HYBRID SOLS AS INTERMEDIATES TO INORGANIC-ORGANIC NANOCOMPOSITES

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ABSTRACT

For the preparation of inorganic-organic hybrid materials, synthesis processes have been developed to fabricate so-called hybrid sols, which contain an inorganic core (ceramic or glass) with nano-scale dimensions surface modified by organic groupings. These groupings have been reacted to the particle surface either by amino functional silanes (e.g. in case of iron oxide nanoparticles for amino group containing silanes) reacting with aliphatic acids to make surfaces unreactive and reduce the particle-to-particle interaction by acids, or silanes with polymerizable groupings reacted with organic monomers. In the paper a summary of the recent work and the development of structural models is given. Moreover, it could be shown that surface charges can be generated in the particles within already gelled systems and thus, particles can be transported by electric fields to form gradient index materials.

INTRODUCTION

Inorganic-organic hybrid materials fabricated by the sol-gel process are looking back now on an almost 20 years old history. However, the idea of a synthesis of organically modified inorganics or inorganically modified silicones (heteropolysiloxanes) is much older and goes back to the synthesis of silicones [1, 2], but never was exploited systematically for the synthesis of new materials for industrial applications. In [1], synthesis of heteropolysiloxanes is compared to silicon preparation, and silicones have been judged to be more advantageous. In [2], titanium dioxide was incorporated into silicones to improve the temperature resistance, but not much success was obtained. In the 80's, pioneered by D. Uhlmann and G. Wilkes, polycerams and ceramers were developed in order to improve mechanical properties of polymers. Schmidt developed heteropolysiloxanes, ormosils and ormocers for very special uses, such as contact lenses, functionalized surfaces for immunoassays or special adsorbents [3 - 5]. Slowly, the field was gaining increasing interest from the scientific community, and more and more types of materials and applications were proposed [6 - 8], and in various conferences so-called hybrid materials started to play an increasing role [9 - 13]. More and more materials have been developed and are already used in industry or are being developed.

One of the most interesting questions remaining is the structure of these materials, especially related to the phase dimension. Most of the materials still are considered to be molecular composites where an inorganic component exists in a molecular dispersion within a polymer type of network [14]. In this type of structure (e.g. SiO_4^{4-} tetrahedron), the function of the inorganic unit is to act as a three-dimensional crosslinker, leading to more brittleness. Due to the hydrolytic stability of SiC bonds, silicon has an exceptional position within these materials. Other elements have to be incorporated by different mechanisms, such as by forming complex compounds, e.g. ß-diketones or amines in order to disperse them molecularly. Inorganic properties resulting from the electronic properties of the inorganic component, of course, can be

incorporated into polymeric networks, too (e.g. spectroscopic properties in transition metals). But all properties to be attributed to solid state inorganic materials properties are excluded in the molecular type of composite. That means, the range of property tailoring of molecular inorganic-organic hybrid materials is rather limited. Despite restrictions, very interesting applications have been developed based on the molecular approach, e.g. porous materials [15] or scratch-resistant coatings on plastics [16]. Due to the small phase dimensions, all these materials can be prepared with highly transparent properties, and they have been proposed for optical applications [17, 18].

The question, however, arises, by using sol-gel techniques can composite materials be obtained with larger phase dimensions but still showing high optical transparency. For this reason, in order to avoid disturbing Rayleigh scattering, as a general rule the phase dimension of the dispersed phase should be below 1/20 of the applied light wavelength, meaning particle sizes below 5 - 8 nm in the visible range. From these considerations the concept of the so-called nanocomposites have been developed. These composites, if the phase dimension of the inorganic part is below the Rayleigh scattering limit, should be able to be prepared in the form of transparent materials and, due to the extended inorganic phase their solid state properties (e.g. refractive index), should be able to be incorporated. Additional quantum size effects of small particles (e.g. semiconductor or metal colloids) become of interest as well as properties of the interfaces, which can become significant due to the interfacial volume.

The aim of this paper is to give some basic ideas of nanocomposite synthesis, properties and materials tailoring and to summarize some interesting results.


GENERAL ASPECTS

In order to exploit the possibilities of nanocomposite properties, it is necessary to develop methods for a cost-effective synthesis and for a perfect dispersion of the particles in a polymeric or inorganic-organic network. The composite can be considered as a nanoparticle-reinforced, nanoparticle-modified or a simple nanoparticle-containing polymeric network and shall be called "Nanomers" (nanoparticle and organic component containing polymer type materials).

Synthesis of Nano-Scale Particulate Phases

As described elsewhere, the sol-gel process can be used advantageously for the preparation of ultrafine particulate systems in the lower nanometer range [19, 20]. This route seems to be quite simple since if one starts from a molecular solution in a system able to precipitate, for example, after nucleation a growth reaction takes place involving all size ranges. If the thermodynamical parameters are suitable, large crystals can be formed. One of the major objectives of the sol-gel process, however, is to keep small particles in solution in order to carry out various moulding processes, such as film or coating formation. Due to the surface area, small particle size and the high number of particle interactions, the integral particle forces per volume unit becomes very large (e.g. van der Waal's forces). Therefore, a system has to be generated in which the agglomeration by attraction of the particles can be controlled. In general, in sol-gel ractions this is carried out by pH control which produces surface charges (Stern's potentials) [21], ending up with repulsing forces between the charged surfaces. In order to form compact materials from sols, the system has to be destabilized, either by change of pH, loss of solvent (overcoming the critical radius for repulsion from the Stern's potential), or by generating chemical reactions between the particles. In all cases where these reactions do not run under

controlled conditions, random arrangements of the particles are formed, leading to gels with low density microstructures. The stabilization condition for sols is that the surface free energy generated by any type of surface active medium (e.g. electric charges) generates a lower Gibbs free energy minimum than the aggregation. This is demonstrated in fig. 1.

Fig. 1: Schematics of the stabilization of sol particles by electric charges and destabilization followed by aggregation.
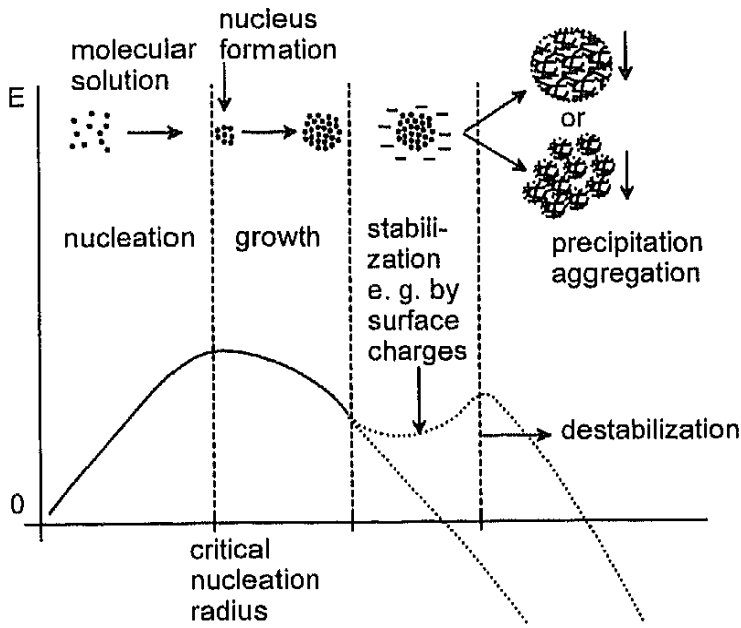
This type of sol-gel process (colloidal type) is typical for most of the elements being able to form insoluble compounds starting from a solution. The only difference between a precipitation process and a sol-gel process is that the sol-gel process, in general, is carried out far away from the point of zero charge (pzc). If well-crystallized precipitates shall be obtained, the reaction has to be carried out close to the point of zero charge. One of the disadvantages of charge-stabilized systems is that after the removal of the charges the forces between the particles in solution are not only van der Waal's forces, but in most cases (especially with sol-gel materials with reactive OH groups) also are based on hydrogen bridges or even the formation of chemical bonds. This leads to so-called hard agglomerates and gels if the whole volume is agglomerated "monolithically", which cannot be redispersed. For this reason, we have introduced [22, 23] the concept of chemical surface modification with the possibility to establish controlled interaction between the particle surfaces. The schematics are shown in fig. 2.

Fig. 2: Schematics of the chemical surface modification to stabilize sols and redispersion.
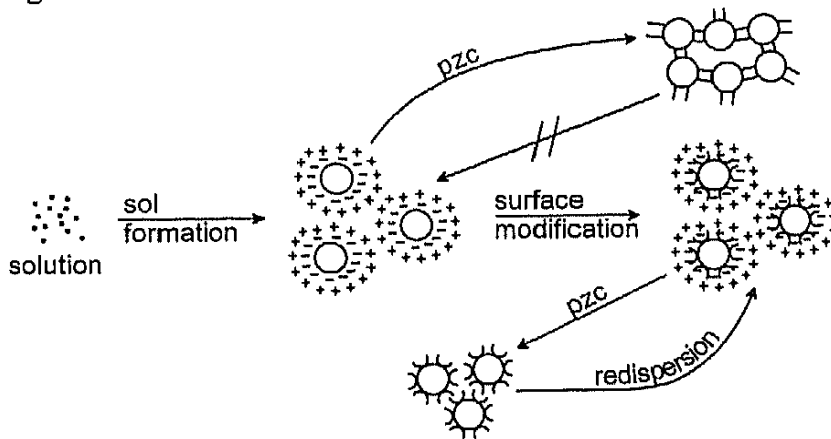
The chemical stabilization in addition to the charge stabilization also allows establishment of specific surface reactivities to control the polarity of the particles and by this, to control the interaction of the particles to other components (such as organic monomers) as well as to protect the surface from undesired reactions like absorption of components from the solution.

This concept leads to new type type of a sol-gel precursor, the so-called hybrid sols, which can be considered as a specific type of sol-gel precursor suitable for various reactions.

The preparation of this type of sols can be carried out by different routes. Some of them will be described.

Modification of Alkoxides

This route describes a more or less stoichiometric formation of alkoxide complexes, as described elsewhere [24]. Interesting complex formers with an interesting potential to act as surface modifiers for nanoparticles are ß-diketones or ether alcoholates, alkoxides or carboxylic acids for oxidic, and amines or aminoacids for transition metallic systems.

In order to obtain appropriately modified particles, this route requires very special conditions. First, a complex bond to the alkoxide precursor has to be possible. The above mentioned compounds are stable in many alkoxides [24]. Second, the stability of the bond has to be low enough to allow hydrolysis, condensation and growth. Third, the bond has maintained to the particle surface during the growth process and still has to be intact if small particles are formed. If all of the three conditions are fulfilled, this method can lead to chemically surface-modified colloidal particles. The schematics of this assumption are shown in figure 3. If the bonds to the surface are stable enough, they should be able to be established even after the colloid formation, thus replacing electric charges.
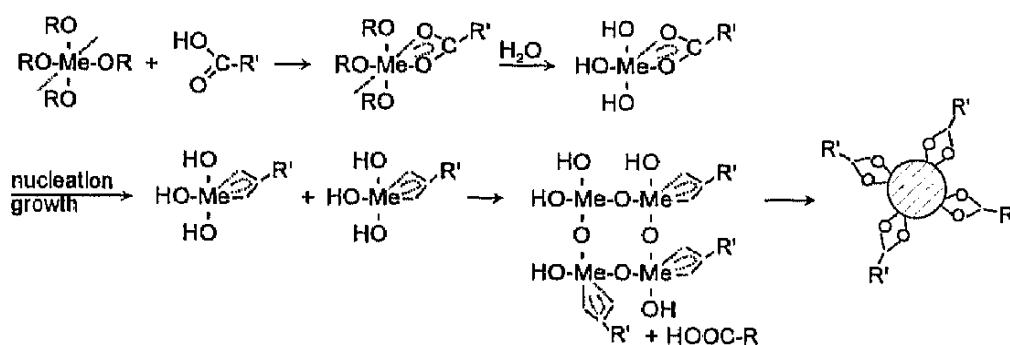

Fig. 3: General scheme of modification of alkoxides with subsequent hydrolysis and condensation with carboxylic acids as example.

It has been shown elsewhere [25] that even already weakly agglomerated nano-scale systems can be redispersed using this approach, for example agglomerated commercially available nano-scale boehmite refluxing with carboxylic acid groups such as propionic or acetic acid. The resulting system is a boehmite powder covered with carboxylic acid groups, which are stable enough not to be washed away by water. Sols prepared from these surface-modified systems do not show a gel point but only a slowly increasing viscosity up to more than 50 vol. % solid content (fig. 4). Without acid, gelation takes place in any cases [26]. Identical results are obtained for propionic acid. These systems can be moulded by plastic deformation and have been used for extrusion of tubings [27]. The surface modification can be followed by IR spectroscopy.

The $>C=O$ frequency is shifted from the 1700 cm^{-1} regime of the free acid to the carboxylate form below 1600 cm^{-1}, typical for salts.

This example demonstrates the usefulness of chemical surface modification of nano-scale particles in order to enable appropriate processing.
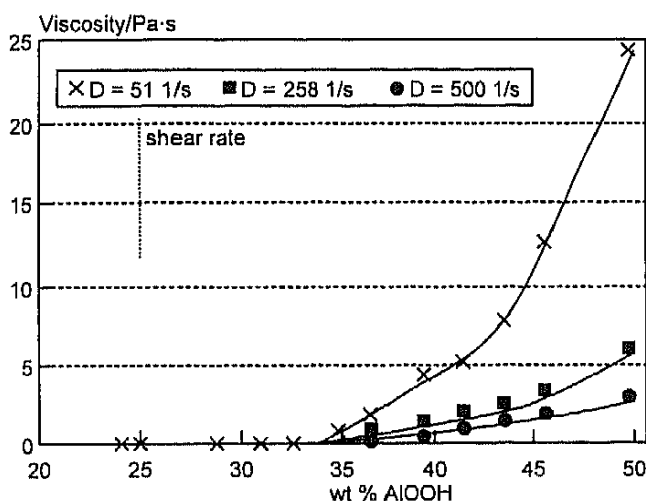
Fig. 4: Rheological behavior of aqueous boeh- mite sols with 15 nm particle diameter, surface modified with 1 wt% acetic acid.
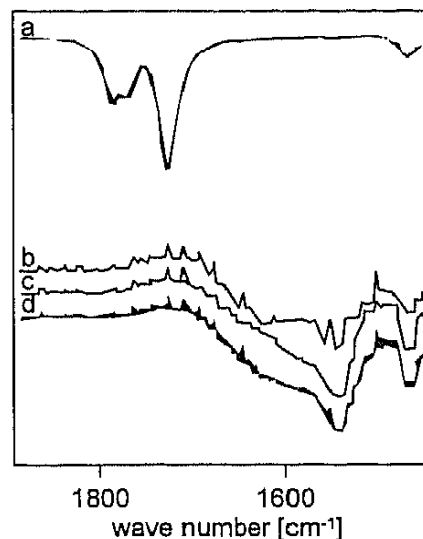
Fig. 5: IR spectra of a: propionic acid, b: 1 wt%, c: 2 wt%, e: 5 wt% boehmite + propionic acid; Al propionate.

For the surface modification of small particles, different prerequirements have to be fulfilled. One of the most important is the use of small molecules in the range of below 10 or 15 carbon atoms; otherwise the volume required by the surface modifiers (e.g. if polymers are used) leads to a drastic decrease of the nanophase content of the whole system, and ceramic processing, for example, becomes very difficult, due to the volume required by the absorbed surface modifiers. If small molecules are used, the binding force to the surface has to be high enough to avoid high concentrations of the surface modifiers in the surrounding liquid. For this reason, the above mentioned systems have proven suitable for a variety of modifications.

Another type of surface modification is the reactive type, for example, the reaction with silanes which directly form bonds to the surface or which can be reacted in a way to surround particles with a coating. An interesting example for this type of surface modification has been developed by Lesniak et al. [28] who were able to develop a surprisingly hydrolytically (be- tween pH 1 and 11) stable aminosilane coating by reacting it on the surface of 10 nm magnetite particles by using ultrasonic energy in the presence of γ-aminopropyl triethoxysilane to cover the magnetite surface completely. In fig. 6 the ξ potential of modified and unmodified magnetite particles are given, clearly showing the effect of modification.
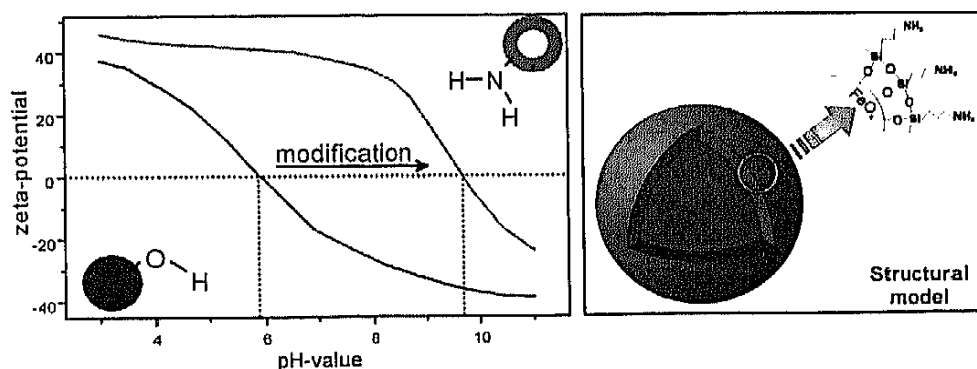

Fig. 6: ξ potential curves of surface mo- dified and unmodified magnetite particles.

As known from the literature [29], polycondensed

aminosilanes rapidly depolymerize in aqueous solutions and never form stable systems. The high stability of the coated magnetite is attributed to a very high degree of polymerization of the aminosilane shell, since the Fe-O-Si bond is very sensitive to hydrolysis.

This material represents a variable precursor for different reactions. It can be used as a sol-gel precursor easily incorporated into sol-gel glasses to obtain superparamagnetic glasses. It also can be used as a precursor for polymer fabrication, for example, together with epoxides, to produce superparamagnetic polymers. Another way of attaching reactive bonds to the surface of iron oxide particles again utilizes carboxylic acids. The first successful sample has been obtained from reacting the iron oxide sols under ultrasonic treatment with citric acid [30]. These samples are hydrolytically stable at room temperature as well as in aqueous solutions, but now show -COOH groupings at the surface.

The modification of oxidic nanoparticles by reaction of carboxylic acids with zirconia particles has been described elsewhere [31 - 33]. The use of carboxylic acid with functional groups such as methacrylate leads to hybrid sols with a potential to be copolymerized with a variety of organic monomers and, of course, hybrid precursors such as silanes containing polymerizable groups, e.g. methacryloxysilanes. This route is started by reacting alkoxides with carboxylic acids and methacrylic acid. The question arises, however, how far during the subsequent hydrolysis and condensation does the bond between the particle surface and the carboxylic acid remain intact, and how much of an oxidic network is formed. As shown elsewhere [34], under conditions of hydrolysis and condensation and subsequent polymerisation when methacrylic acid is used as carboxylic acid, monoclinic nanoparticles (≈ 2 nm) are formed. Various optical materials have been prepared using this approach [35 - 36]. The evidence for the existence of Zr carboxylic acid bonds throughout the process could be shown by IR spectroscopy.

In figure 7, the IR-spectra of ZrO_x/methacrylic (ma) acid system is shown in various states. It shows that the $>C=O$ frequency remains unchanged throughout all processing steps (complexation, hydrolysis, polymerization) and that the reaction of ZrO_2 surfaces with carboxylic acids leads to the same $C=O$ frequency.
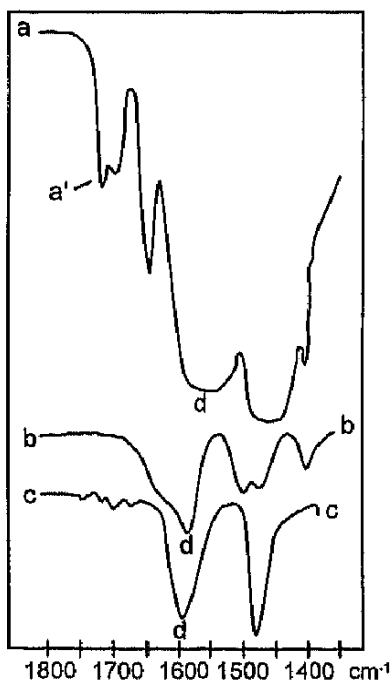

Fig. 7: IR spectra of a: $Zr(OR)_4$ complexed with excess of ma ($>$ 2:1); b: sub μm ZrO_2 reacted with aliphatic carboxylic acid; c: after hydrolysis and condensation; a': $>C=O$ frequency of the free acid; d: of the carboxylic and reacted to the particle surface.

One of the interesting questions in this connection is related to the polymerization mechanism since the "molecular weight" of „monomers" consisting of nanoparticles linked to double bonds is high compared to organic monomers. As shown by Krug [35], the polymerization kinetic of a mixture of ma-reacted ZrO_2 nanos and methacryloxy silane (MPTS) is slower than that of pure MPTS, but high conversion rates are obtained (up to 95 %). This leads to the conclusion that the nanoparticles show rather high diffusion rates almost comparable to those determined in polymerizing systems. From these findings, the question was asked how nano-scale particles in soft organic matrices can be used to provide selective diffusion in order to enforce phase separation in such systems. Mechanistic examinations during the fabrication of optical gratings or microlense arrays by holographic methods

proved that a selective diffusion of nano-scale particles can be initiated by a photopolymerization process with an intensity gradient of the light beam [37]. The schematics of the process are shown in fig. 8, indicating the enrichment of areas with increased nanoparticle contents schematically.

mixed with monomers → → film formation

↓ ↓ ↓ ↓ mask

↓ photo polymerisation ← diffusion of nanos

I

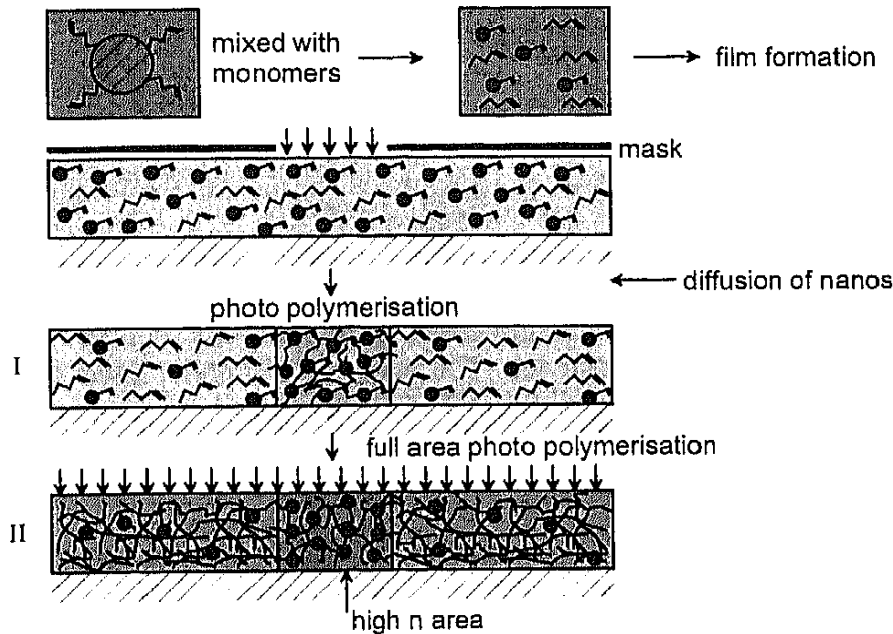↓ full area photo polymerisation

II

↑ high n area

Fig. 8: Schematics of the preparation of gradients in photopolymerized nanocomposite films.

If this assumption is true, after full area polymerization, a difference in the refractive index in preliminary radiated and non-irradiated areas should remain. Moreover, the Δ n should depend on particle size (due to differences in diffusivity) and particle content. Oliveira et al. [37] have shown that the diffusion of ZrO_2 nanoparticles can be followed by on-line determination of the diffraction efficiency during an irradiation process using the interference pattern of a two-wave mixing process to generate intensity fluctuations. He found that the diffusivity increases by decreasing particle size. Moreover, in these experiments the ma coated ZrO_2 particles have been copolymerized with methacryloxy silane, and the diffractive efficiency also depends on the ZrO_2 content. With $C_{ZrO_2} = 0$ (pure methacryloxy silane) a diffractive pattern could be obtained in the first step due to the Colburn-Haines effect. After full area polymerization, however, the diffractive efficiency returns to zero. These findings actually prove that ZrO_2 nanoparticles are "transported" by the attached double bonds due to a concentration gradient established by the "consumption" of double bonds through the photopolymerization step. Moreover, the concentration gradient of ZrO_2 could be directly measured by micro-Raman spectroscopy as well as by scanning EDX. This increase of nanoparticle content (in this case ZrO_2) is accompanied by an increase of the refractive index up to $1.5 \cdot 10^{-2}$ depending on composition [37].

Additional experiments have been carried out by the use of artificially generated gradients of the chemical potential, or even another potential within a material, to initiate diffusion processes and to fabricate gradient materials. Using this approach seems to be attractive, as shown by the example of an holographic process using the diffusion of high refractive index nano-scale particles. Another approach would be to use electric fields and for this case, the system described in [37] was used to investigate how electrophoresis can be used for building gradients. In fig. 9 the experimental set-up for this investigation is shown.

The question arises how nanoparticles in non-densified organic or composite matrices can be "moved" by other means. If charges are present on the nanoparticles, they should be able to move in an electric field. Various possibilities may exist with respect to the changed particles (fig. 9). Depending on the degree of surface coverage, residual $\equiv$ZrOH groupings may exist, leading to negative surface charges. In this case, the particles should move to the anode. If the
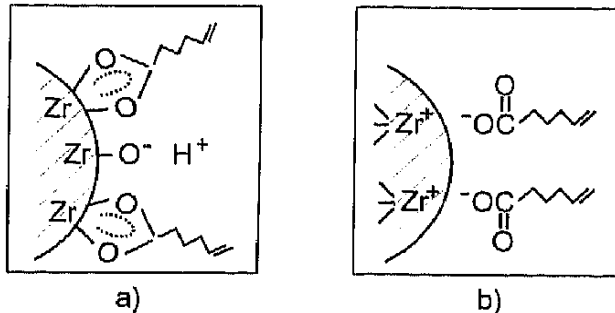

a)   b)

Fig. 9: Different models for surface charges on ZrO₂ nanoparticles.

salt form is dominant, the particles should move to the cathode. In fig. 10, the schematics of the electrophoretic system are shown. The set-up was used to produce GRIN lenses.

To produce the lenses, a cylindrical receptacle has been filled with the photopolymerizable composite containing nano-scale ZrO_2 particles. The composite material used in the experiment is based on methacrylpropyl trimethoxysilane (MPTS), zirconium n-propoxide (ZR) and methacrylic acid (MA) in 10/2/2 (MPTS/ZR/MA) mole-%. Irgacure 184 (Ciba) was used as a photoinitiator in concentration of 0.4 mol%/C=C. The synthesis of the basic composition is described in [37].

The convergent lens has the radial concentration gradient of the ZrO_2 particles pointing to the geometrical center of the lens. To induce this concentration gradient of the positive ZrO_2 by electrophoresis, the window of the receptacle were defined as the cathode and the centered gold wire the anode. The voltage was employed for 36 hours.

The photopolymerization process using a Hg-Xe lamp was divided in two steps. First, the nanocomposite was gelated by a two minute treatment with a UV, and the cathode, consisting of a 50 μm gold wire, was removed. The second step includes the complete polymerization of the sol with subsequent 8 minutes of UV irradiation. After photopolymerization, the rod was cut into disks, and the refractive index was measured by Spectroscopic Ellipsometer (ES 4G-Sopra). A n was detected to be 0.07 (fig. 10). Since the particles move to the anode, the model a) in fig. 9 is more likely.
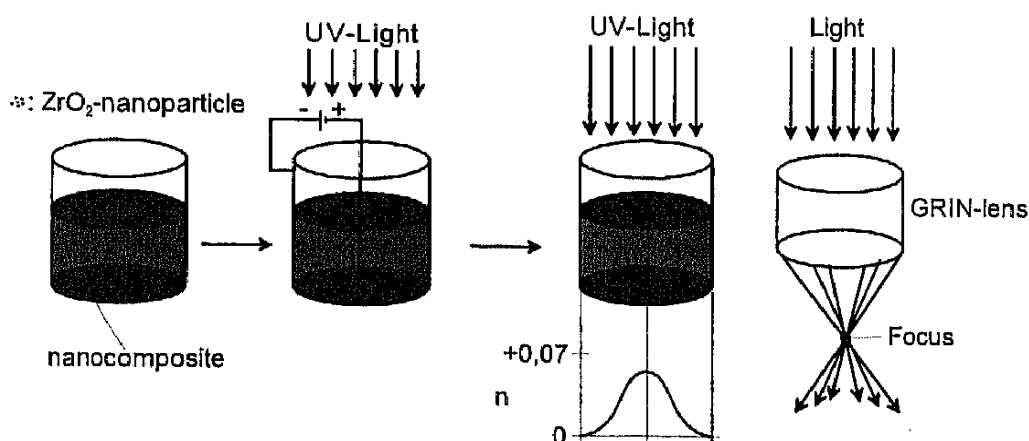

Fig. 10: Experimental set-up for electrophoretic gradient material fabrication (direct current voltage).

One of the most important issues of materials synthesis using surface-tailored nanoparticles is to prevent aggregation, especially if high optical quality (transparency) is required. Another reason for looking for high dispersion is to implement high interfacial volumes into materials properties. Whereas interfacial phases, in general, do not play an important role in systems with micrometer-size particles, the interfacial phase can become a remarkable component if particle size decreases to the nm range. In fig. 11 this is demonstrated on a simple example.
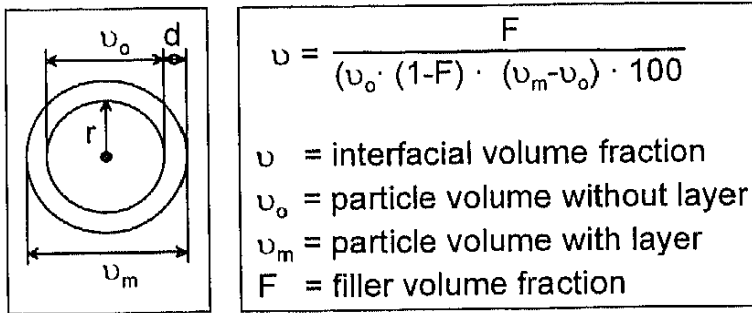

$$\upsilon = \frac{F}{(\upsilon_o \cdot (1-F) \cdot (\upsilon_m - \upsilon_o) \cdot 100}$$

υ = interfacial volume fraction

υ_o = particle volume without layer

υ_m = particle volume with layer

F = filler volume fraction

Fig. 11: Estimation of the volume of interfacial phases in nano-composites. Assumed data: d = 2 nm, F = 0.15 nm, r = 7.5 nm. Calculated value for v = 30 % [after 38].

As one can see, for the assumed filler volume fraction F = 0.15, the volume of the interfacial phase exceeds the degree of filling by the factor of 2 if the thickness of this phase is estimated to 2 nm. These data are estimated according to investigations of Kendall and coworkers [39]. This means that in nano-scale particle filled polymers effects have to be expected caused by an interfacial phase. In fig. 12 the storage modulus of three types of composites are compared. The composite is a copolymer of MMA (metal methacrylate) and HEMA (hydroxyethylmethoxylate) [40].
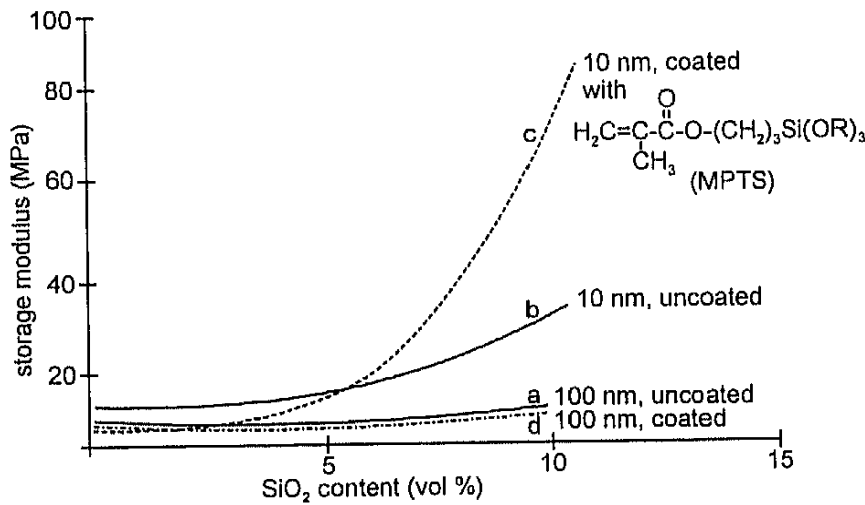

Fig. 12: Storage modulus as a function of the coating of 10 and 100 nm particles of SiO₂ with meth-acryloxy silane and subsequent poly-merization.

A one-to-one composition of MMA to HEMA was used. Azubis-isobuty-ronitril (AIBN) was used as a thermal initiator. Fig. 12 shows clearly that 10 % filler that 100 nm, uncoated as well as the coated species, curve a and d, do not effect the mechanical properties. The use of 10 nm particles gives a slight increase of the storage modulus, but the particles coated with MPTS results in a strong increase of the storage modulus. Especially the difference in the coated and the uncoated case leads to the conclusion that these effects cannot only result from the pure filling effect since the degree of filling is very low at 10 %. The formation of a interfacial structure is postulated (curves b and c). It has to be mentioned that the composite systems b and c both are completely transparent, and no light scattering can be measured.

In the uncoated case the good dispersion can be attributed to the presence of HEMA which generates SiO₂ interactions with the surface OH groups by the alcoholic OH groups of the hydroxyethyl group. If one compares the Tg values (obtained by thermomecanical analysis from

the tan δ maximum) for 100 nm coated and uncoated, for the 10 nm MPTS and APTS coated and 10 nm uncoated particles, corresponding results are obtained (figure 13).
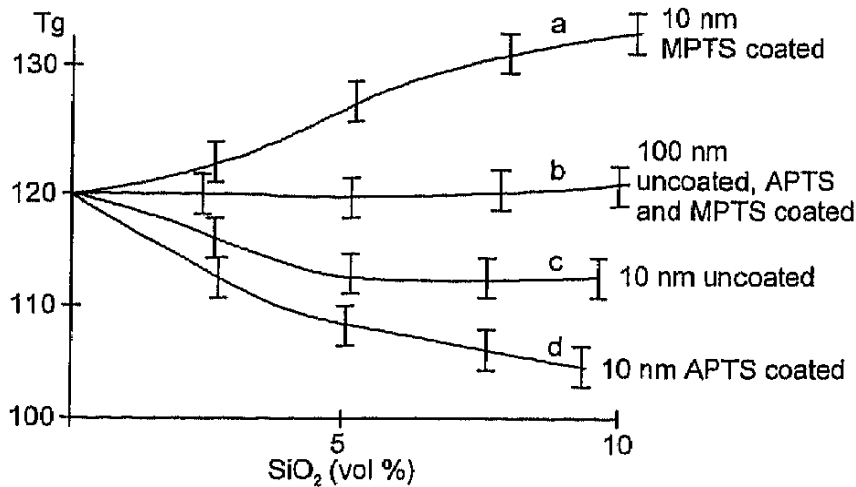

Fig. 13: Tg values of different SiO₂ MMA/ HEMA copolymer composites.

As expected from the storage data, the 10 nm MPTS composite leads to increased Tg values, whereas the 100 nm systems are almost unaffected by the composite formation. For the 10 nm uncoated system, a slight decrease in the Tg value is observed, which does not match exactly with the storage modulus observation. However, in the 10 nm case, if another surface modifier is used, in this case acetoxypropyl trimethoxysilane (APTS), the Tg value decreases. This is attributed to the formation of a "softer interface", due to the fact that no bonds are formed between the matrix and the particles, which seems to have less order than the polymer by itself. A model is given in fig. 14.
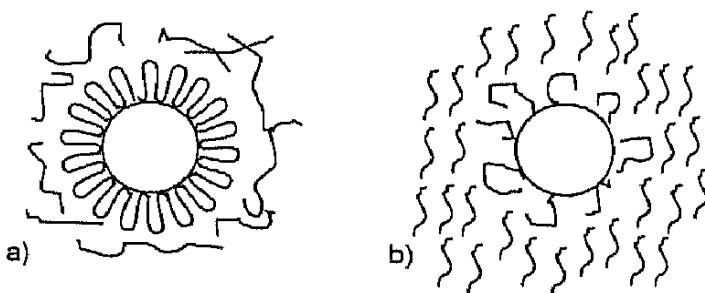

Fig. 14: Model for the formation of "soft" and "rigid" interfaces around nanoparticles by different surface modifiers. a): polymerizable, b): unpolymerizable.

These results can only be interpreted by the presume of a remarkable volume fraction attributed to an interfacial phase, too, according to figure 11. These first experiments show that by using nanoparticles as fillers in a perfectly dispersed state, it seems to be possible to use interfacial structures for tailoring polymer properties, which can be used as a new approach for manipulating polymer properties. But these investigations still are at their infancy.

As shown by work of Mennig and Nass, hybrid sols, that means nano-scale particles with tailored surfaces dispersed in solutions, not only can be used for ceramic polymer nanocomposites, but also for metal polymer composites [41] for the fabrication of high χ^3 value composites, or for colloidal processing of ceramics with extremely low sintering temperatures [42].

CONCLUSION

It can be concluded that the sol-gel process is a suitable means for the fabrication of nanoscale inorganic particles. If chemical surface modification with organic molecules is used for steric or electrosteric stabilization instead of charge stabilization, the hybrid sols are obtained.

These hybrid sols are characterized by functionalized surfaces which can be used for a variety of materials tailoring, for example, superparamagnetic composites, optical gradient materials or new types of interfacial phase-determined ceramic polymer composites. This class of materials can be considered nanoparticle-containing organic polymers (nanomers).

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