Organically Modified Silicates and Ceramics as Two-Phasic Systems: Synthesis and Processing

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Abstract. Based on the concept of controlling the particle size by the surface free energy, the growth of sol-gel derived nanoparticles (Al_2O_3, TiO_2, ZrO_2) has been investigated in presence of molecules with binding ability to the growing particles. The investigations show that the use of silanes, carboxylic acid or β-diketones allows to replace electrostatic sol stabilisation by steric sol stabilisation and through this, high solid content sols can be obtained. The introduction of these sols into organic or ormocer type of matrices leads to nano composites with degrees of filling up to 40 wt.-% without agglomeration and with high optical quality. Already developed TiO_2 containing bulk materials, ultrahard coatings on plastic and adhesives for fiber to chip coupling are examples for the usefulness of this alternative sol-gel route. The nanocomposite materials show interesting mechanical and thermomechanical properties such as high hardness or low thermal expansion compared to unfilled systems.

Keywords: sol-gel chemistry, nanoparticles, surface modified nanoparticles, inorganic-organic nanocomposites

1. Introduction

Inorganic-organic composite materials prepared by the sol-gel process are known for almost two decades [1,2]. Meanwhile the field has widened, and various interesting directions have been developed [3–8]. These developments are mainly based on $\equiv$Si—O—Si$\equiv$ bonds as links between the inorganic backbone and the organic part of the composite, and the $\equiv$Si—O—Si$\equiv$ network plays the role of the basic construction unit of such materials. As shown by Sanchez [9], molecular composite systems can be synthesized by using complexed alkoxides as precursors with complex formers having polymerizable groupings (e.g., allyl substituted β-diketones) and processed to composites. However, in this type of composite (molecular type), the influence of the inorganic component on the overall properties of the material results rather from the property of the specific inorganic molecular species, e.g., SiO_4^{4-} or TiO_4^{4-} units with its molecular (e.g., spectroscopic) or network forming properties but from its inorganic material properties, which are typical for crystalline or amorphous inorganic structures. Hydrolysis and condensation in typical sol-gel reactions, with the exception of acid catalysed tetraalkyl orthosilicates, lead to the formation

of particulate sols with crystalline or amorphous structures, depending on the system or reaction conditions. The formation of precipitates, in general, is prevented by the stabilisation of the sols by generating electric charges on top of the particles by adsorption of ions (e.g., H^+ or OH^-) through proper choice of the pH value. Change of pH or up-concentration, in general, lead to gelation or precipitation and create problems for obtaining highly concentrated sols or for incorporating the sol particles into matrices with different polarity without agglomeration. This leads to the question how far the modification of the growing particle surface by chemical means as an alternative stabilisation principle can be used for overcoming these problems and how far this is an appropriate route for composite formation. In this paper, some results of the present work on the synthesis of inorganic-organic particulate precursors and the processing of them to composites is summarized.

2. Basic Considerations and Control of Particle Size in Sols

In general, sol-gel reactions are carried out at conditions away from the point of zero charge. Otherwise

aggregation and uncontrolled growth will take place, since there are no thermodynamical or kinetic reasons for the growing particles not to grow together if no barrier is present. The small size of sol particles in the range of several to 100 nm is of interest for several reasons, for example, the question arises how far the reactivity of small particles can be used advantageously for material development and processing. Due to their small particle size, various interesting properties can be expected, such as quantum confinement or plasma frequencies in semiconductors or metals, low sintering temperatures in nano-scale ceramic green bodies and high transparencies in transparent matrices even with high degrees of filling due to the neglectable Rayleigh scattering. In order to obtain the described properties, particle size and aggregation have to be controlled carefully. As shown by Sanchez and In [9], Naß [10] and Schmidt et al. [11], the size of colloids can be influenced by additives during the hydrolysis and condensation process. The model suggested in Ref. [11] so far is related to a control of the surface free energy σ during the nucleation and growth process.

In a nucleation process the nucleation frequency I is the most important step. It can be expressed by Eq. (1), [12, 13]

$$I = A \cdot e^{\frac{-(\Delta G_n + \Delta G_D)}{kT}} \qquad (1)$$

where ΔG_n is the Gibbs free energy to form a nucleus and ΔG_D the kinetic barrier. A is the pre-exponential factor, which can be expressed by Eq. (2),

$$A = 2n_v \cdot v^{1/3} \cdot \frac{kT}{h} \cdot \sqrt{\frac{\sigma}{kT}} \qquad (2)$$

where n_v is the number of units (atoms or molecules) per volume unit, v is the volume per formula unit, h the Planck constant and σ the interfacial free energy. The question arises how far molecules with the ability to interfer with one of the crystallizing or condensing components of growing nuclei or colloidal particles such as complex formers can affect nucleation and growth reaction. It can be expected that using components reducing σ may slow down the nucleation frequency, but also the further deposition of the component responsible for the growth of the nuclei. If this is the case, the addition of surface interferring components should influence the formation of sol particles, e.g., the growth rate. It can be assumed that molecules interferring with a particle surface, require a specific area the size of which, in order to obtain a surface free en-

ergy minimum, is depending on the chemical nature of the surface and the absorbed molecule as well as the type of bond to be formed. Based on this consideration, at least one optimum coverage should exist for each system in order to provide this minimum. If σ is the driving force for obtaining this minimum, and if the system has the ability to exchange components through the liquid phase, an equilibrium state should be formed in a way that, depending on the concentration ratio r of the nucleating and growing component to the ligand and the bonding isotherm θ of the ligand to the surface, a monodispersed particle should be formed, the size of which depends on r and θ. Since θ is a constant for a given system, the particle size d can be expressed by (3)

$$d = \frac{1}{F} \cdot 6V \qquad (3)$$

and is independent of the particle shape. $F =$ the total surface area of the particulate system, which, at an assumed complete coverage of this surface by the ligands is equal to the area required by these ligands, or to their number times a constant A, and V is the total volume of the particulate system which is equal to the concentration C_c of the crystallizing or condensing species times a constant B (4)

$$d = A \cdot \frac{1}{n} \cdot 6B \cdot C_c \qquad (4)$$

with $n =$ number of ligands. As one can see from Eq. (4), in the case of a low remaining ligand concentration n_l in the liquid phase ($n_l \ll$ corresponding to total adsorption), the particle size only should depend on the concentration ratio of ligands and condensing species. The type of curve then should follow an equation like $y = 1/xK$, with K as a constant including all constant parameters. If the adsorption is depending on ligand concentration, Eq. (4) changes to Eq. (5):

$$d = \theta \cdot A \cdot \frac{1}{n} \cdot 6B \cdot C_c \qquad (5)$$

with θ representing the adsorption isotherm function. A series of experiments have been carried out to investigate the influence of various additives during hydrolysis and condensation and to find out how far the particle size can be influenced. In Figs. 1(a)–(c) three curves based on data obtained by Krämer [14] are shown, with alkoxides of Zr and Ti reacted with different complex formers after hydrolysis. In order to find out how far the $y = 1/x$ function can be used, the theoretical curves were calculated. As one can see, in the case of
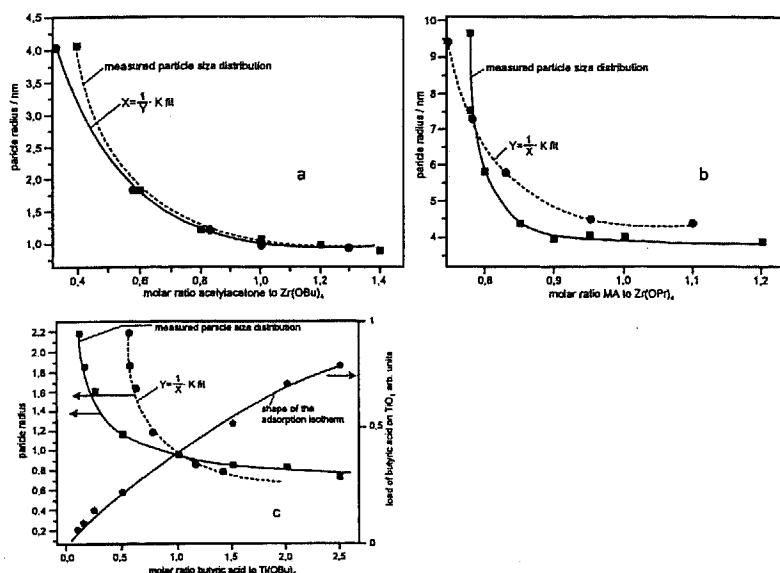
Figure 1. Dependence of sol particle size determined by photon correlation spectroscopy and $y = 1/x \cdot K$ fits of three systems: (a) $Zr(OBu)_4$/ acetylacetone (acac); (b) $Zr(OPr)_4$/methacrylic acid (MA); (c) $Ti(OBu)_4$/butyric acid [after 14]; particle distribution $\pm 10\%$ in diameter.
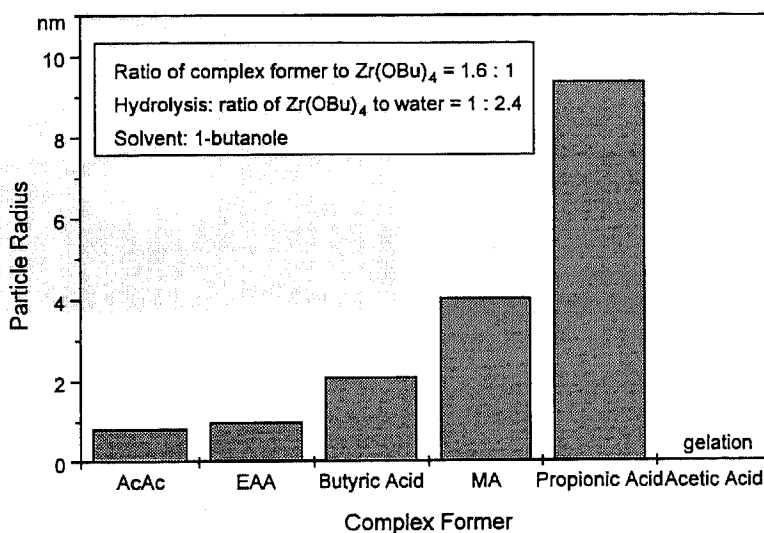

Figure 2. Dependence of particle size on ligands [after 14]. AcAc: acetyl acetate; EAA: ethyl acetoacetate; MA: methacrylic acid.

$Zr(OR)_4$/acac, the theoretical curve is close to the measured one, indicating the validity of the hypothesis for a σ driven reaction and an almost complete adsorption of the acac by the particle surface. In the other two cases the fitting is rather poor, indicating a weaker bond of the acids to the surface, which could be expected. In the case of Ti, from the mismatch an adsorption isotherm could be estimated, showing increasing adsorption with increasing butyric acid concentration. Independent on the problems of determining the exact equation of the

dependence of particle size on ligand concentration, it is possible to control the particle size by the reaction parameters. As also shown in [14], in one and the same system and under consistent reaction conditions, the particle size also can be varied by the type of ligand only. The different effect of the modifying molecules is attributed to their different sizes, $\ominus$ functions and pH values. As one can see, the typical complex formers based on ß-diketones show the lower particle size, indicating the strongest surface interactions.

In further experiments, it could be shown that this principle also could be used for the metal colloid formation (e.g., Ag, Au, Pd, [15]), if metal and amine complexes were reduced to the metals. Due to the weaker adsorption of amines to the metal surface, much higher ligand concentrations had to be used (1 : 20–1 : 100).

In order to fabricate materials based on surface modified nanoparticles or to process them into a matrix, it is of importance to know how far bonds stable enough to survive such processes can be obtained. For this reason, the system Zr(OR)₄/MA was investigated, since this system already has been used for synthesizing nanocomposites so far [16, 17]. In Figs. 3(a)–(b) the IR spectra of the hydrolysed ZrO₂/MA system obtained from the MA complexed alkoxide and the electron diffraction patterns after polymerisation with (RO)₃Si-methacrylate are shown [16].

During complex formation the C=O frequency of MA is shifted to the methacrylate form and remains unchanged during hydrolysis and condensation. The electron diffraction patterns show clearly that crystalline ZrO₂ (monoclinic modification) particles are formed and that the methacrylic acid is still bonded to the particle surface even after polymerisation indicating that MA is pushed to the particle surface during condensation. Similar results have been obtained with alumina either modified with carboxylic acids [19], ether ethanolates [20] or β-diketonates [10]. Similar results have been obtained with nano-scale particles modified after preparation (Fig. 4). In Fig. 4(a), IR spectra of ZrO₂ (30 nm) and in Fig. 4(b) of AlOOH (15 nm) [19] after surface modification are shown. The =C=O frequency indicates a carboxylic "salt" formation ("colloidal salts") since the =C=O frequency of the "carboxylic acids" bonded to the
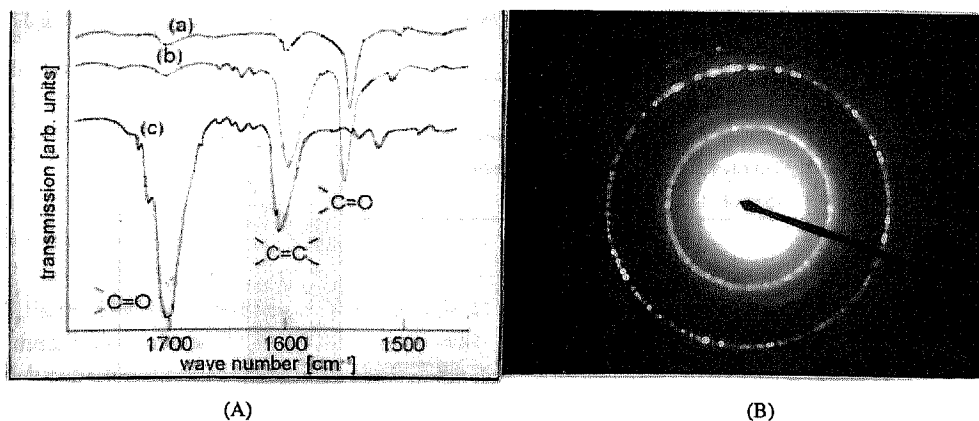

Figure 3. (A) IR spectra of (a) methacrylic acid, (b) Zr(OR)₃/MA; (c) after hydrolysis, condensation and polymerisation of the double bond and two weeks water exposure; (B) electron beam diffraction pattern of the polymerized system. Particle size ≈ 2 nm [16, 18].
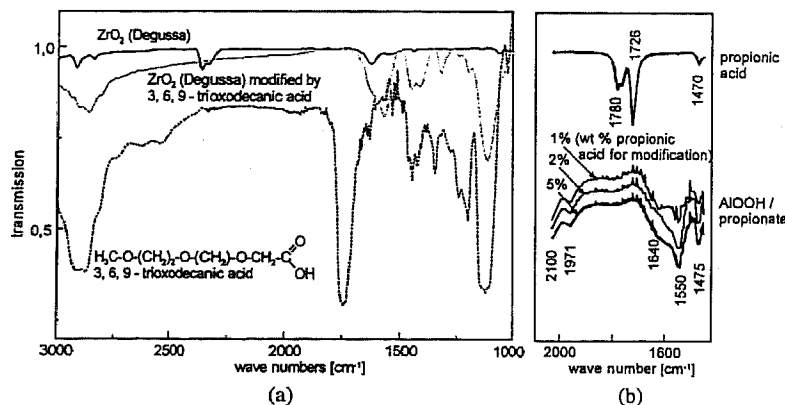

Figure 4. IR spectra of colloid carboxylates; (a) ZrO₂/decanates; (b) AlOOH/propylate; treatment: refluxing for 24 hrs in toluene with excess acid, filtering, washing and drying; IR by DRIFT (diffuse reflectance FTIR).
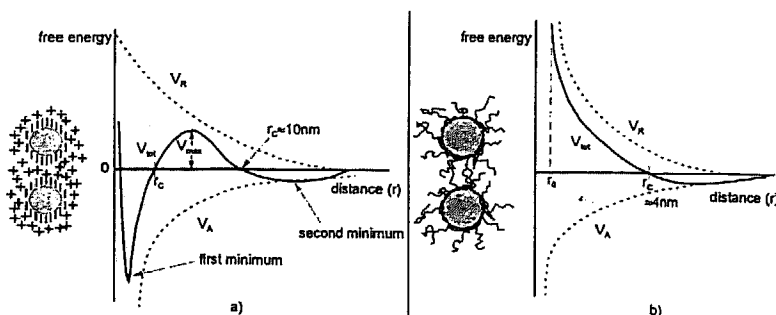
Figure 5.   Dependence of the repulsion/attraction on the distance between two particles after [21]; (a) electrostatic; average value: depends on the ionic strength of the liquid phase which, in sol-gel processing, is intended to be kept low; distance decreases with increasing ionic strength; (b) steric model.

particle surfaces are almost identical with the corresponding ionic carboxylates Al(i-propionate)$_3$ and ZrO(carboxylate)$_2$. These bonds do not disappear during further sol-gel processing or incorporating into polymer or ormocer matrices, which means that these systems can be used for material fabrication.

Another route of surface modification is the reaction of already formed nanoparticles with reactive silanes (Eqs. (6) and (7)).

(6)

(7)
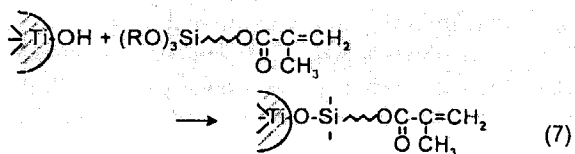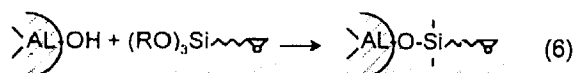
or by reaching SiO$_2$ nanoparticles with ammines (8):

(8)
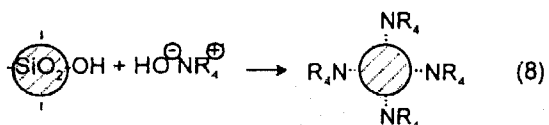
As one could see from the previous results, the described modifications, beside the fact that sol particles are surface modified and outfitted with interesting chemical reactivities, the ligands also act as stabilisers, preventing the sols from agglomeration. As already pointed out, charge stabilized sols are difficult to be processed in a very controlled way. In addition to this, the question arises how concentrated these sols can be prepared, which strongly depends on the interaction distances.

In Fig. 5, a consideration after Stern's model [21] is shown, depicting the energy potential of charged particles as a function of the particle-to-particle distance. For the electrostatic stabilisation (Fig. 5(a)) a critical distance r_c exists, at which the repulsion switches into attraction. This can be enforced, for example, by up-concentration (e.g., by solvent removal), and this plays an important role in film formation by dip or spin coating, leading to remarkably higher gel densities compared to corresponding bulk systems. In bulk processing, the gelation has to be initiated by either further condensation (e.g., in acid SiO$_2$ sols) or by neutralisation of surface charges and subsequent aggregation. Due to the fact that the repulsion by electric charge is in the range of about 10 nm, the maximum density of these sols remains low. In Fig. 5(b) the case of the so-called sterical stabilisation is shown. In this case, the equilibrium distance r_c caused by van der Waal's forces is in the range of 4 nm with long chain polymers and can even be reduced by use of small molecules. But it is more important that the nature of the attracting forces can be tailored to be of the van der Waal's type, if appropriate surface modifyers are used. Since the van der Waal's forces are much weaker than chemical or hydrogen bonds, only weak agglomerates, if so, should be formed.

Using the type of modification shown in Eqs. (6)–(8), surprisingly high solid contents could be obtained in sols and gels, for example, 40 wt.% of boehmite in liquid mixtures of glycidyloxypropyl triethoxysilane/ TEOS/Al(OR)$_3$ without gelation [20, 22] 50 wt.% of SiO$_2$ by the surface modification of 6 nm SiO$_2$ sols by (RO)$_3$SiCH$_3$ or NR$_4^{\oplus}$OH$^{\ominus}$ [23] (boehmite: 45 vol%; ZrO$_2$: 35 vol%) [24, 25]. In the case of boehmite, weakly agglomerated powders have been prepared which could be completely redispersed in liquids.

R   = organic non-reactive, polymerizable or organofunctional groupings
~   = organic chains with charged groupings
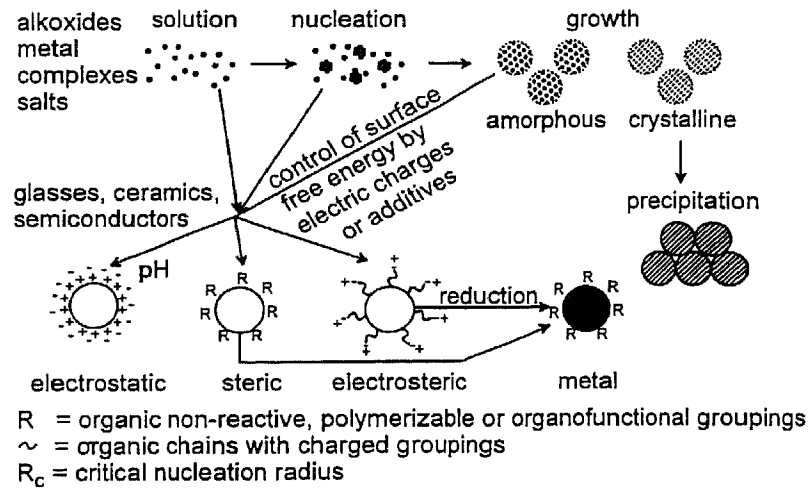R_c = critical nucleation radius

Figure 6.   Reaction scheme for the fabrication of nano sols for different types of stabilisation.

Summarizing, one can say that the steric stabilisation can lead to remarkable advantages compared to electrostatic stabilisation in sols. In the flowchart in Fig. 6, the various reaction routes are summarized.

The chemically modified sols have been used for the preparation of high density ceramic green bodies with low temperature sintering [26] for the synthesis of composite materials, characterized by an organically modified inorganic nanoparticle, so-called organically modified nanocomposites (ORMONANs). With colloidal metals (Au, Cu), transparent composites with high χ^3 values [27, 28] up to 10^{-5} esu have been synthesized already.

In the following, material developments based on organic-inorganic nanocomposites are presented. For this reason, especially if high optical quality is required, a perfect dispersion of the nano particles is indispensible. Steric stabilisation seems to be the adequate means, since the interface of the particle can be adjusted

to the matrix. This is of specific importance for higher volume fractions of fillers.

3. Material Fabrication with Modified Sols

3.1. TiO₂ Containing Nanocomposites

TiO₂ particles have been synthesized from Ti(OBut)₄ by hydrolysis and condensation at low pH values by charge stabilisation, the experimental procedure of which is described elsewhere [29], and nano-scale particles of about 2 nm have been obtained (Fig. 7(a)). These sols have been reacted with 3-methacryloxypropyl trimethoxy silane (Eq. (7)) changing from the charge stabilisation to a steric stabilisation and subsequently mixed with methacrylate monomers and polymerized by thermal initiators. The viscous precursor system was poured into moulds and completely
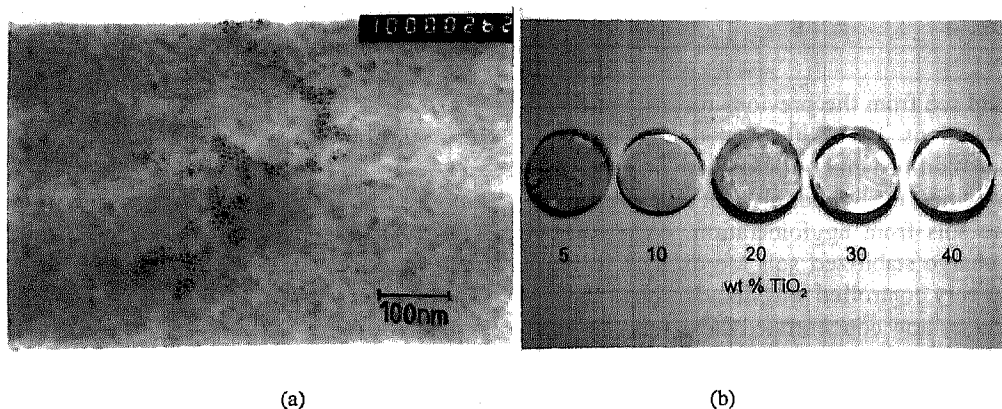

(a)   (b)

Figure 7.   (a) HRTEM image of nano-scale TiO₂ particles; (b) bulk materials with various TiO₂ contents.
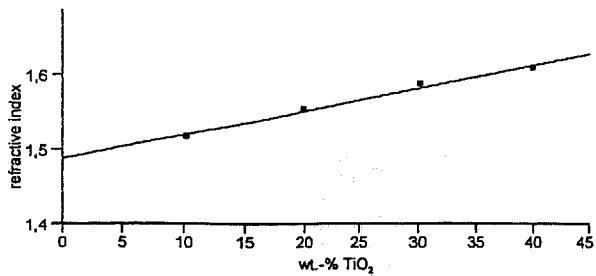
Figure 8. Dependence of refractive index on TiO₂ content in a TiO₂ bulk nanocomposite.

polymerized under temperature controlled conditions. Clear colourless bulk materials had been obtained with TiO₂ contents up to 40 wt.% (Fig. 7(b)). The materials can be sterilized under H₂O pressure and show an intrinsic scratch resistance comparable to usual hard coatings. The refractive index of these materials varies almost linearly with the TiO₂ volume fraction between 1.48 and 1.61, as shown in Fig. 8.

3.2.   SiO₂ Containing Nanocomposites

SiO₂ containing nano composites have been synthesized by using commercially available SiO₂ sols

(Nissan Chem. Corp., Bayer AG) of about 6 nm in diameter, which have been modified by organic ammonium compounds according to Eq. (8). These sols, having a methyl or ethyl group containing surface, show excellent dispersing properties in epoxide and methacrylate precursors and mixtures of them [30].

In Fig. 9, a nanocomposite with 6 nm SiO₂ dispersed in an epoxy methacrylate commercial sealing agent is shown [31]. The unmodified SiO₂ system (upper part) leads to an inhomogeneous, cloudy material, due to the SiO₂ agglomeration. The modified system is homogeneous and highly transparent. The thermomechanical behaviour determined at the homogeneous system depends on the SiO₂ content. The decay of the mechanical properties above T_g is remarkably lower compared to the unfilled system, showing a rubbery plateau (Fig. 9(b)). This is surprising since, in general, this is explained in inorganic-organic composites by a continuous inorganic phase only, not undergoing structural changes at T_g of the organic phase. Since in the nanocomposite system no continuous inorganic phase is present, this interpretation cannot be taken into consideration. The phenomenon has to be interpreted by a percolating interfacial phase around the particles, formed by a special polymer interface structure
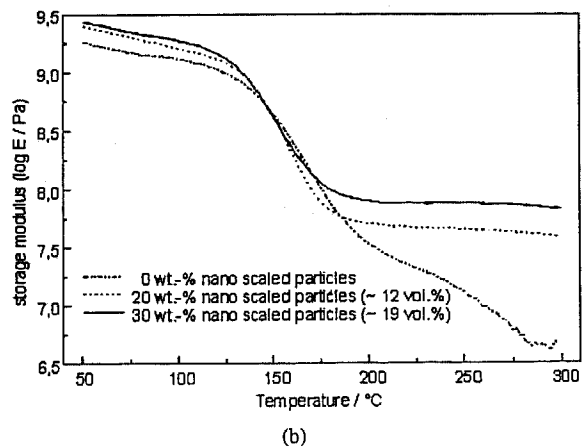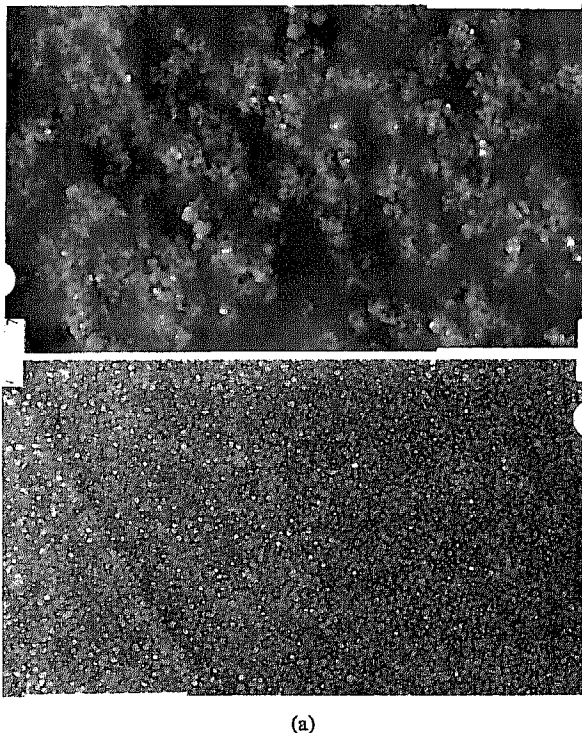

(a)

(b)

Figure 9.   a) HRTEM image of two different SiO₂ nanocomposites; 5 vol.% poorly (a) and 15 vol.% (b) homogeneously dispersed; b) thermodynamical properties of SiO₂ nanocomposites with various SiO₂ contents.
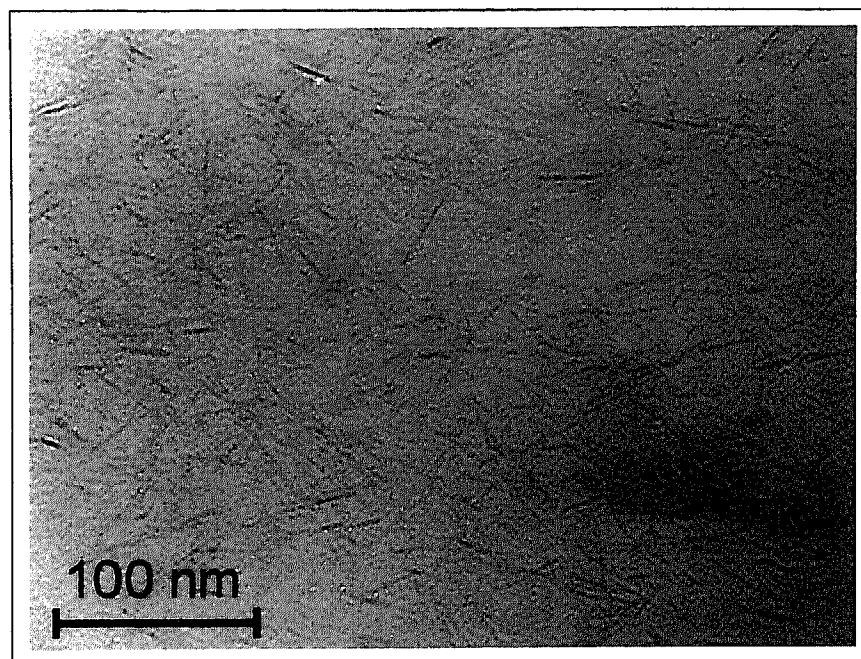
Figure 10.   HRTEM image of a boehmite/epoxy-silane nanocomposite.

(interfacial phase determined material). The system is used as a seal for high performance fiber-to-chip coupling in microoptics.

3.3.   Boehmite Containing Nanocomposites

As already shown in Eq. (6) and described elsewhere [20], the "coating" of boehmite with epoxy silanes leads to the prevention of agglomeration up to 40 wt.% solid content in epoxy group containing liquid precursors. Furthermore, as also described, boehmite nanoparticles are able to catalyse the polymerisation of epoxide groups of epoxy silanes, and it is supposed that by reacting the silane with boehmite, a structure with AlOOH particles embedded in PEO chains is formed. This was proved by NMR spectroscopy [20]. In Fig. 10 a HRTEM micrograph of this nanocomposite is shown, demonstrating the homogeneous distribution of the needle type boehmite in the matrix. The composites are highly transparent, show a good adhesion on various polymeric substrates, can be cured at 130 to 150°C to ultrahard coatings (1000 cycles taber abrader, ≤2% haze) and are used successfully since July 1994 for ophthalmic lenses on CR 39 with curing temperatures of about 90°C.

4.   Conclusion

The controlled sol-gel processing with surface interacting additives is an interesting alternative to the classical route, using electrostatic stabilisation. Moreover, the steric stabilisation with appropriate molecules allows to control the particle size during synthesis, to control agglomeration and dispersion, and to increase the solid concentration of sols, as well as to establish desired reactivities, e.g., polymerization. In opposition to the classical inorganic-organic (ormocer) composite route with "molecular" phase dimensions, the solid state properties of small particles can be used as tool for material property tailoring without losing transparency for new interface determined organically modified nanocomposites (ORMONANs).

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