

Invited Lecture

NOVEL ORMOCERS AND NANOMERS FOR COATINGS

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Nanoparticles produced by a microemulsion for a controlled growth precipitation technique (ZrO_2 , $AlOOH$) have been surface modified and incorporated into inorganic/organic composite matrices made from epoxy or methacryloxy silanes. For this reason, the nanopowders have been surface modified with carboxylic acids in order to obtain full dispersibility necessary for high optical quality coatings. ZrO_2 was used for obtaining high refractive index coatings. By adjusting an appropriate zeta-potential the particles in a not fully cross-linked matrix have been upconcentrated electrophoretically to obtain graded index optical lenses. Methacryloxy grouping containing particles have been used for the preparation of UV curable hard coatings containing $AlOOH$. SiO_2 and TiO_2 particles allow the fabrication of antireflective hard coatings on plastic surfaces by UV curing methods.

1. INTRODUCTION

Nanocomposite materials have gained increasing interest in the past. Several interesting results from industrial applications already have been reported, for example the layered silicate type of nanocomposite¹ or nanocomposite type of hard coatings². These nanocomposites have been prepared by dispersing nanoscale inorganic powders within a more or less polymer type of matrices. Other types of nanocomposites where metals are dispersed in sol-gel matrices have been reported by Mackenzie³ or by Mennig⁴. Semiconductors such as cadmium sulfide also have been dispersed in the gold matrices^{5,6}. The objective of these investigations was either the increasing of the mechanical strength of materials⁷, the increasing of the hardness of polymer matrix while remaining transparent due to the small particle size² or to introduce properties specifically related to the nanoscale such as quantum size or plasmon effects.

In situ preparation of nanostructured systems have been reported by Krug and Tiefensee^{8,9} where zirconia nanoparticles have been prepared in organically modified sol-gel matrices during hydrolysis and condensation under the protective effect of complex formers to zirconia and zirconia colloidal particles such as β -

diketones or methacrylic acid whereas the in situ fabrication leads to partially crystallized systems which are suitable for many applications (for example volume and relief phase gratings, Fresnel lenses, micro lens arrays, GRIN lenses, laser coupler, storage media). Completely and fully crystallized systems are not easy to prepare using this route for many compounds. But for many purposes fully crystallized particles seem to be of high interest for example for obtaining high refractive indices or for ceramic applications.

In order to fabricate nanoparticles the sol-gel process seems to be an interesting route since in most cases hydrolysis and condensation of appropriate soluble precursors lead to particulate sols which, in general, are electrostatically stabilized by absorption of ions to the particle surfaces, generating the so-called Stern's potential¹⁰. If the concentration of the particles is low enough, the Stern's potential is sufficient to stabilize sols since the average distance of the particle is high enough not to break through the Stern's potential and cause attraction and aggregation. However, as already mentioned above, in most cases the particles are not very well crystallized. Moreover, these particles always possess electric charges as "surface modifiers". In order to process these colloidal particles to materials such as ceramic coatings or composites, especially not only extremely thin layers are required. Difficulties arise due to the fact that by removal of the electric charge rapid condensation between the particles takes place, leading to irregular and inhomogeneous structures difficult to be densified to compact materials outside of thin films.

Nanoparticles also can be generated as an in situ reaction within a polymer type of matrix or sol-gel derived composite matrices for example prepared from organoalkoxysilanes having functional groupings to be polymerized to polymeric chains such as methacrylates or epoxides^{8,11}. This reaction as demonstrated with a zirconia aconic sample leads to partially crystallized small particles in the range of several nanometers. However, as mentioned above, no full crystallinity can be achieved.

For receiving the full benefit from the physical or other crystalline properties of nanoparticles, an adequate route would be to synthesize particles, to crystallize them and to surface-modify them in order to get the appropriate surface reactivity. This requires routes to prepare nanoparticles, routes to crystallize nanoparticles

while maintaining the full dispersibility and to avoid hard agglomerates and to outfit them with appropriate surface properties to provide further reactions. In this paper a summary of different investigations is shown in order to demonstrate a complete route from the sol-gel nanoparticles synthesis to coatings for different applications.

2. EXPERIMENTAL

To generate high refractive index nanoparticles, 21 g of tetra-isopropylorthotitanate was slowly dropped into a mixture of isopropanol with 9.3 g glacial acetic acid and 1.2 g water under stirring at 25 °C. The solution was stirred for 12 hours at 25 °C. To silanise the surface of the formed TiO₂ nanoparticles 0.5 g 3-glycidoxypropyl-trimethoxysilane (GPTS) were mixed with 200 g TiO₂ sol under reflux and vigorous stirring at 50 °C for 5 hours. A part of isopropanol (10 g) was removed from the sol by vacuum distillation at 10 mbar and 25 °C and 20 g of 2-isopropoxy-ethanol were added. UVI 6974 (Union Carbide) was mixed in proportion of 3 wt.% in reference to the GPTS concentration.

The SiO₂ nanoparticles (low refractive index component) were synthesized by base catalyzed hydrolyses and condensation of tetraethoxysilane (TEOS). 63.0 g TEOS were mixed with 10.58 g de-ionized water and 14.04 g ethanol to give a homogeneous solution. 4.23 g NH₃ (25 % in water), were added under vigorous stirring at 25 °C. The mixture was heated up to 50 °C under stirring for two days until no more residual TEOS was detected (IR-spectroscopy). This silica sol was concentrated by vacuum distillation to 30 wt% of SiO₂ in water. After adding 2-propanol and 0.5 wt % of glucose as stabilizer, the sol was concentrated by vacuum distillation to 20 wt% of SiO₂ and the water was removed to 0.3 wt% (Karl-Fischer titration). The silanisation of the SiO₂ nanoparticles was carried out with 1 g of methacryloylpropyl trimethoxysilane (MPTS) for 3.94 g of SiO₂-nanoparticles with the MPTS was slowly dropped into the SiO₂ sol at reflux and the mixture was stirred at 80 °C for 3 hours. To complete the nanoparticle coating process, the sol was stirred for 24 h at 25 °C. Initiator Irgacure 184 (Ciba) was mixed in proportion of 2 wt.% in reference to the MPTS concentration. The size distributions of TiO₂ and SiO₂ nanoparticles were measured by PCS technique (ALV-5000 Multiple Tau Digital correlator - ALV Laser mbH).

All films were applied on PC-substrates of a size of 10 x 10 cm². Before the coatings were applied, the substrates were cleaned with in a 20 mol% KOH-H₂O solution for 10 min. After cleaning the substrates, the films were prepared by spin-coating in controlled atmosphere (30% relative humidity at temperature of 25 °C) in a clean room. The photopolymerization was performed in a Beltron UV conveyer equipment by simultaneous UV and IR treatment (0.4 W/cm² and 80 °C). For the high and low refractive index films, an intensity of 21 J/cm² was adjusted, the primer was photocured with 4 J/cm². After the photocuring process, the film stacks were additionally stored at 80 °C for 10 min.

For the fabrication of UV curable hard coatings to 136.84 g (43 wt.%) nanoscaled AlOOH (Sol P3, particle size: 15nm, Degussa) 248.8 g (1 mole) MPTS (Dynasilan MEMO, Hüls) are added. After slow addition of 36 g (2 mole) deionized water, the suspension is cooled for 2.5 h at 100 °C. After cooling down the hydrolyzed product is diluted by adding 282 g 1-butanol to a solid content of 45 %. 3.5 g (0,5 wt.%) Byk-306 (Byk) as a levelling agent and 5.46 g benzophenone (3 mol% per C-C double bond, Fluka) as UV initiator are added. After application of the coating material by spin-coating onto PMMA, the coating is irradiated for 2 minutes by UV light of a Hg high pressure lamp. The coating shows excellent primerless adhesion onto PMMA (CC/TT=0/0) and good abrasion resistance with haze values of 11 % (after 1000 cycles, CS 10F rolls, 5.4 N).

The materials used to produce GRIN structures were synthesized from methacryloxypropyl trimethoxy silane (MPTS) methacrylic acid (MA) and zirconium-n-propoxide (ZR). A zirconium-n-propoxide/methacrylic acid complex was formed by reacting the alkoxide with methacrylic acid. After addition of prehydrolysed silane (MPTS), hydrolyses and condensation were performed by the addition of an appropriate amount of water. A detailed description of the synthesis procedure is described elsewhere^{12,13}. Irgacure 184 as a photoinitiator was added in concentration of 0.5 mol%/mol C=C and the material was photocured by illumination with a Hg-lamp.

A cylindrical electrophoretic cell with a diameter of 10 mm made from polyethylene was used. The front and back window of the cell were made both from fused silica. The center electrode and the circular electrodes were made from silver. The three circular electrodes were fixed at diameters of 10, 8 and 4 mm from the

center on the fused silica windows. The wires of the front and rear window were connected to each other with fine adjustment features of potential to produce a radial electric field inside of the cell. The GRIN-lens was realized applying an electric field of 100 V. After 5 h, the material was photopolymerized by the Hg-light source (50 J/cm^2) and the fixed radial gradient of the refractive index was measured with a Mach-Zehnder interferometer. The concentration profile of Zr in the photocured bulk material was measured by Energy Dispersive X-Ray (EDX).

3. GENERAL ASPECTS

Due to the specific surface chemistry of inorganic oxides the exhibited zeta-potentials depend on the pH value. In this connection the point of zero charge also depends on the surface chemistry, for example for SiO_2 particles it is around $\text{pH}=3.5$ and for alumina or zirconia it is close to neutral. This means, for example, that in order to stabilize colloidal silica a pH value below 3.5 or distinctively above 3.5 has to be established, for alumina distinctively below or above neutral. For industrial applications, however, a low pH in the acid regime leads to corrosion problems of the equipment which, for example, is one of the draw backs for large area sol-gel coatings on glass. For this reason it is suitable to develop surface coatings which allow to shift the zeta-potential into the desired direction, for example to obtain sufficient electric charges in the neutral regime in order to stabilize small particles under any desired pH conditions. This can be obtained by the so-called electrosteric stabilization that means the fixation of small molecules on the particle surface, having a different zeta-potential which is schematically shown in figure 1. Electrosteric stabilization with groupings not leading to hard agglomerates also leads to more densely packed green bodies, as shown by Naß¹⁴. An example on how the zeta-potential can be shifted by the surface modification of silica particle diamino groupings is given in figure 2.

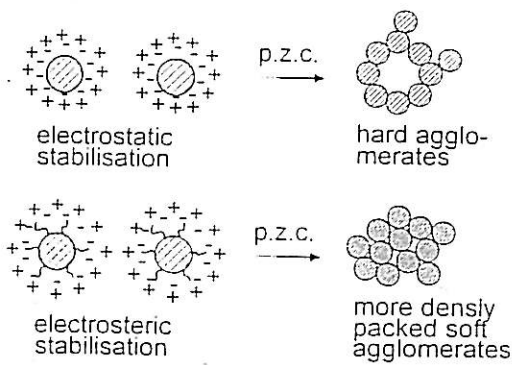


Figure 1: Principles of electrostatic and electrosteric sol stabilization

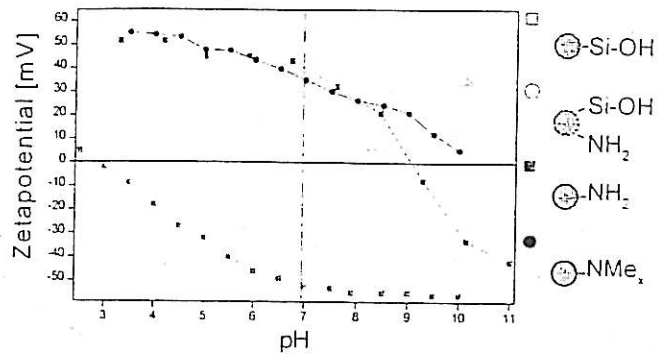


Figure 2: Effect of the surface modification of SiO₂ particles on the zeta-potential¹⁵.

Another interesting effect, resulting from the electrosteric stabilization is the possibility to make sol-gel colloidal systems easily processable in water. In connection with slowly hydrolyzing silanes, for example silanes of the type (RO)₃Si-R', where R' is a grouping having hydrophilic groups, e.g. amino, diamino, epoxy, OH, etc, exhibiting an equilibrium in connection with aqueous systems, for example by having hydrophilic groupings such as aminosilanes, these colloids can be used in order to synthesize fully aqueous based systems as shown by Schmidt et al.¹⁵ Thus, the electrosteric stabilization for sol-gel systems seems to be an interesting route for precursor and intermediate technology.

An important parameter for surface modification is the interfacial free energy, which can be used as a thermodynamical approach to control the surface free energy and the surface reactivity of the particles. The basic principles of this approach have been shown elsewhere¹⁶. It can be used for controlling nucleation and growth reaction of small particles under the control of surface modifiers which allow to control particle size and distribution as well as to avoid aggregation¹⁶. This route works perfectly where systems are prepared which tend to crystallize rather well, for example boehmite. In other cases like zirconia or titania, not very well crystallized particles are obtained by sol-gel precipitation processes, so methods have to be developed to crystallize these systems after preparation but still avoid crystallization. For these reasons two different routes have been compared as shown elsewhere^{17,18,19}.

In this experiments hydrothermal or solvothermal treatments have been investigated in order to obtain full crystallinity¹⁷. However, in order to avoid

agglomeration completely, small organic molecules, in general, do not bond sufficiently to the organic surface during the hydrothermal process to avoid agglomeration as shown with acetylacetone and zirconia²⁰, which is a strongly binding complex former for Zr^{4+} or zirconia surfaces.

As shown in conventional ceramic processing polyelectrolytes are interesting candidates for a surface modification because they possess a high number of active sites leading to a strong bond of the molecule to the surface, even if only a part of the active sites is bound to the surfaces. With nanoparticles, however, the coating with oligomeric molecules leads to a dramatic increase of the organic content, which may disturb further processing, so the question arises, how far it is possible to use oligomeric molecule protection of colloidal particles in order to perform complete crystallization and to remove the protective molecules in order to allow further processing. For these reasons investigations have been carried out with OPE as an oligomeric compound. was chosen, since it was proved for OPE to be effective as an emulsifier in micro-emulsion processes as well as for control of particle size in the precipitation process, especially for and ZrO_2 ^{21,22}. The basic reactions of this process and the procedure are shown in figure 3. The details of the processes are described elsewhere^{18,19,21,22,23}. The water-in-oil micro-emulsion represents a sol-gel nanoreactor. Both processes shown in figure 3 lead to particle sizes in the lower nanometer range starting from nitrates or alkoxides. OPE acts as a growth controlling and surface protecting agent at the same time. Both systems have been treated solvothermally (70 bar, 250°C) in a mixture of ethanol and water and no particle size increase has been observed in the precipitation process and only a very low particle size increase has been observed in the case of the microemulsion derived powders. So it was possible to produce for example ZrO_2 or Y- ZrO_2 powders below 10 nm in diameter, completely agglomerate-free due to the OPE surface coating. In order to remove the OPE surface coating, the polymeric ester can be removed under alkaline conditions, now leading again to an electrostatically stabilized slurry, in which by adding carboxylic acids, for example, the OPE could be completely exchanged now by small molecules (figure 4). Figure 5 and 6 show the obtained powders and the particle size distribution measured by laser back scattering. In figure 7 the change of the zeta-potential from the OPE modified to the electrostatically stabilized powder is shown.

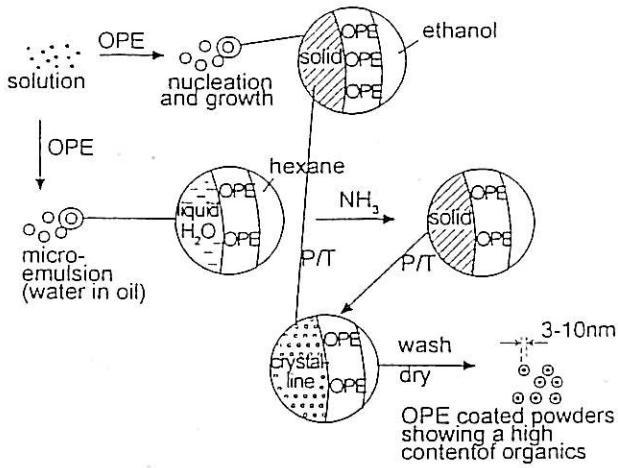


Figure 3: Effect of OPE for nanoparticle fabrication by precipitation and micro-emulsion processes.

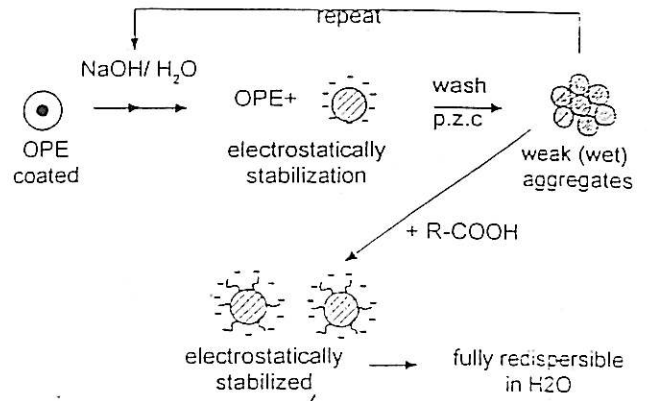


Figure 4: Scheme of the ligand exchange (OPE against carboxylic acids, e.g. tetra-oxodecanic acid)

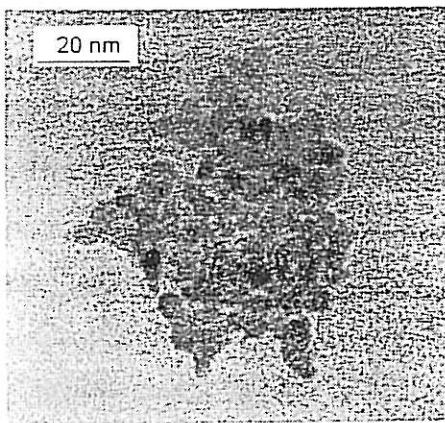


Fig. 5: HRTEM micrograph of Y_2O_3/ZrO_2 after hydrothermal crystallization (250 °C, 75 bar, 3 h), surface modifier: OPE.

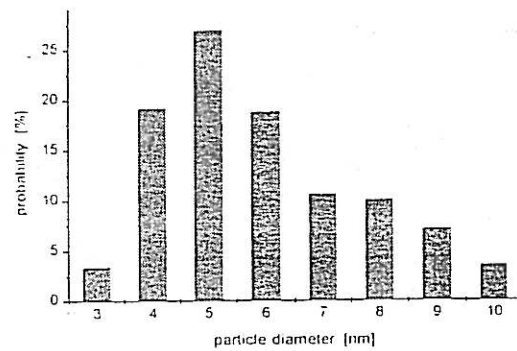


Fig. 6: Particle size distribution calculated from HRTEM micrograph of hydrothermal crystallized Y_2O_3/ZrO_2 (250 °C, 75 bar, 3 h) surface modifier coated with OPE.

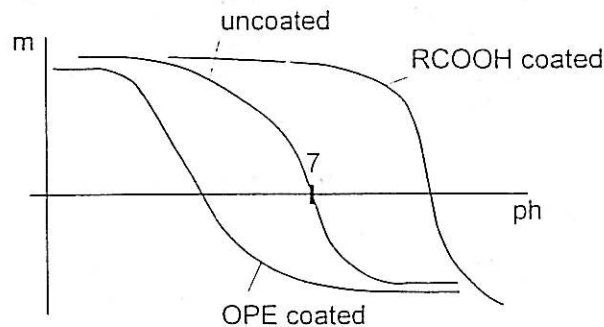


Figure 7: Shift of zeta-potential

The zeta potential of uncoated particles was measured after repeated washing. The important fact is that the electrostatically stabilized powder now shows a high zeta-

potential at neutral. This leads to a complete redispersibility of this powder for example in aqueous solutions. This aqueous solutions have been added to hard coatings based on TEOS, boehmite epoxysilanes² and Al(OR)₃ which then lead to high refractive index hard coatings¹⁹. At the same time the ZrO₂ powders also can be used for being redispersed in alcoholic or aqueous solutions. The organic content of these powders after recoating is down to <5wt.-% compared to 15 to 20 wt.-% with OPE.

These considerations show that it is possible to produce surface protected nanopowders, the zeta-potential of which can be chosen by an appropriate surface modification leading to completely redispersible powders suitable for composite fabrication.

4. USE OF NANOPARTICLES FOR THE FABRICATION OF NANOCOMPOSITES AND COATINGS

The use of nanopowders for making coatings is of interest for various reasons. Polymeric coatings, when they have to be used for optical applications, in general, are very soft since no inorganic fillers can be used due to the light scattering effects. So coatings with increased refractive index only can be originated from organic groupings with high molar refraction according to the Lorentz-Lorenz equation. Inorganic fillers only can be used if the particle size is below the Rayleigh light scattering limit which is in general below 1/20 of the used wavelength. This means that the particle size has to be below 20 nm at least, since the scattering efficiency also depends on the difference between the refractive index between the particle and the matrix. It is, however, not sufficient to reduce only the particle size, since the Rayleigh scattering also depends on the correlation length of the different phases compared to the wavelength. That means that even weakly agglomerated particles are counted as large particles and contribute to light scattering. So a homogeneous dispersion of the particle and the matrix is required. The dispersion of particles in polymeric or liquid matrices normally is carried out by intensive mixing or compounding by employing high shear rates. Simple calculations, however, show that with particle sizes in the nanometer range the Van-der-Waals forces or other weak interactions between particles require forces, normally leading to the destruction of the polymer. So the thermodynamical approach has to be used.

meaning that the surface free energy between the particle surface and the matrix has to be at its minimum or has to be at least distinctively lower than the interfacial free energy between two particle surfaces.

An interesting aspect for the application of nanoscale particles distributed in a transparent matrix is the question of the improvement of the scratch resistance in combination with increased refractive indices.

Especially zirconia particles, when fully crystallized, may be used as refractive index increasing additive since crystalline ZrO_2 has a high refractive index (2.20). Since the photocatalytic activity of zirconia is dramatically lower than that of titania, it may be preferable to use nanodispersed zirconia instead of titania. The surface modified ZrO_2 powders, as described above, have been used as refractive index increasing additives, the experimental results of which are described elsewhere¹⁹. For this reason boehmite nanoparticle containing hard coatings as described elsewhere² have been used as a basis. These boehmite modified coating systems are synthesized from epoxysilanes, TEOS, $Al(OR)_3$ and, in order to slow down the condensation reaction, by a weak complex former on the basis of an ether-ethanolate complexing the aluminium alkoxide and providing a sufficient shelf life. Since these systems are processed from aqueous suspensions of boehmite, the basic system is mixable with zirconia powders dispersed in water, leading to zirconia contents between 10 and 40 wt.%. With 30 wt.% zirconia clear coating liquids have been prepared by dip and spin coating processes have been used for coating polycarbonate lenses. With 30 wt.% of zirconia the refractive index of the coating could be adjusted to about 1.6. While maintaining the very high scratch resistance of the basic coating system which is in the range of 2 - 4 % haze (using 1000 cycles taber abraser test, Al_2O_3 filled wheels with 500 g load) which is an extraordinary high value. These examples show how nanopowders can be used for fabrication of optical coatings by very simple preparation routes, once the nanopowders are prepared with a surface coating guaranteeing 100 % dispersibility. The optical properties of these coatings meet all the requirements for ophthalmic lenses.

Other possibilities to modify the surface of nanoparticles are based on silanes, for example on polymerizable silanes like methacryloxypropyl triethoxysilane (MPTS). As described elsewhere²⁴, various nanopowders, for example titania or silica, have been modified with MPTS as described in the experimental. These nanoparticles

have been dispersed in alcohols as solvents to completely clear liquids. Dip coating processes have been carried out using these particles on various plastics, for example PMMA or polycarbonate. The coating thickness can easily be adjusted between several micrometers and 50 nm. By addition of UV initiators²⁴, such as Irgacure (Ciba), the coatings can be polymerized within several minutes by UV curing. The scheme of this process is shown in figure 8. This leads to a crosslinking of the nanoparticles and the abrasion resistance obtained by these systems is in the range of 10 % haze at 1000 cycles, which is a very good value for UV curing systems. The refractive index to be obtained by titania nanoparticles is at 1.9, and from SiO₂ particles at 1.45. Antireflective coatings have been prepared by two-layer coatings with titania, coated by silica. The scheme of the process is shown in figure 9.

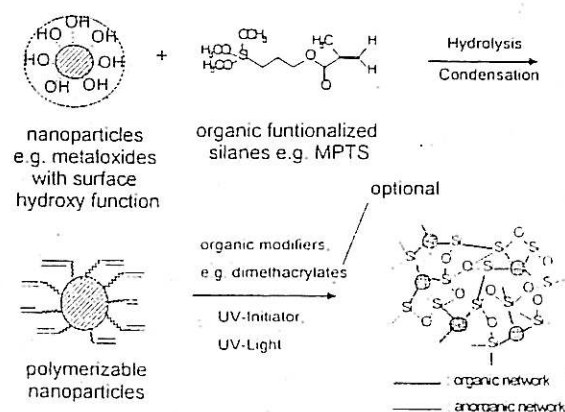


Figure 8: Scheme of the reactions to UV crosslinked coating systems.

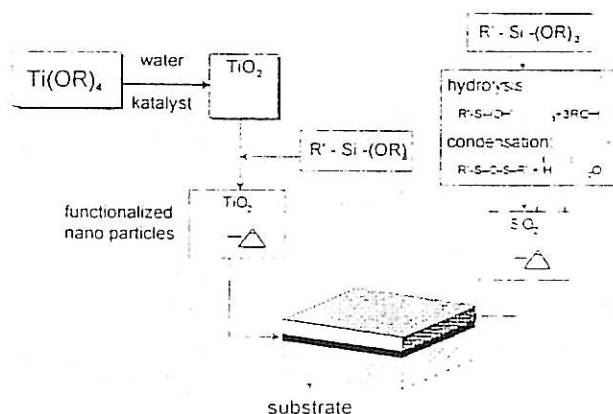


Figure 9: Preparation of anti-reflective coatings by two-layer coatings with titania, coated by silica

In figure 10 the antireflective effect of this coating is shown and compared with the calculated curve. As one can see, the system approach can be used to provide antireflective coatings having almost the theoretical value on plastic substrates. using the polymerizable nanoparticle approach through UV polymerization.

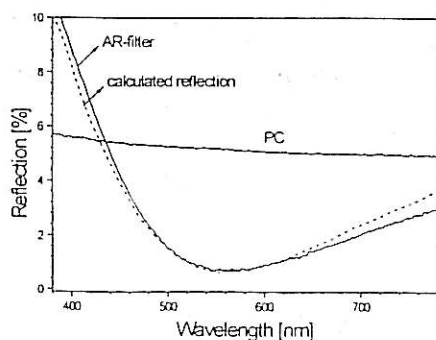


Figure 10: Measured and calculated reflection on polycarbonate.

At the same time these coatings are very scratch resistant and fulfill the function of a mechanical protective system at the same time. As already mentioned above, the surface modification of the nanoparticles can also be used for electrosteric stabilization, meaning that the coated particles are not able to undergo further condensation. Due to the fact that by the surface modification the charge carriers, for example from OH-groups, are still present in sufficient concentration, despite the surface modification, a zeta-potential can be established, even if the modifying molecule does not have a functional grouping with sufficient polarity. As shown elsewhere²⁵, it could be proved that zirconia nanoparticles modified with methacryloxic acid can be electrically sufficient to undergo electrophoretic processes in matrices not fully polymerized. For this reason, a system has been synthesized which consists of methacryloxy silane, some functional organic methacrylates and methacrylic modified zirconia particles. The details are described elsewhere²⁵. Negatively charged zirconia particles have been established by appropriate pH values during the sol-gel process of this system. It leads to a viscous liquid if hydrolysis and condensation reactions are controlled by the appropriate water concentration under NMR control, so that the degree of condensation is low enough not to lead to gels. If an electric field is employed to this type of system, a selective electrophoretic process takes place where the zirconia particles move to the positive electrode, leading to an upconcentration of the nanoparticles with a correlating increase of the refractive index.

This basic approach has been used to develop a method for the fabrication of graded index lenses. For this reason, a system of contactless electrodes developed by an electric field modeling process was simulated. Based on this simulation, a cylindrical electrophoretic cell with three concentric ring electrodes on the planar windows of the electrophoretic cell was produced.

With this process the electric field line density can be adjusted to various shapes. In case a parabolic shape is used, it is expected that the concentration follows the electric field line densities. In the next figure the concentration of zirconia particles, the refractive index and the parabolic curve are shown, which are matching quite well.

After finishing the electrophoretic process, the system is polymerized using UV curing agents and the whole system is solidified. This allows the production of planar focal lenses as shown in figure 12. The whole process at present takes only several hours, compared to several day processing in the area of the fabrication of graded index lenses by diffusion processes.

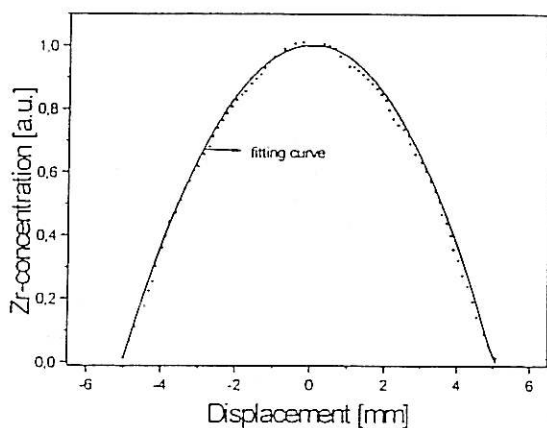


Figure 11: Parabolic curve of the concentration of zirconia nanoparticles produced by electrophoretic diffusion

organic nanocomposites
electrophoretically
the composite material

10 mm

Figure 12: GRIN lens (diameter 1 cm and 1.3 cm thick) made in the material system MPTS/Zr/MS/TEGDMA (5/1/1/5 in mol%) by electrophoretically controlled diffusion of the ZrO_2 nanoparticles after fixation of the index profile by photo-polymerization.

5. CONCLUSIONS

The investigations show that by using surface modified nanoparticles, a different type of processing and effects are possible, since these principles can be generalized and employed to almost any other nanoparticles. The basis for very interesting material developments has been worked out.

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Section F - *Non Conventional Routes to Ceramics*

Section G - *Ceramic Composites*

Section H - *Ceramic Joining*

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