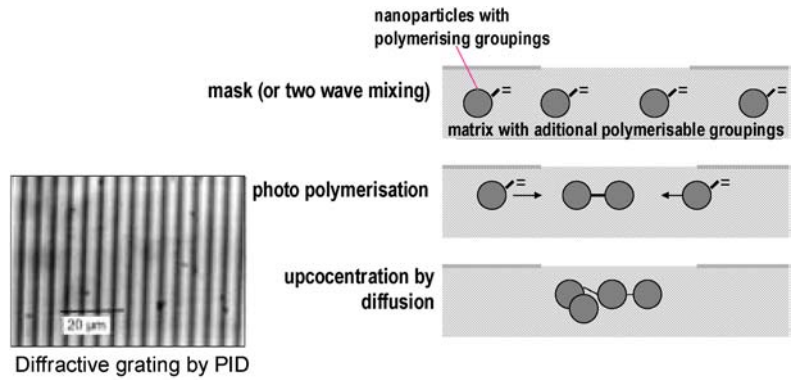


Fig. 9 Results of abrasion test of the PU "star" polymers

5.2. Gradient formation by directed nanoparticle diffusion

As already shown elsewhere [42], the diffusion rates of nanoparticle in soft films are rather high and comparable to organic molecules. This phenomenon has been used to develop the process of the photo-induced nanoparticle diffusion. The process is described elsewhere [43]. In this process, a film containing nanoparticles surface modified with polymerizable groupings, such as methacryloxy silanes, is

Fig. 10 The concept of photoinduced nanoparticles diffusion (PID)



covered with a mask. The film also contains photo initiators. By UV irradiation, nanoparticles diffusing into the irradiated areas, are polymerized and form nanoparticle clusters. Using nanoparticles having higher refractive indices than those of the matrix material leads to holographic patterns. The film matrix contains in addition to these organic monomers, and these organic monomers then can be cross-linked after removal on the mask, fixing the matrix as well as the nanoparticle clusters. Based on this process, the technology has been developed by Mennig and Oliveira [44] in which a continuously working production process is used for the fabrication of large area foils having so-called light guiding pipes. These light guiding pipes are essential elements in many displays since they are able to enhance the light yield or to direct light emitted from these displays. Another interesting application is the increase of sight light independent reflectivity of project screens. In Fig. 10, the basic principles of the PID process are shown. The diffusing nanoparticles are

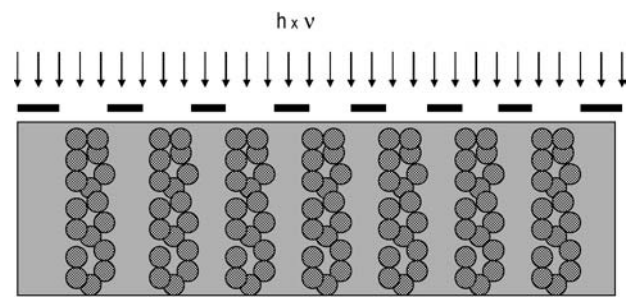


Fig. 11 Generation of light guiding pipes

trapped in the irradiated sections and generate high refractive index segments (holographic process). The fabrication of light guiding pipes schematically is shown in Figs. 11 and 12 shows the basics of a continuous production process for light guiding foils suitable for many display applications. This is a commercial product now. A cross section of an asymmetric light guiding film is shown in Figs. 13 and 14

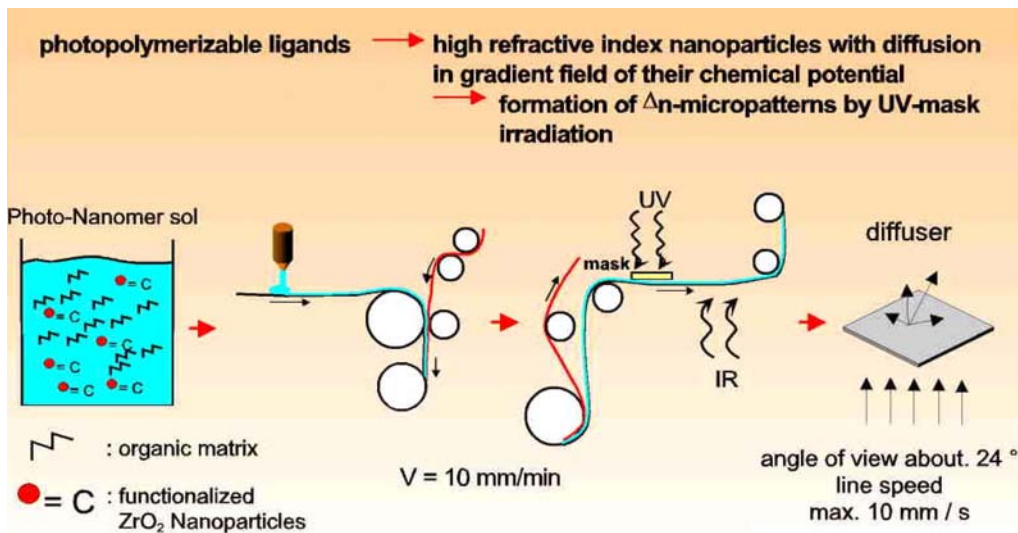


Fig. 12 Technology development for display diffusors

Fig. 13 Microstructure of the light guiding film; controlled asymmetric diffuser [after Zimmermann, AZ Company]

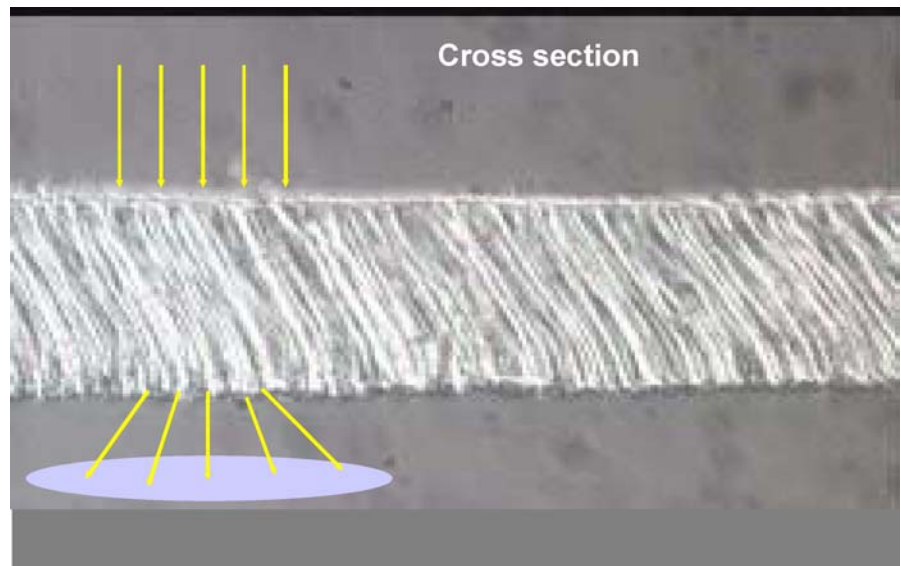


Fig. 14 Effect of the reflection enhancement for projection TV screens [after Menning/Oliveira]



shows the light enhancement effect of a projection screen. The whole advantage of this type of a screen is the fact that incident daylight from the sight does not reduce the reflectivity, an indispensable requirement for daylight projection TV [45, 46].

5.3. Flexible SiO₂ containing systems

5.3.1. Flexibilization of sol-gel films

As pointed out by Lange [47], there seems to exist a critical thickness for sol-gel systems for the fabrication of crack-free films. As many sol-gel scientists have pointed out, it seems to be very difficult to produce single step inorganic coatings

above 1 μm . In Eq. (2) (Critical thickness for crack-free films), the considerations of F. Lange are demonstrated.

$$t_c = \frac{E \cdot G_c}{A \cdot \sigma^2} \quad (2)$$

E is the E-modulus, G_c is the energy for crack formation, A is the material constant, σ^2 is the stress, t_c is the critical thickness.

The important problem seems to be the relaxation behaviour of films during the densification which is uniaxial and requires a considerable flow within the coating material since the densification of a film only permits the shrinkage in one direction. The important constant is A since beside E it seems to cover also plastic deformation. Based on this con-

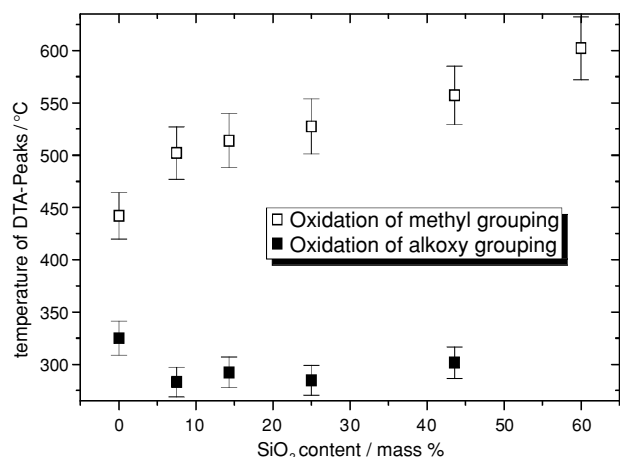


Fig. 15. Effect on $-\text{CH}_3$ Loss

sideration, investigations have been carried out in order to increase the plastic deformation by the reduction of the network connectivity. In sol-gel materials as already described elsewhere [48], in organically modified systems using methyl group containing silanes, the addition of SiO_2 nanoparticles leads to a strong increase of the critical thickness. In Fig. 15, the addition of SiO_2 nanoparticles (6 nm in diameter) on the temperature affected loss of methyl groups is shown. The figure clearly shows that with increasing SiO_2 content, the loss of methyl groups is dramatically shifted to higher temperatures. There is no good explanation for the increase of temperature stability, but this provides an explanation for the enhancement of the critical thickness. The addition of methyl group containing silanes to SiO_2 nanoparticles may lead to a coating of these particles reducing their interaction and enhancing the plastic deformation as it is schematically shown in Fig. 16. The effect of the addition of nanoparticles to methyl group containing system is remarkable. The critical thickness (defined as thickness obtained in a single step coating with subsequent firing to 500°C for one hour without any cracks) is increased from below $1\ \mu\text{m}$ to $15\ \mu\text{m}$. Moreover, these sols show sufficient flexibility to act as a sol-gel binder for glass fibre mats maintaining a high elasticity as shown in Fig. 17. This glass fibre insulation mat is a commercial material (URSA Glass

Fig. 16 Suggested sol structures with and without nanoparticles

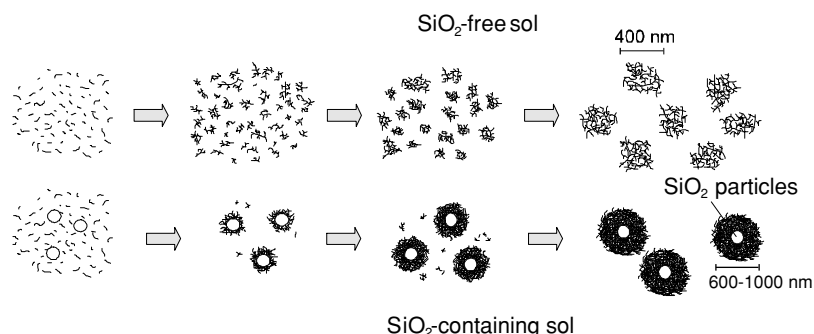


Fig. 17 Elastic glass fiber mats with highly inorganic sol-gel binders

Fibre Company, Spain). The advantage of this glass fibre is its high temperature stability up to 500°C and in case of fire, almost no toxic organic decomposition products appear as it is the case if conventional phenolic resin binders are used.

Other applications of these technologies (with appropriate variations) have been used for the development of interlayer systems for flame retarding architectural glazing [49] where SiO_2 nanoparticle composite systems have been used. This also led to commercial products and, as an example, the new airport of Dubai is completely outfitted with this type of glazing. The advantage is that the interlayers are only 3 mm thick, very effective (2 h fire protection) and light weight, so that large buildings can be equipped with this system.

The introduction of alkaline ions in addition to the nanoparticulate systems below 6 wt.% leads to sodium silicate glasses which, in opposition to other glass, are of high chemical resistance. Coatings up to $10\ \mu\text{m}$ in thickness applied on stainless steel lead to a glass layer which can be deformed after firing at 500°C , for example, for mounting these types of steel by threedimensional moulding onto other substrates. This was used for the development of a completely new type of high value sols for iron plates which is commercialized by Rowenta Electric Company, a subsidiary of the SEB group. The results of plastic deformation of relatively thick glass like sol-gel coatings is attributed to the structure of this system where the network modifiers are located around

Fig. 18 (a) Nanoglass coated iron plate and (b) coated waste gas controlling valve of a diesel engine in a car

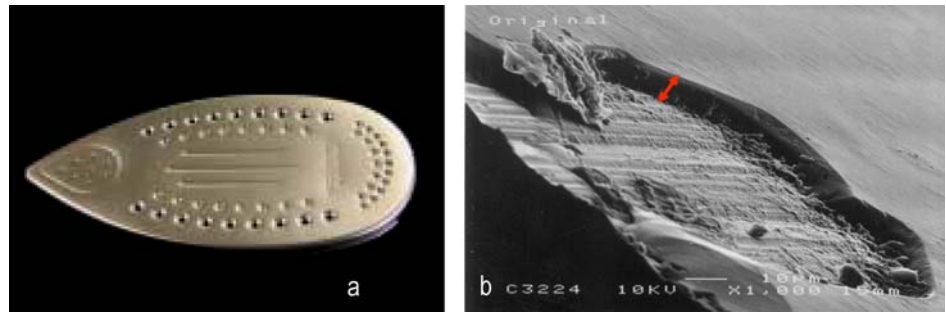
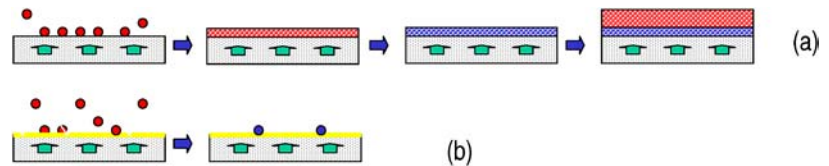


Fig. 19 (a) Principle of biofilm formation and (b) prevention of biofilm formation by use of additional anti adhesive layer



the SiO₂ nanoparticles, thus substituting a part of the covalent bonds by ionic bonds deleting to a higher deformability.

In Fig. 18, the application of this type of glass coating for iron plates (a) is shown. (b) shows the coating of a stainless steel valve in a waste gas controlling system of a diesel engine in a Renault car. It clearly can be seen that the coating smoothens the metal surface remarkably. This leads to a extremely low adhesion of cracking products from the waste gas and the avoidance of blocking the pneumatically or magnetically operated valves by cracking product deposition.

5.4. Antimicrobial coatings

Antimicrobial coatings are investigated intensively on many substrates in order to avoid the deposition of fungi and bacteria, LG and viruses. For this reason, many different concepts have been used and silver has been proved to have a very important oligodynamic effect [50–52]. This effect is known since a long time and the toxicity of silver for humans is a few orders of magnitude lower than especially for bacteria. For this reason, silver has been incorporated into polymers and, by diffusion of silver ions to the surface, bacteria may be killed. The problem, however, is that the killed bacteria still stay on the surface and form a good substrate for this settlement of other microbes on top of it. By this, a so-called biofilm is formed. The schematics of this process is shown in Fig. 19 (a), where by diffusion of silver ions to the surface, the deposited bacteria (left side of (a)) act as a substrate (right side). In order to avoid the adhesion of oncoming bacteria to the surface as well as the adhesion of dead bacteria, it seemed to be suitable to deposit in addition to the silver a thin antiadhesive layer on top of the system. This technology is described elsewhere [53]. It leads to the formation of an enrichment of side chain fluorinated silanes on top of a layer by thermodynamic reasons during the drying of the

film. ESCA profiling (Fig. 20) clearly proves an enrichment of the fluorinated side chains at the surface by a factor of approximately 10. This leads to the design of a nanocomposite coating (nanoparticles in the structure were supposed to improve the abrasion resistant of these types of coatings) as shown in Fig. 21 (a). It shows the nanocomposite coating with the antiadhesive layer on top, nanoparticles dispersed in the coating material structures as well as silver nanoparticles in between. The silver nanoparticles act as a reservoir for a diffusion of silver ions to the surface. The matrix was supposed to be composed of a hybrid sol-gel material in order to control or establish the right hydrophilicity or hydrophobicity suitable to control the silver ion diffusion rate, too. Figure 21 (b) shows the HRTEM micrograph of a film including silver nanoparticles. In order to obtain a simple application technology, silver nitrate, silver complexed with amino silane was used as a precursor in the sol-gel hybrid ma-

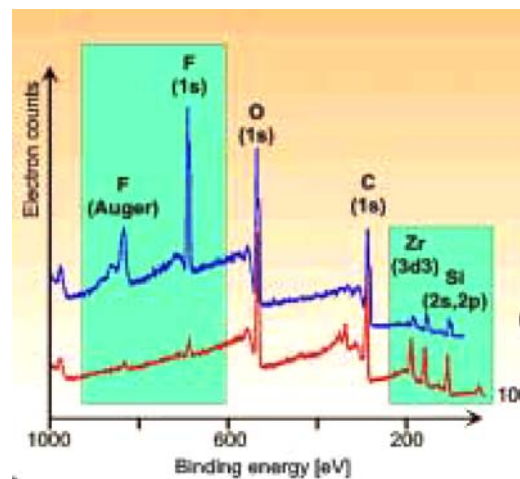


Fig. 20 ESCA profiling of hybrid gradient coatings

Fig. 21 (a) Design of a gradient forming nanocomposite coating with controlled release properties of Ag^+ ions and (b) HRTEM micrograph of the Ag nanoparticle containing coating

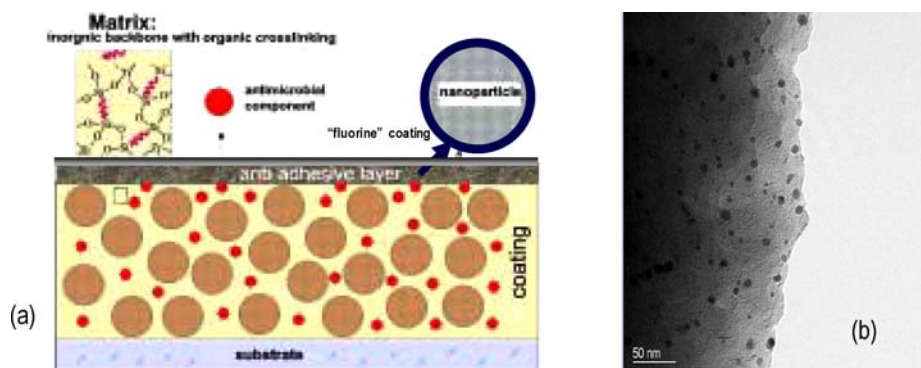
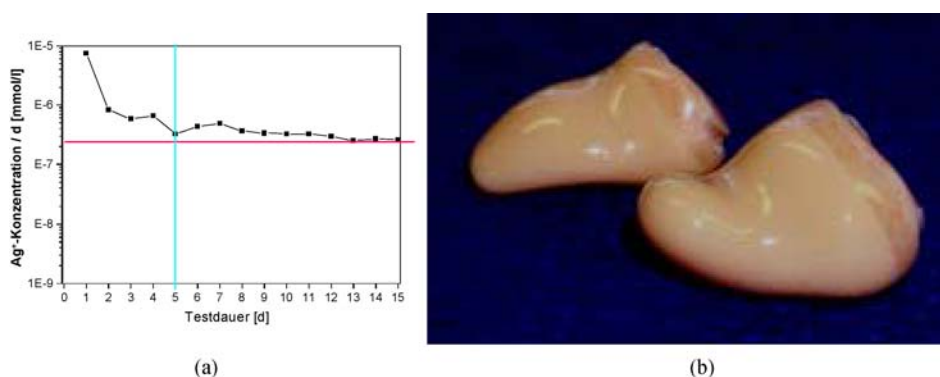


Fig. 22 (a) Release kinetics in simulated body fluids and (b) coated in-ear hearing aids



trix because this precursor stabilizes the silver ion during the whole sol-gel processing step. By UV radiation, a nucleation process is started which, by a heat treatment between 80 and 120°C, leads to a growth process to silver nanoparticles. By concentration of the silver precursor and the duration of the UV treatment, the nucleation frequency can be controlled and the size of nanoparticles can be tailored. As already mentioned, the diffusion rate of silver ions can be controlled by the hydrophobic/hydrophilic balance of the matrix. This system can be employed in a one step coating process and by UV irradiation and heat treatment tailored for appropriate purposes. The experimental investigations show that these coatings can be tailored for controlled release behaviour of silver in the oligodynamic concentration between 6 months and 5 years. As an interesting application, the system was tailored for the use on in-ear hearing aids. In-ear hearing aids are almost invisible since they are mounted within the ear, but, due to the blocking of the access of air “humid climate” is generated in the inner ear and bacteria and fungi grow very well in this environment leading to serious problems. With 160 patients, it was demonstrated that with a new coating, all inflammations and problems can be avoided. In Fig. 22, the established release behaviour is shown and it is of high interest that after an initial period, the release curve becomes very flat. On the right side of the picture, the coated hearing aids are shown. The system is commercialized and well accepted worldwide on the market.

Other applications have been developed for self-sterilizing pharmaceutical containers for liquid applications like nose, ear and eye drops.

5.5. Other applications

- These are writing, resistant and transparent abrasion resistant coatings on check cards: In this case, a photo curable nanocomposite coating with alumina nanoparticles has been established which allows the laser writing on check cards with the individual information after coating the plastic sheets. This leads to an increased security as well as to an optimal fabrication technology because it is possible to coat the plastic sheets before cutting.
- Superparamagnetic iron oxide nanoparticles for cancer treatment (collaboration with Magforce/Center for Nanobiotechnology, Berlin). It was investigated how far it is possible to coat 10–20 nm iron oxide nanoparticles (maghemite/magnetite), so that these nanoparticles are able to discriminate between healthy and tumor cells. By a silane coating put on top of the iron oxide nanoparticle by a sono-chemical process [54], surface modified nanoparticles with a point of zero charge at pH 8.5 could be synthesized which are strongly discriminating between tumor cells and healthy cells (10 to 1), having a colloidal stability under physiological conditions and are able to take up a maximum of energy at a frequency of 100 kHz

alternative magnet fields. Injected into the tumors, the nanoparticles diffuse into tumor cells and don't touch healthy tissue. By magnetic field employment, the tumor cells get heated up and die (directed hyperthermia). The clinical phase 1 with over 60 patients has been successfully performed. The clinical phase 2 is going on at present.

- Magnetic separation system for viral DNA: In this technology, mica coated with superparamagnetic iron oxide nanoparticle was coated by a sol-gel glass composition (zinc containing glass) [55, 56]. The composition was optimized to absorb selectively viral DNA according to its surface potential distribution. After the lysis of the viruses by putting in the coated mica, a selective absorption of the viral DNA on top of the particles takes place and they can be removed by magnets. A large scale technology for the fabrication and coating of the mica was established (spray drying technology) and by Roche Diagnostics, kits were fabricated and widely used for the detection of hepatitis and aids viruses.

These few examples about the flexibilisation of sols and the consolidated products show that with colloidal (nanoparticulate) sols and surface modification, interesting commercial applications can be obtained.

All these development examples which, in all cases, led to an industrial or medical application, only have been possible by following the vertical interdisciplinarity, that means starting from the basic investigations and following the development down to a turnkey technology. All these companies which now are producing these systems, did not have any skills in sol-gel or nanoparticle processing and product development. The described examples are only a few from over 60 successful product developments. The examples show that by building up the appropriate development and production structures, sol-gel and nanoparticle processing can lead to new products with successful market expectations. Meanwhile, 12 start-up companies have been founded and 3 major groups with international marketing and sales activities have been settled down.

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