Nanoparticles for Ceramic and Nanocomposite Processing

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Nanoparticles of various compositions have been fabricated by chemical processes. Sol-gel processes and precipitation processes have been used to prepare the nanoparticles and surface modifiers act as vehicles to tailor surface chemistry, the ζ-potential and to avoid agglomeration. In the first described industrial product development, SiO_2 nanoparticles have been modified with CH_3 groupings and materials with high adhesive strength, being flexible despite the low organic content have been obtained and a binder system for glass fiber mats, temperature resistant up to 500°C has been developed. The second development is based on SiO_2 nanoparticles coated with methacrylic groupings and TiO_2 nanoparticles coated with epoxy groupings. The corresponding sols form high density coatings (≈65 % kg volume) and are densified by crosslinking of the organics. These coatings have been used for the fabrication of interference layers (SiO_2: n≈1.45; TiO_2: n≈1,92) on plastic and glass.

Keywords: nanoparticles; nanobinders; glassfibers; interference layers; AR coatings on plastic

INTRODUCTION

Nanomaterials have become a very interesting area of wide spread research. First of all, the interesting properties of nanostructured materials as shown by Gleiter [1] have attracted many researchers. Soon, however, it became clear that the fabrication of nanostructured materials has to be carried out on a rational cost effected basis. Chemistry has been identified to be an interesting tool for the preparation of nanoscale materials or nanoparticles due to the fact that during a precipitation process, a nucleation step takes place followed by a growth process. The nucleation starts on a level of a couple of atoms or molecules and during the growth process, the nanoscale state is reached. But in general, the system doesn't stop on this level. If appropriate means are undertaken to stop the growth on this level, for example by stopping the feed for the growth process, nanoscaled particles can be obtained. Another route, known as sol-gel process, has been used for reaching this state. In this case, by controlled feed and the development of electric charges on the particle surface, so called sols are obtained, which represent a colloidal solution which is electrostatically stabilized. The physics of this process have been described by Stern [2] in the early nineties. Due to the electric charge of the particles, they can be moved with an electric field, and the velocity of the movement depends mainly on the effective electric field at the location of the particle, which is influenced by the electric charge and the dielectric constancy of the particle. The surrounding media by the effective charge, which is a residual charge from the charge directly on the particle and the surrounding space, the particle size and the viscosity of the liquid medium. The response of the particles to an external electric field can be used for determining the overall electric charge on a particle and can be expressed by the so-called zeta-potential. In general in protoic liquids (water, alcohols and similar solvents or mixtures), the zeta-potential strongly depends on the pH. So, by an appropriate choice of the pHvalue, electric charges can be built up on top of the particle, which prevent the contact of the particles as long as the particle-to-particle distance is large enough not to overcome the repulsion barrier. If the critical distance of the repulsion barrier is overcome, the repulsion changes into an attraction and agglomeration takes place. The strength of agglomeration strongly depends on the inner particle forces which may be of chemical or physical nature. If chemical bonds are built up (condensation processes between hydroxyls or hydrogen bridges), the agglomeration may be very strong and reversible. If only dipole-dipole interaction or Van-der-Waals forces exist, the agglomeration in most cases is reversible if an appropriate solvent is used. Sol-gel materials, which in most cases are oxides, in general suffer from an irreversible agglomeration due to the condensation process of hydroxides. So, it is very difficult to use the sol-gel process as a route to produce processible nanoparticles. The colloidal part of the sol-gel process, that means the reaction of precursors like alcoxides or halides or hydroxides to oxidic colloidal particles in solution, is very simple and easily to be done. However, the processing of these colloids to desired materials, for example glasses, ceramics or composites, requires a specific chemistry since otherwise only gels are produced, which have a view interesting application but are not materials for the fabrication of components.

GENERAL ROUTES FOR NANOPARTICLES

In order to overcome these difficulties, it is necessary to surface modify the reduced colloids by compounds which prevent reversible aggregation. If this can be obtained, there is a reasonable route for the fabrication of materials through nanoparticles. Nanoparticles are of specific interest for many materials, and in table 1, a survey is given with respect to the material tailoring potential of nanoparticles.

TABLE 1: Interesting properties of nanoparticles and resulting material properties

property	useful for	material property
size	no Raleigh scattering	transmission in optical composites (active-passive)
size	high surface area	catalysts, sensors, adsorbents
size	large interfaces in composites	polymer matrix composites with 3rd faces (structured interfaces)
size	large surface area	adhesive and sticking properties, binders, adhesives
quantum size effect	metals	plasmon resonance, non-linear (χ^3) materials, colors, glasses and polymers
quantum size effect	semiconductors	non-linear optical materials, photorefractive materials
size	lasing particles	composite laser materials
size effects	superparamagnetic materials	optical switching. Hysterysis free magnetic materials

This short overview, which is of course not complete, gives some impression about the potential of nanostructured materials based on nanoparticles. Chemical routes for the fabrication of nanoparticles have been of interest since long time and many authors have investigated these routes [3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18].

Based on these considerations, general processing routes for the fabrication of nanoparticles have been developed, the fundamentals of which have been published elsewhere [19,20]. A thermo-dynamically induced model has been developed in order to produce nanoparticles of various type by a combined precipitation sol-gel route which at the same time provides the appropriate surface modification. The surface modification of the particles can fulfill different purposes. First of all, it has to make sure that no undesired hard agglomeration takes place, that means that redispersibility is given. Second, the surface modification also has to provide a sufficiently low interfacial free energy which is desired for the next step of processing, for example if the particles have to be introduced in a matrix system. Third, the surface modification also may provide sufficient reactivity, for example if the particles have to be polymerized or reacted into a matrix system, for example into polymers, gels or others. Forth, the surface modification can be used for further reacting the surface in form of a coreshell system or to bind specific new substances on top of these surfaces. In figure 1, a general survey over these four basic directions is given.

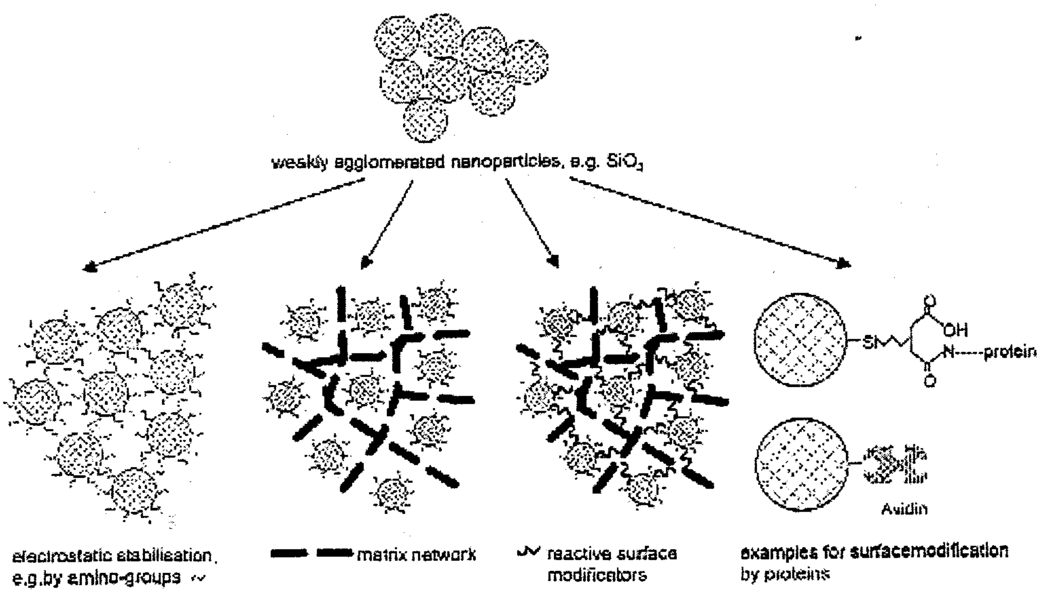

FIGURE 1: Schematic survey about basic directions for surface modification on nanoparticles, see text.

These reactions in general are carried out in presence of surface modifiers or surface protectors, which in many cases organic oligomers are used in order to give a perfect protection [21]. Due to the fact that these precipitations or sol-gel processes, for example if one starts from a titanium alcoxide and precipitates the alcoxide by hydrolysis and condensation, in general this does not produce very well crystalline particles. The same is the case with zirconium. For this reason, it might be useful to follow up with a hydrothermal treatment which in general leads to a strong increase of the particle size. However, in this case, surface modifiers strongly bond to the surface like functional oligomers have to be used as shown in [19]. The oligomers have to be exchanged by other surface modifiers, which is able to be done by the removing of the oligomer, the flocculation of the system by appropriate pH change, washing the precipitate, redispersing the precipitate and then surface re-modifying. The process according to [19] is shown in figure 2. According to this approach, it is possible to produce various types of nanoparticles. A survey is given in table 2 (According after [20]). The nanoparticles have been used for a variety of material tailoring. In the following, some important examples are given.

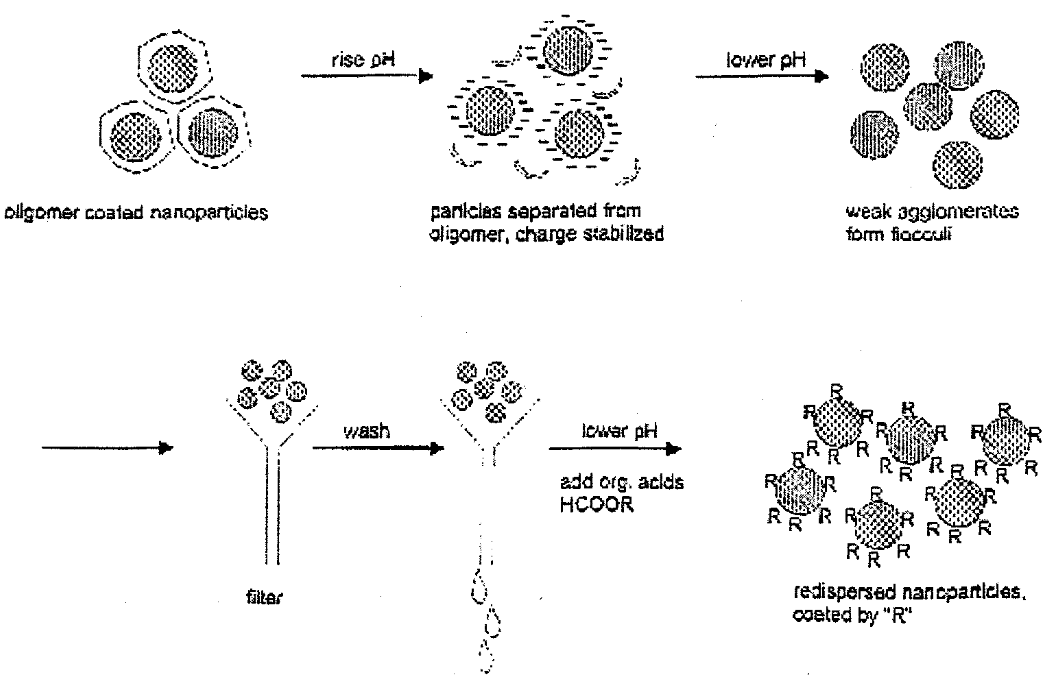

FIGURE 2: process for processing hydrothermally treated nanoparticles

TABLE 2: State of the nanopowder technology by chemical processery routes

System	Primary Particle Size [nm]	Dopants [mole %]	Redis-peritivity to primary particle size	Applications
ZrO_2 (2)	5-10	Y^{3+}, Pr^{3+},Sc^{3+} 0-8	completely	filter membranes SOFC, gas sensors scratch res. coatings
SnO_2 (2)	3-5	Sb^{3+}, 0-10	completely	sensors, electrodes
In_2O_3 (2)	ca. 10		completely	IR protection electric conductivity
ITO (2)	ca. 10	Sn^{4+}, 1-10	completely	IR protection electric conductivity
ATO (2)	3-5	Sb^{3+}, 0-10	completely	IR protection, electromagn. shielding
PZT (1)	50-100		not yet completely	sensors, actuators
Y_2O_3 (1)	10-20	Eu^{3+}, 0-3	no data available	luminescent pigments, display technique
TiO_2 (1)	8	Al^{3+}, 0,5	completely	UV protection in coatings and polymers, cosmetics waste water purification
α-Al_2O_3 (1)	90		not yet completely	filter membranes, ceramic substrates
HAP (1)	5-30		not yet completely	bioceramics, bioactive films
Fe_2O_3/Fe_3O_4 (1)	5-10		completely	medical data storage
ZnO (1)	5-10	Al^{3+}, 0,1 5	no data available	UV-IR protection varistors
Talcum (1)	x,y: 500 z: 5-10		not yet completely	seeds,for nucleation in polymers, filler of polymers
Zn_2SiO_4 (1)	10-20	Mn^{4+}, 0,1-10	no data available	luminescent pigments, display technique
$BaTiO_3$ (1)	10		no data available	condensators, sensors
$CaWO_4$ (1)	5 - 10		completely	luminescent pigments, display technique

(1) lab scale

(2) pilot scale

MATERIAL DEVELOPMENTS

Coatings based on polymerizable nanoparticles

Polymerizable nanoparticles as described in [22] have been surface modified by methacryloxy groups and epoxy groups. For SiO_2, methacryloxy groups, and for TiO_2, epoxy groups have been used. The SiO_2 and TiO_2 sols were prepared by base catalyzed hydrolysis and condensation of tetraethoxysilane (TEOS) mixed with isopropanol. 65 g TEOS were mixed with 100 g alcohol, 34 g ethanol and 10 g methacrylic acid to give a homogeneous solution. 4 g H_2O, were added under vigorous stirring at 35 °C. The mixture was heated under reflux at 45 °C with stirring for two days, these coating materials employed by a dip coating process and after addition of photocatalysts can be photopolymerized to relatively dense layers. To generate the high refractive index component TiO_2, 2.1 g of tetraisopropylorthotitanat was slowly dropped in to a mixture of isopropanol with 0.981 g con. HCl (37 wt%/H_2O) and 0.205 g water under stirring at 25 ^{0}C for 24 hours. To silanise the surface of the formed TiO_2-nanoparticles 2g GPTS was mixed with 200 g of the TiO_2-sol under reflux and vigorous stirring at 50 ^{0}C for 5 hours. To produce films with different refractive index, GPTS (prehydrolyzed with 0.1 N HCl) and 2 wt% of UVI 6974 (in relation to the GPTS species) were added to the particulate sol [23]. The package density determined by is 56 vol.-% in the case of SiO_2 and 63 vol.-% in the case of TiO_2 and the layer formation is shown schematically in Fig.3.

This means that the package density is close to the theoretical package density of spheres. These are high values, if one takes into account that only photopolymerization is used without thermal treatment. This process has to be used to produce anti-reflective coatings on polymers like polycarbonate as shown in the following figure (Fig. 4) [23].

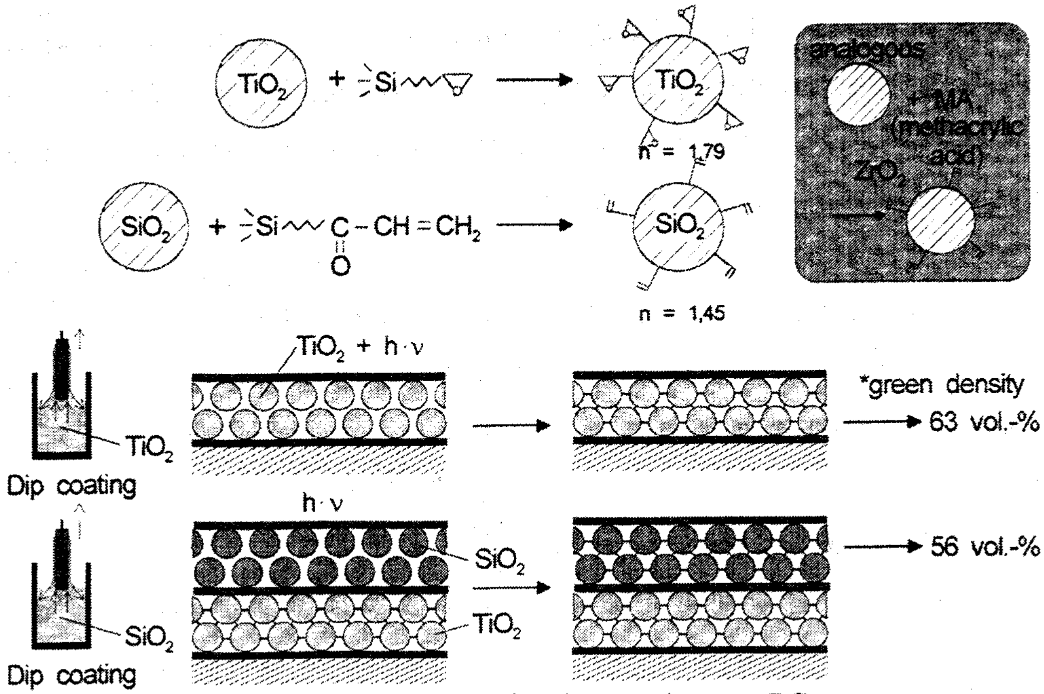

FIGURE 3: Process to produce anti-reflective coatings on PC.

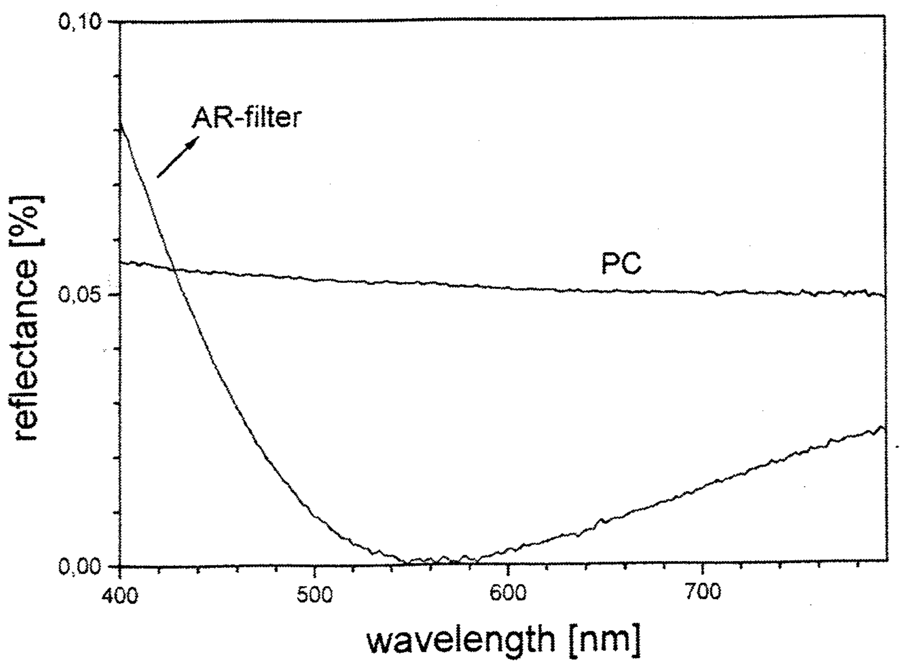

FIGURE 4: Reflectance of a stack of $\lambda/4$-TiO_2 and $\lambda/4$-SiO_2 -layers on PC and of uncoated PC.

This fabrication technique for anti-reflective coatings also can be used on glass. One of the major advantages is that using the intermediate photopolymerization step, it is not necessary to fire layer by layer. Up to seven consecutive layers can be fired in one step (stack firing). If conventional sol-gel techniques are used, the density of the layers is low due to the strong particle-to-particle interaction during the drying process leading to a gel type of structure. This leads to low density ending up in a high shrinkage which in general leads to crack formation in conventional sol-gel layers. Due to the high density of the film and the flexibility, due to the surface modification, the layers possess a high relaxation power leading to the possibility of a one-step firing.

Flexible sol-gel-binders

The concept of the reduction of the particle-to-particle interaction for better processing of nanoparticles is more or less universal. In the next example, as already shown by Mennig and co-workers [24], very thick layers can be made from one step dip coating processes from SiO_2 for the fabrication of optical wave guides.

In this case, SiO_2 sols with particle diameters of 6 to 10 nanometers have been treated with methyltrioxysilanes, which leads to a "flexible gel" (the details of which are described elsewhere [25]), the structure of model is given in the next figure.

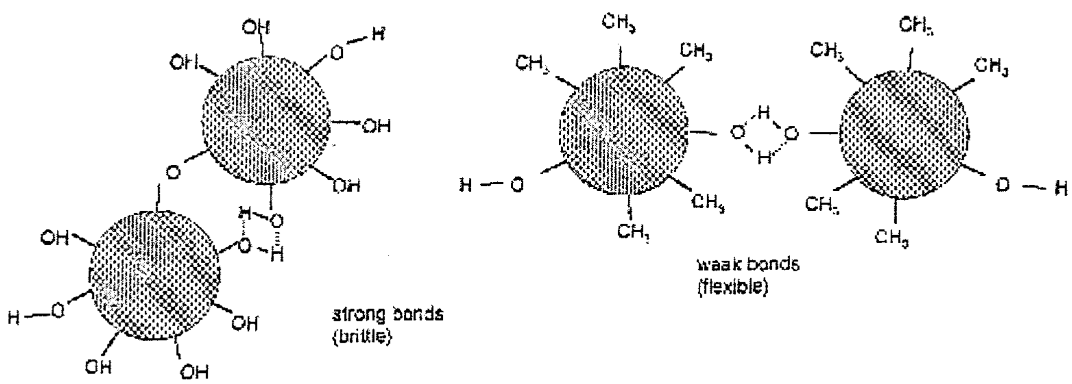

FIGURE 5: schematic model of the structure of brittle and flexible gels.

Sols of this type have been used for the binding of glass fibers and it could be shown that glass fibermats can be produced in an industrial process by spraying the sols on uncoated glass-fibers just in the production process. The resulting glass fibermats are white, the flexibility and elasticity of the mats is similar to mats bond by phenolic resins but they withstand heat up to 500 to 600 °C and do not exhaust toxic volatiles in case of heating up, as it is known from phenolic resin bond mats. The binder content of these materials is about 5 %, the organic content is in the range of about 1 %. In case of heat, the methyl groups are slowly burned to water and carbon dioxide. In figure 6, the thermal behavior of coated fiber rovings is shown and the elongation is determined as a function of the temperature and compared to commercially available inorganic glassfibers coatings. The interesting fact is, that the sol-gel coating leads to a shrinkage of the glass fiber starting form T > 600 °C. This is attributed to a further densification of the methyl group containing coating system during burnout of $-CH_3$, which is continued up to 900 °C (burnout end). This is confirmed by DTA/DTG measurements. Between 700 and 1050 °C, the coating is strong enough to maintain sufficient stability of the fiber, that no elongation takes place. Above 1050 °C, the coating softens and the elongation takes place. In figure 7 the decay in strength between phenolic resin bond fibermats and SiO_2 nanoparticle bond fibermats is compared.

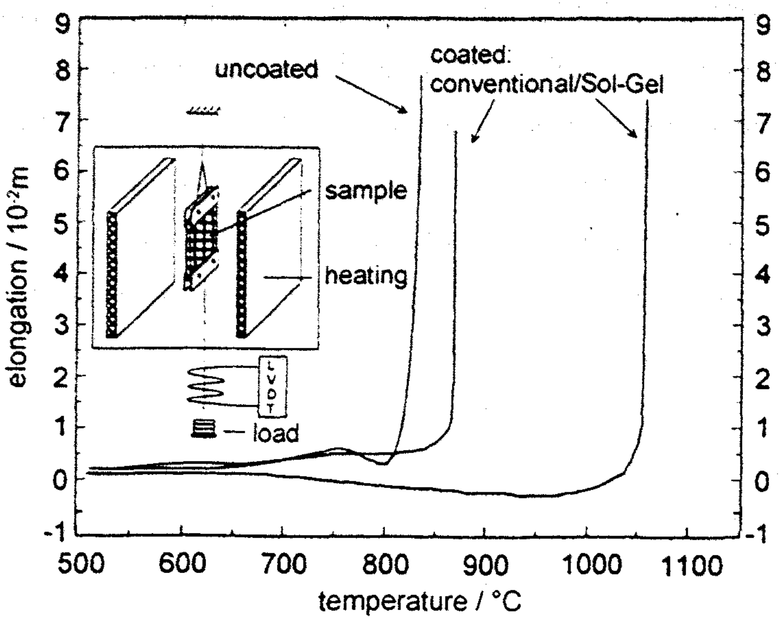

FIGURE 6: Elongation of sol-gel bonded glassfibers in respect to those bonded by phenolic resins after [25].

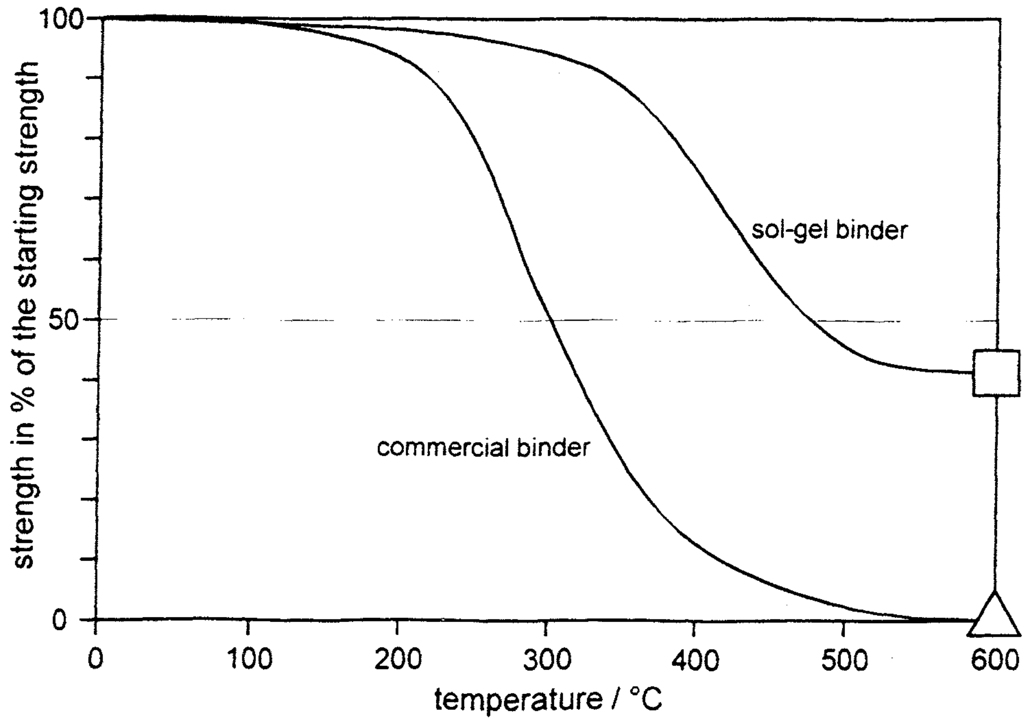

FIGURE 7: Strengthening of sol-gel bonded glassfibers in respect to those bonded by phenolic resins. Flexure strength: △ phenolic resins: very low ; □ sol-gel binder 40%.

As one can clearly see, the phenolic resin bond mats loose completely their strength where even at 500 °C , the SiO_2 bond mats keep ≈ 40 % of its original strength, which is sufficient for most application. This means that with this type of glass fibermats, new application in high fire-resistant type of construction materials are possible.

Due to CH_3 groupings, the glass fiber mats are highly hydrophobic. But after 24 hours of dipping under water, the hydrohobicity decays. If hydrophobic coatings according to [26] (fluorinated silanes) are used in addition to this, the fibermats don't take up water as shown in the following figure, so that these materials also can be used under wet conditions.

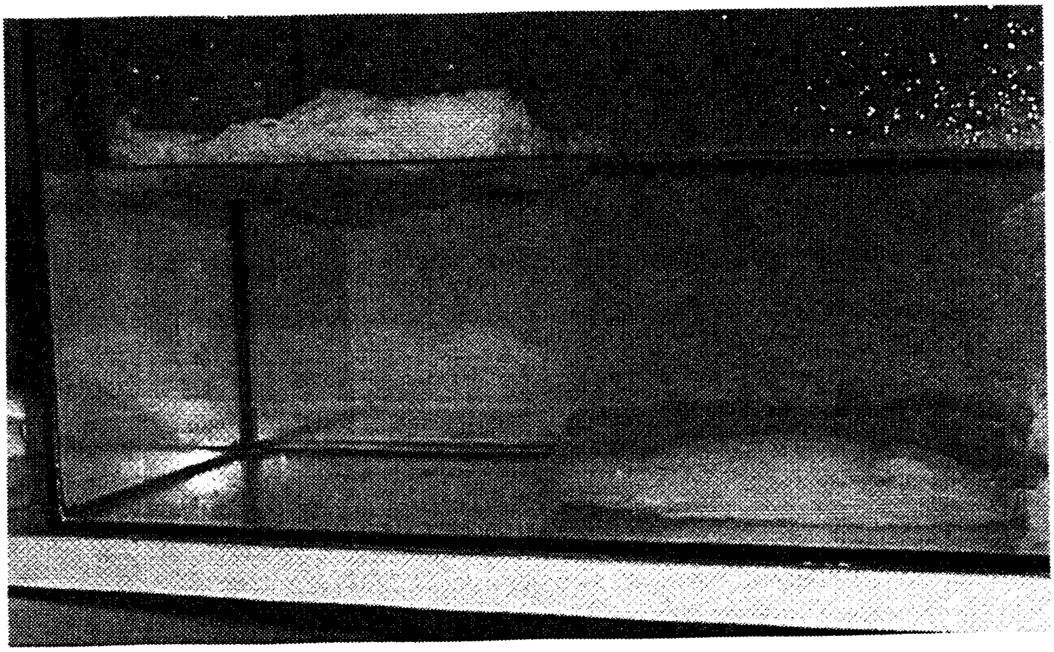

FIGURE 8: glassfiber mats: left: coated with hydrophobic coating; right: uncoated

CONCLUSION

The described examples show that through nanoparticle technologies, interesting new materials can be prepared. The key issue, of course, is the nanoparticles surface chemistry, since this chemistry defines the processing and final product properties to a great deal. The key issue of the surface modification is to reduce the particle-to-particle interaction, so that typical gel properties (high rigidity in combination with low strength) can be overcome. If this is achieved, sol-gel materials even can be used as adhesives or binders with adjustable mechanical properties (e. g. elasticity) and interesting technical products can be built up. Another interesting feature is the increased package density which can be obtained by reduced surface interactions and which leads to interesting optical properties with respect to refractive index. Tailoring and for obtaining interference layers with optical properties, otherwise only achievable in sol-gel systems by high temperature firing. This type of new anti-reflective coatings have a great potential on surfaces of plastics (infrared, reflective or AR-coatings). Nanoparticle technology by chemistry at present is still at its enfancy and the potential is not exploited yet.

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