

Inorganic-organic nanocomposites for optical coatings

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ABSTRACT

The fabrication of nanoparticles by the sol-gel process and their use in polymeric or sol-gel-derived inorganic-organic composite matrices opens up interesting possibilities for designing new optical materials. Two different routes have been chosen for preparing optical nanocomposites: The first is the so-called "in situ route", where the nanoparticles are synthesized in a liquid mixture from Zr-alkoxides in a polymerizable system and diffractive gratings were produced by embossing uncured film. The second is the "separate" preparation route, where a sterically stabilized dry nanoboehmite powder was completely redispersed in an epoxy group-containing matrix and hard coatings with optical quality on polycarbonate were prepared.

Keywords: Optical sol-gel materials, nanocomposites, diffractive gratings, embossing, optical hard coatings

1. INTRODUCTION

Sol-gel materials have gained a reasonable significance in the development of optical materials. One of the most important reasons is that, due to sol-gel processing, the particle size of precursor material can be kept below the Rayleigh scattering limit, which is roughly about 1/20 of the wavelength to be used. Due to the processing parameters, which, in general, lead to electric charge-stabilized small particles in the lower nm range, sols can be prepared, which are transparent¹. If the distance between the particles can be kept large enough so that, according to Stern's potential, the repulsion between the charged particles can be maintained, no aggregation takes place, and the transparency also can be maintained³. By reducing the particle distance (for example, by solvent evaporation after a dip coating step) or by changing the electric charge (e.g. by pH change), the repulsion of the particles or oligomers turns into attraction. If the resulting microstructure still has dimensions below the Rayleigh scattering limit (pores and particles), the gels still are transparent. If by heat treatment, crystallization takes place and the crystallites also are in the nano range, as it has been shown with various oxides⁴⁻⁶. The resulting materials still are transparent and suitable for optics. The fabrication of large components can be carried out also by this way, as shown by Hench⁷. The problems related to these techniques, however, do not result from problems to obtain optical homogeneity, but from the problems to maintain precise dimension in large scales.

Another problem related to sol-gel processing for optics is the problem to fabricate films with appropriate thicknesses, especially if thicknesses above 1 μm are required. If purely inorganic materials are prepared, several obstacles occur. One of them, especially in coatings, is the fact that, due to the poor relaxation of the three-dimensionally cross-linked systems and small pores, capillary forces lead to the crack formation during drying. This is also dependent on the solid content, which, in gels, also is rather low, that means, within the range of about 20 % by volume as a maximum⁸. The system also allows to fabricate coatings of optical quality. Applied on polycarbonate (PC), a high abrasion resistance results, which opens up new optical applications on PC.

There is numerous work carried out to combine inorganic systems with organics⁹, which shows that through organic modification, more flexibility can be provided, and the problem of cracking can be avoided completely. But these systems now have more or less properties related to the organic residues (for example, low hardness, gas permeability and, in general, low index of refraction). However, these materials then can be processed more or less like organic polymer films. The majority of these hybrid systems contain inorganics more or less molecularly distributed. This means that solid state properties attributed to a crystalline or an inorganic glassy phase cannot be observed in these materials. Recently, papers have been published which show that well-defined inorganic nano-scale phases can be obtained by an independent processing of the inorganic phase and then mixed to organically modified or pure organic phase¹⁰⁻¹², which allows the combination of functional inorganic as well as organic phases in optical application. In the present paper, a general consideration about these combined routes and some examples for material developments are given.

2. GENERAL CONSIDERATIONS

As pointed out in the introduction, it has been shown that the introduction of nanoparticles into inorganic-organic composite materials can be used for tailoring materials properties without losing optical transparency. Basically, different preparation routes can be used. An overview is given in fig. 1. In this draft, two different routes are shown, the so-called

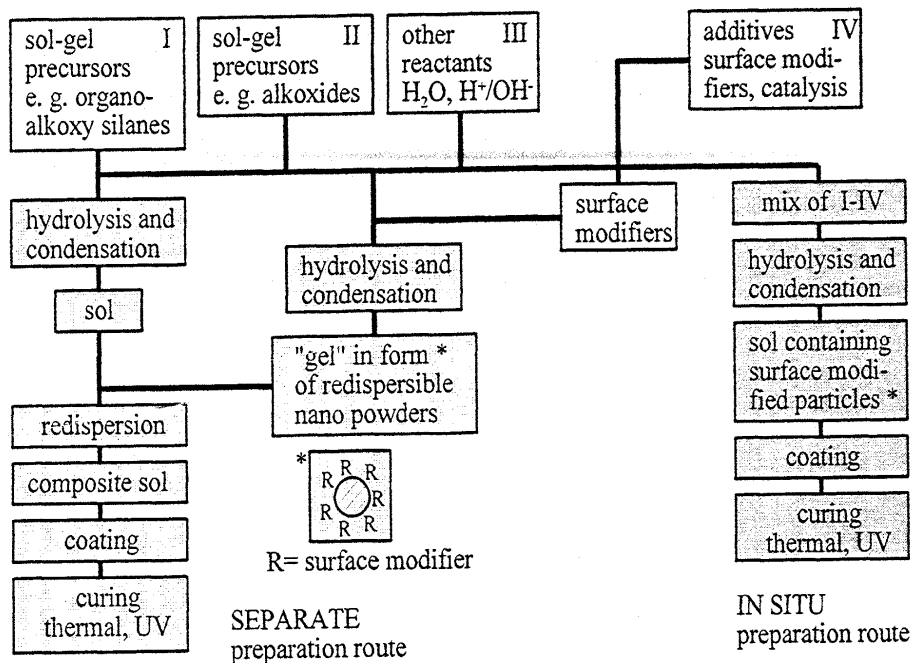


Fig. 1: Basic routes for synthesizing inorganic-organic nanocomposites.

separate preparation route and the in-situ preparation route. The most important issue is that agglomeration of nanoparticles have to be avoided at any rate, because otherwise the turbidity would not be avoidable. The effect of the surface modifiers during hydrolysis and condensation is described in detail elsewhere¹¹. From both routes, various types of material have been prepared (for example, zirconia-containing nanocomposites¹³ or various hard coatings¹⁴). The basic

difference between the two routes is that in the separate preparation route, nano-scale particles have to be prepared in a way that a guaranteed redispersion takes place in the corresponding liquid media. The advantage of this route is that the particles can be prepared independently and added to various matrices. Methods for particle preparation have been described elsewhere¹⁵⁻¹⁶. In the in-situ preparation route, the modifier not only acts as a sterical stabilizer of the growing particles, preventing them from growing together, but also interferes with the nucleation and growth process^{11,17}.

In addition to the stabilizing effect of the surface modifiers, they also can be used for linking the particles into the matrix as far as they are reactive. So, for example, polymerizable silanes have been used for connecting nanoparticles to a polymerizable matrix or particles modified by acrylates with polymerizable groupings¹⁶ or methacrylic groupings¹⁸. Both routes have been investigated for their potential of the production of optical materials. One example for the effect of the surface modifiers is shown in fig. 2 and 3¹⁹. As one can clearly see, the unmodified particles are agglomerated, and the resulting composite is cloudy. On the other hand, the coated particles disperse very well in the composite, and these materials are completely clear, that means in this case suitable for optical application. The results are interpreted in a way that by coating of the SiO₂ nanoparticles with the methacryloxytrimethoxysilane the interfacial free energy between the particles and the matrix, also containing methacryloxy groups, is reduced in a way that the dispersed state shows a lower free energy value than the agglomerated state. Without surface modification, the opposite takes place. As shown elsewhere^{13,18,21}, zirconia easily can be dispersed in methacryloxysilane-containing matrices if it is surface-modified by methacrylic acid. In these cases, the in-situ route is suitable since during the sol-gel process, the methacrylic acid is bonded to the surface of the zirconia nanoparticles, and the size of them can be tailored by the concentration ratio of zirconia to the methacrylic acid¹¹. With increasing ratio of zirconia to methacrylic acid, the particle size also is increasing. So an excellent tool existst for keeping the particle size in the nano range. This type of composites already have been investigated for their optical properties, and it has been shown¹³ that waveguides and gratings can be fabricated. In the following, a process will be described which already is introduced into industry.

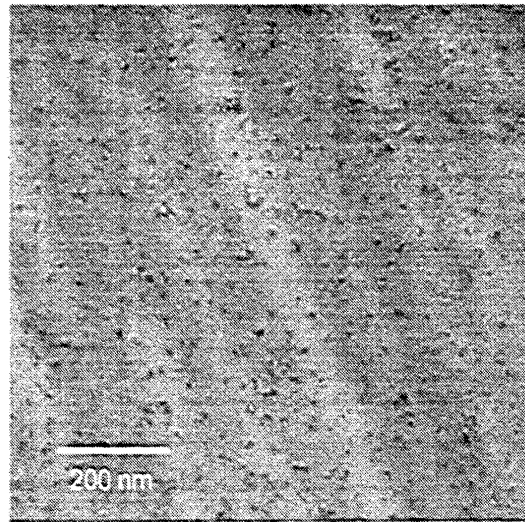
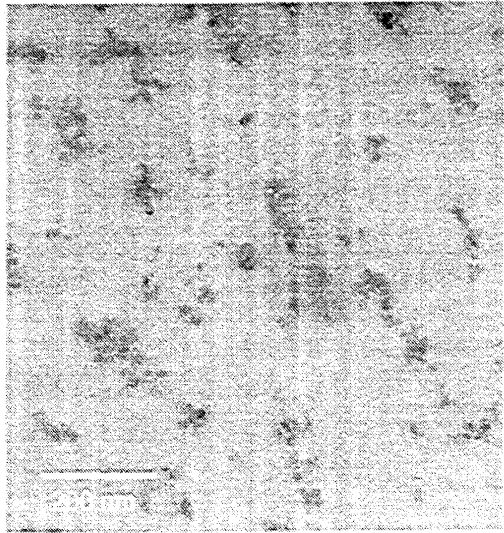


Fig. 2: TEM micrograph of a poly-MMA*-HEMA**/hydroxyethylmethacrylate/SiO₂ nanocomposite with 10 nm SiO₂ particles added before radical polymerization^{after 20}.
* methylmethacrylate
**hydroxyethylmethacrylate

Fig. 3: TEM micrograph of a poly-MMA/HEMA/SiO₂ nanocomposite with 2 vol.-% of SiO₂ particles coated with methylmethacryloxysilane before mixing^{after 20 Ann. Rep. 1995}.

3. MATERIAL AND PROCESS DEVELOPMENT

3.1 Experimental

The nanocomposite material was synthesized from methacryloxypropyltrimethoxysilane (MPTS), methacrylic acid (MA), zirconium-u-propoxide (ZR) and perfluorooctyltrimethoxysilane (FS). The ZR component was complexed with the MA component in a mol-ratio of 1 : 1. The MPTS component was prehydrolyzed with an acid catalyst and the MPTS and ZR/MA components were mixed. The formation of ZrO₂ nanoparticles is initiated in situ of the MPTS matrix by catalytic hydrolysis and condensation of the ZR/MA component. Additionally, the FS component was added. The detailed synthesis procedure is described elsewhere²². A photoinitiator (Irgacure 184) was added to perform photocuring of the materials by radical polymerization. Alternatively, a thermally activated radical initiator has been used.

Thin films were prepared by spin-coating with film thickness < 7 nm because this thickness reveals excellent resistance of the film at high humidity (85 %) and high temperature (120 °C) over several days²³. Embossing of grating structures was performed in a vacuum chamber to avoid inhibition of the polymerization by oxygen. The stamper was pressed on the film with well defined force and the sample was illuminated during the embossing step through a fused silica window. The embossing step took less than 1 minute. After switching off the UV light source, the stamper was lifted and the embossed substrate was removed from the chamber. Detailed description of the process can be found in²³. The synthesis of boehmite-containing films based on epoxysilane is described in¹⁰.

3.2 Results

High-quality optical gratings are of interest for many applications, for example, for optical devices or as basic parts for instruments of ultraprecise positioning of parts for surface finishing. Embossing of polymers is one of the routes which are used in praxis, but in this case, thermoplastics have to be used which above T_g do not show a good stability and, in addition to this, these thermoplastic polymers in many cases are sensitive to organic solvents, and the temperature stability is restricted mainly to temperatures below 100 °C. As shown elsewhere, inorganic-organic composites are rather insensitive to organic solvents and can be used at temperatures up to 150 °C¹⁴. Based on these basic properties, a process had to be developed which allows the fabrication of these gratings from this type of materials in a rational way. For this reason, embossing was investigated as a potential method. First investigations have been carried out with a system based on zirconia nanoparticles derived from zirconia alkoxide complexed with methacrylic acid, methacryloxytrimethoxysilane, as described

elsewhere¹³. This system can be cured by radical initiators (thermally as well as photoinitiated¹⁸). For embossing, a liquid film in thicknesses of 1 - 2 μm has been prepared by dip coating or spin coating on glass substrates dried at room temperatures and then embossed with a master made from glass. In fig. 4 a schematic of the process is shown. The system shows a very easy mould release behavior which indicates that no strong adhesion forces are built up between the embossed grating and the glass mould. However, for practical use, glass moulds are not the first choice since the fabrication costs for these moulds are very high and, as an alternative, metallized plastic moulds had to be used. The plastic moulds had been metallized

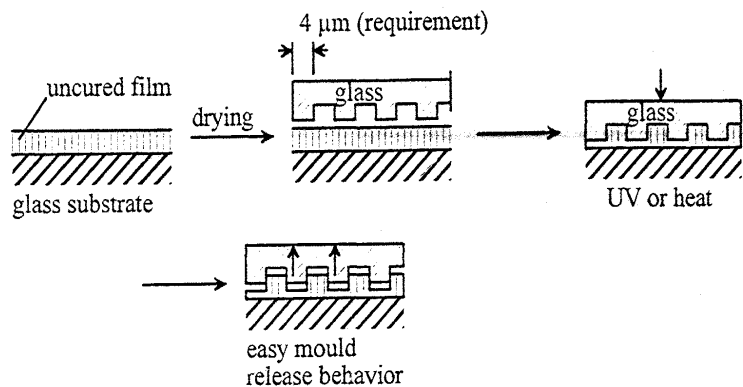


Fig. 4: Scheme of the embossing step with a glass master.

by conventional processes with nickel and used for the grating fabrication, but in this case, a very strong adhesion to the master took place so that no defect-free gratings could be prepared.

In order to solve these problems, two routes are possible in principle: first, to coat the mould with anti-adhesive materials like silicons or teflon, which is a solution with some disadvantages. Silicons have to be renewed and may spoil the grating, and teflon cannot be employed in ultrathin coatings not to change the grating dimensions. In order to solve the problem, fluorinated silanes were added to the coating liquid since, as it has been shown elsewhere, a gradient formation can be expected²⁴.

For this reason, experiments have been carried out how much fluorinated silane has to be added in order to develop an anti-adhesive surface. The effect of the modification has been tested by measuring the contact angle against water. In fig. 5 the development of the contact angle as a function of time and the addition of 1H-1H-2H-2H-perfluorooctyltriethoxysilane is shown. The films have been prepared by spin-coating and were stored in a closed chamber (normal atmosphere, T =

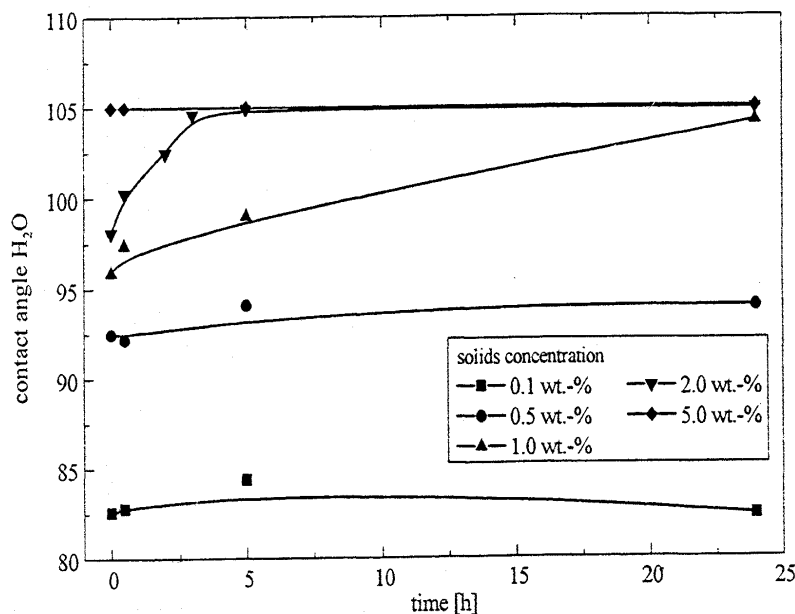


Fig. 5: Contact angle against water of a perfluorated zirconia-containing nanocomposite layer as a function of the fluorine concentration and time.

2 °C). As one can clearly see, very low contents of fluorinated silanes do not lead to a high contact angle. The contact angle is the same as in the unfluorinated sample. At 0.5 % a distinctive increase of the contact angle is observed which increases only slowly with time. With 1 % another increase is observed, and the increase with time is obvious. With 2 % a steep increase is observed at the beginning, which ends at a contact angle of about 105°, which does not change with further increase of the fluorine concentration. So the further experi-

ments have been carried out with 2 % of the addition of the fluorinated silane. The experimental procedure is shown in fig. 6. It has to be mentioned that the adhesion to the substrate glass is not affected by the fluorination. This is attributed to the fact that in the liquid system, sufficient SiOH or SiOR groups are still present, as shown elsewhere²⁵, which are able to react with the glass surface. During the development of the low surface contact angle, a diffusion process takes place where, driven by the thermodynamics of the system, an enrichment of the fluorinated silane groups takes place in the surface.

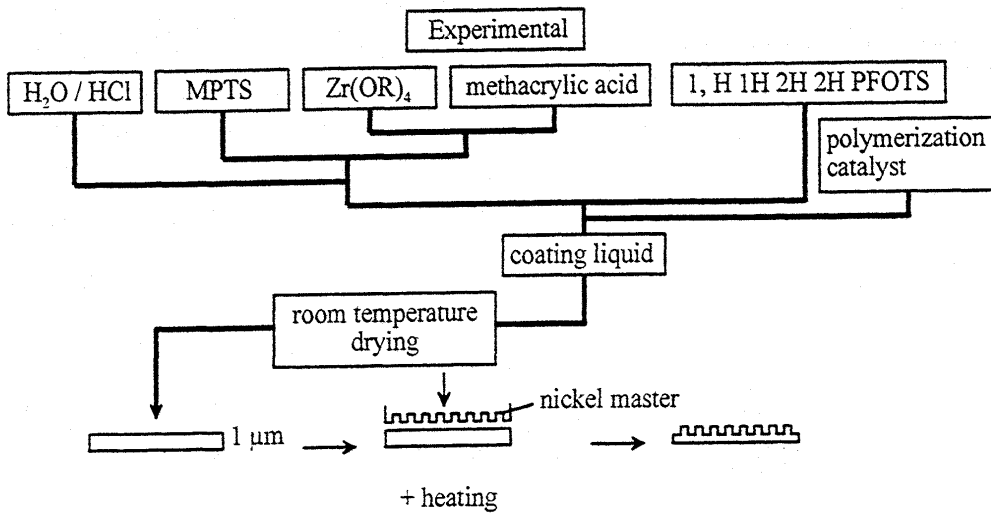


Fig. 6: Draft of the fabrication of the anti-adhesive material system for embossing experiments.

This is schematically shown in fig. 7. The embossing experiments with nickel dyes show that no adhesion

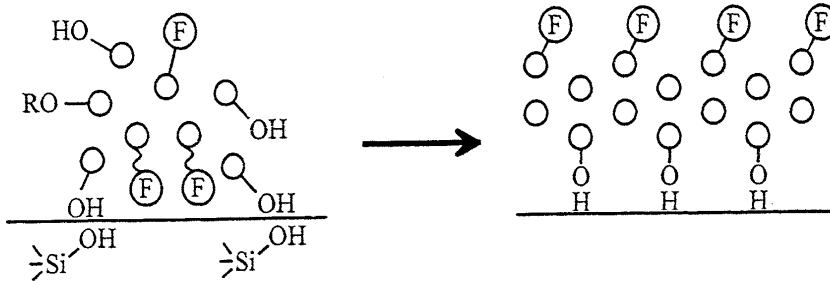


Fig. 7: Scheme of the formation of a gradient after coating with good adhesion to glass surfaces.

problem occurs. In fig. 8 and 9, an atomic force micrograph and the corresponding SEM micrograph is shown. The SEM micrograph shows that a precise grating with 4 μm

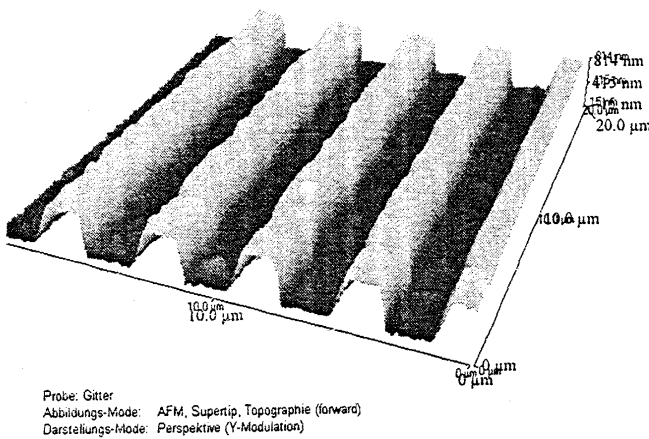


Fig. 8: Atomic force microscope print of an embossed phase grating structure.

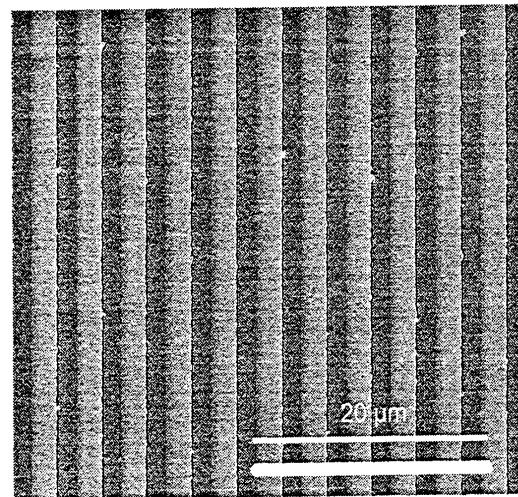


Fig. 9: Scanning electron microscopy of the embossed grating.

width is obtained. The height of the patterns has been calculated from the intensity of the 0-order reflection according to eq. 1. In fig. 10 the reflection spectrum of the embossed phase grating is shown. The evaluation of the height shows

$$I \approx \left(1 + \cos \frac{4\pi \cdot h}{\lambda} \right) \quad (1)$$

that of an average height of 563 nm. This corresponds with the height of the used masters. This development example shows that nanocomposite materials can be used for the fabrication of optical components with simple techniques.

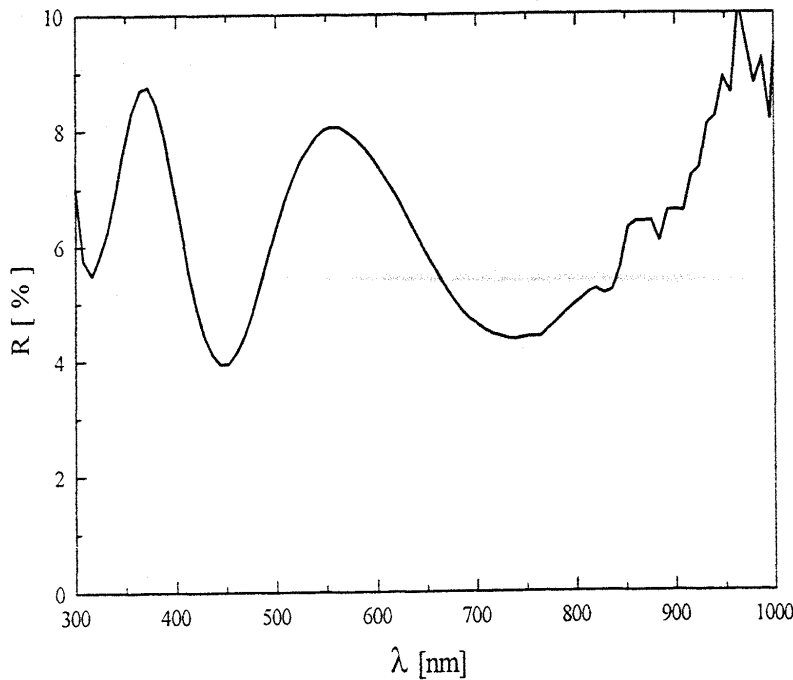


Fig. 10: Reflection spectrum of an embossed phase grating.

The second example is the development of an ultrahard coating for high transparency polycarbonate where the achievement of mechanical properties is the most important part. The aim of this development is to have a coating system with high optical quality for polycarbonate to be used in glazings. The experimental procedure of this coating development is shown elsewhere^{10, 26}. In this case the separate preparation route was used, and boehmite powder stabilized by acetic acid was used as a precursor; the primary particle size of this powder is in the range of 8 - 17nm. A scheme of the stabilization is shown in fig. 11. In this case, instead of methacryloxysilanes,

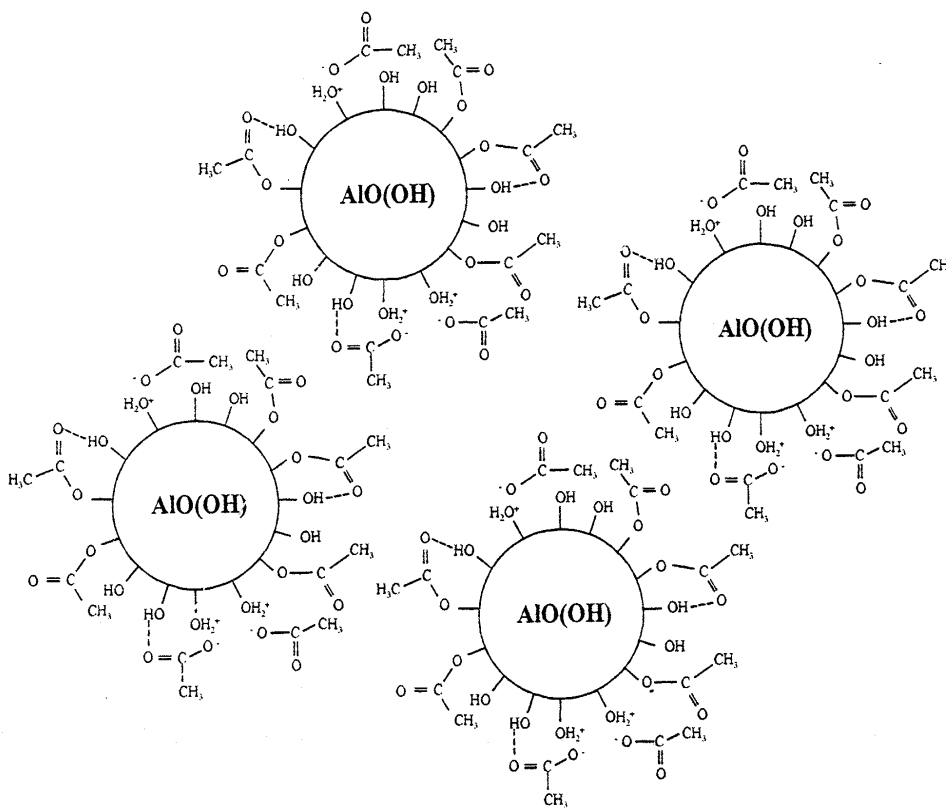


Fig. 11: Scheme of the temporal steric stabilization of boehmite with acetic acid.

epoxysilanes are used together with other precursors like aluminumalkoxides and TEOS. It could be shown¹⁰ that the stabilization of the acetic acid in the boehmite sol is only temporarily if it is dispersed in H₂O/HCl. So the stabilized powder has to be used immediately after dispersion by adding the so prepared aqueous suspension to the precursor mixture. The scheme of the preparation of the boehmite-containing nanocomposite is shown in fig. 12. The aqueous suspension of the stabilized

boehmite is used to hydrolyze the silanes and alkoxides, which, as proved by 29Si-NMR spectroscopy¹⁰ and Al-O-Si bonds to the particles are formed, and the acetic acid is removed.

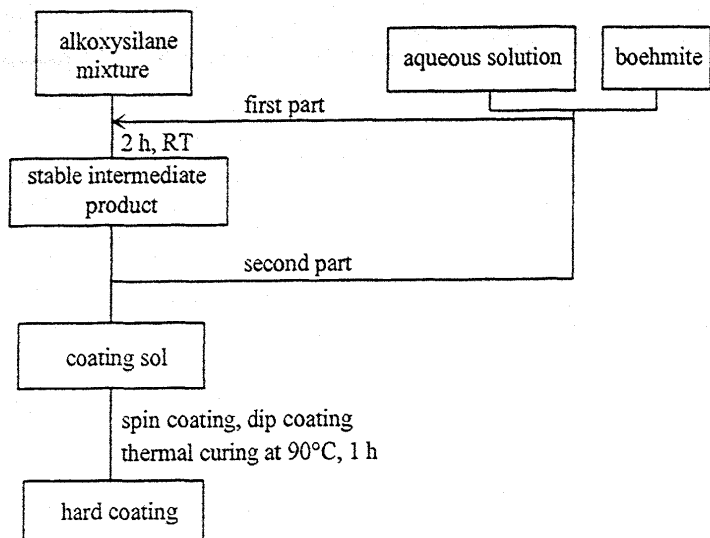


Fig. 12: Synthesis scheme of the boehmite-containing nanomer system.

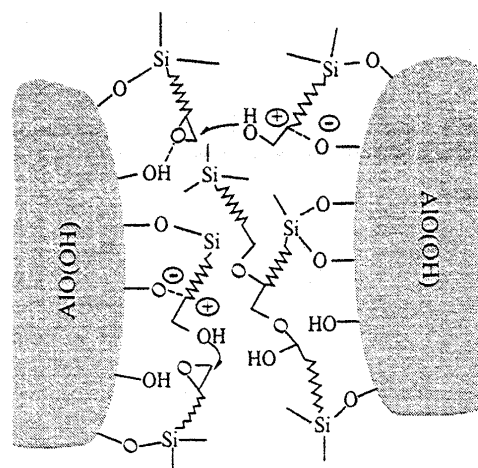


Fig. 13: Mechanistic scheme of the catalytic effect of boehmite on the polyaddition of epoxy groups.

The most interesting results in the synthesis of these materials is the fact that the boehmite particles additionally play the role of the crosslinking catalyst for the epoxides. In fig. 13 the mechanistic approach of the crosslinking activity is shown.

This has been proven by ^{13}C -NMR spectroscopy, as shown in fig. 14. One can clearly see that the crosslinking is catalyzed by boehmite at higher temperatures. For optical applications, it is of great importance that the perfect dispersion of the boehmite nanoparticles is maintained throughout the whole processing, leading to highly transparent coatings.

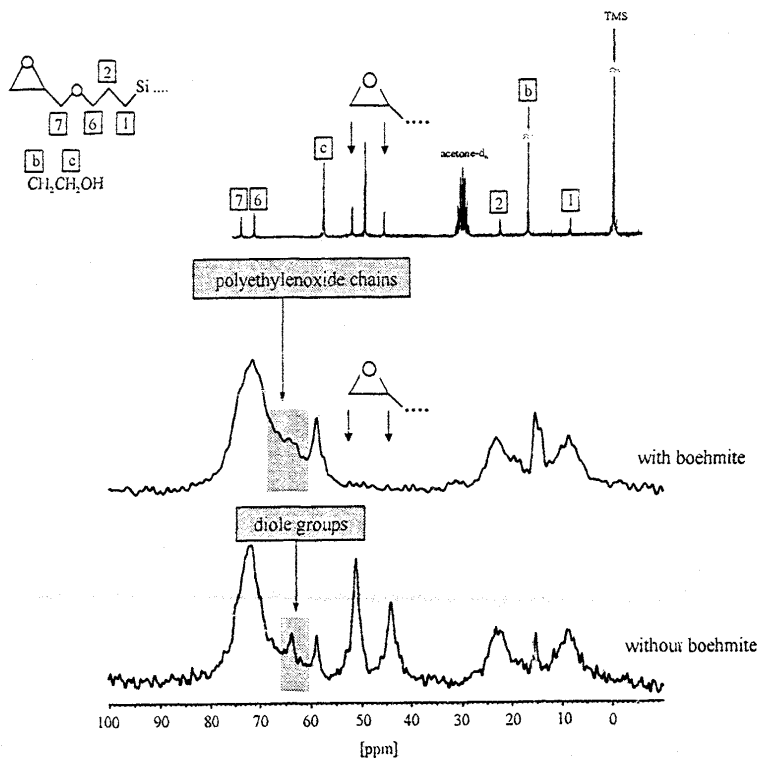


Fig. 14: ^{13}C solid state NMR of the boehmite-containing nanomer (nanoparticle reinforced polymer) system and a similar system without boehmite particles. a: liquid spectrum before thermal curing; b: after thermal curing at 120°C .

It is obvious from the NMR spectrum that only in the boehmite containing system the epoxy ring is no more present. As further shown, the scratch-resistance also depends on the processing route, and the boehmite-containing systems show a much higher scratch-resistance than systems without boehmite (fig. 15). For this reason, the diamond scratch test has been developed. After coating on polycarbonate and curing between 130 and 150°C , a scratch-resistance below 2% haze with 1,000 cycles taber abrader (Al_2O_3 wheel, 500 g) can be obtained. For comparison, floatglass shows after 1,000 cycles 1.5%, and PC 30% even after 100 cycles.

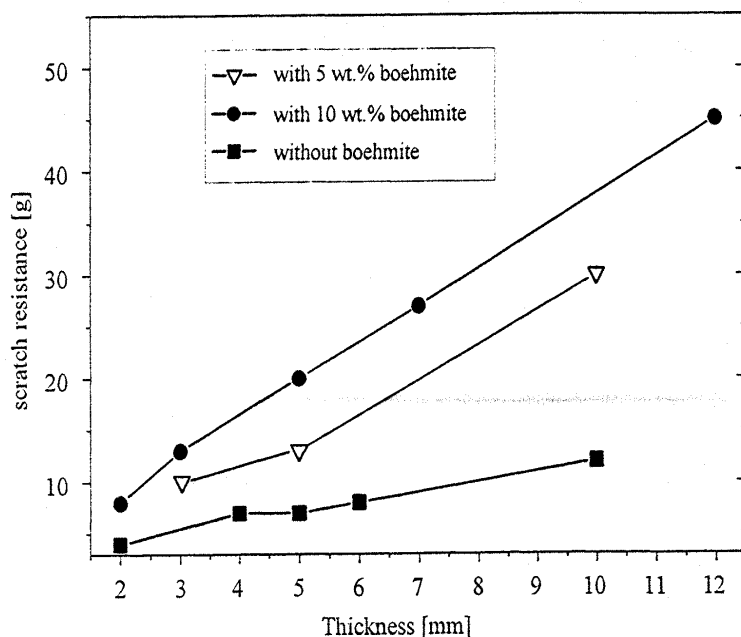


Fig. 15: Results of the scratch tests (modified Vickers test) on composite coatings with different amounts of boehmite particles. A Vickers diamond is scratched over the surface, and the load in g where the scratch becomes visible for the first time under the microscope is used as scratch resistance number.

These examples show that the separate preparation route allows the preparation of optical coatings, and in the described example of very high scratch resistance, which lays a basis for using transparent polymers for glazing purposes.

4. CONCLUSION

As a conclusion, it is to say that sol-gel processing not only allows the preparation of conventional materials for optics, but also the preparation of nanocomposites with interesting optical properties. The described principles, of course, can be extended to a variety of nanofiller materials, as already shown by Mennig²⁷, for superparamagnetic particles²⁸ or for semiconductor quantum dots²⁹. So a generalizable principle has been demonstrated, and good chances for new optical materials are seen.

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