

A NEW TYPE OF A SOL-GEL-DERIVED INORGANIC-ORGANIC NANOCOMPOSITE

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ABSTRACT

A new type of sol-gel-based transparent inorganic-organic nano composites has been developed by increasing the inorganic phase dimension to values just below the point, where scattering can be neglected. For this purpose, nanosized boehmite particles ≤ 50 nm are homogeneously incorporated in a sol based on tetraethoxysilane and an epoxysilane. The nano-scale boehmite particles act as catalysts for the polymerization of the epoxy silane to polyethylene oxide, as proved by ^{13}C NMR, and are linked to the matrix by Si-O-Al bridges, as proven by ^{27}Al -NMR spectroscopy. The synthesized sols can be applied by standard coating techniques on transparent polymers and are cured thermally. The mechanical properties (scratch resistance, hardness) have been substantially improved compared to systems with molecular dimensions of the inorganic phase. The effect is attributed to the special structure of flexibly suspended nano-scale boehmite particles in an inorganic-organic network by a tailored interface.

INTRODUCTION

The sol-gel process for the synthesis of inorganic-organic hybrid materials has gained increased interest for several fields of applications due to its possibility of combining inorganic and organic material properties [1 - 7]. Starting from metal alkoxides, an inorganic three-dimensionally crosslinked network in form of colloidal particles (sols) or polymer type oligomers is synthesized by hydrolysis and condensation in a first step. Organic groups chemically linked to the alkoxides can be homogeneously incorporated. These may be covalent ($\equiv\text{Si-C}\equiv$), coordinative or ionic bonds as shown in [8, 9]. The organic groups can act as network modifiers or network formers in case of polymerizable functions (like vinyl, methacryl or epoxy groupings). Due to increased relaxation properties caused by the organic network modifiers, the densification temperatures can be drastically decreased in comparison to pure inorganic sol-gel materials. Due to the resulting low curing temperatures and improved mechanical properties compared to organic polymers (e.g. scratch and abrasion resistance), transparent inorganic-organic hybrid materials (Ormocers) have been successfully used in industry as hard coatings for ophthalmic lenses for quite a while [10, 11]. This application is based on the tailored properties as an optimized compromise between hardness and elasticity, and it has been shown to be an ideal coating for CR39[®] ophthalmic lenses. The question arises whether it is possible to incorporate nanosized oxide particles into this type of matrices to fabricate heavy duty transparent scratch-resistant coatings, and what structural effects can be expected. As known from SiO_2 fillers, even small amounts increase the viscosity of liquids drastically, due to the particle-to-particle surface interaction. As nano filler, boehmite was chosen, since it is commercially available, and surface modification can be employed to obtain high solid contents at low viscosities, which has been already shown elsewhere [12]. As shown in [13], this type of nano composites exhibits drastically improved properties in comparison to Ormocer materials with molecular or phase dimensions in the range lower than 5 nanometer. In the present paper, the attention is focused on the determination of the structure of this type of materials.

EXPERIMENTAL

Synthesis of the coating material

To a mixture of 118.17 g (0.5 mole) glycidyloxypropyltrimethoxysilane (GPTS) and 62.5 g (0.3 mole) tetraethoxysilane (TEOS) (stirred), 24.3 g of a boehmite aqueous suspension (boehmite suspension: 6.41 g boehmite (Disperal Sol P3, Condea) were added at room temperature to a stirred solution of 64.1 g 0.1 m HCl and ultrasonically treated for 30 minutes). The mixture is stirred for 30 minutes, then cooled down to 0 °C, and additional 46.21 g boehmite suspension are added. After stirring over night at room temperature, the slightly translucent sol is diluted by addition of 20 wt. % n-butanol. The sol is applied by standard coating techniques (dip, spray, spin coating) on corona treated polycarbonate substrates and is thermally cured at 100 °C/ 4 h. The liquid-state NMR spectra are measured with an AC 200 spectrometer, Bruker. The solid-state MAS NMR are performed with an MSL 200, Bruker, Karlsruhe. Microhardness and E-module [14] of 6 μm thick coatings using 1 mN load are determined using a Shimadzu DUH-202.

RESULTS AND DISCUSSION

As a model system for the synthesis of the inorganic-organic composites a system based on a tetraalkoxysilane, GPTS (as a carrier for an organically polymerizable grouping) and an HCl-stabilized boehmite suspension with an average particle size of 50 nm in diameter as a starting material for the nano-scale metal oxide were chosen. This system opens the possibility to follow the hydrolysis and cocondensation of GPTS and the tetraalkoxysilane by ^{29}Si -NMR using the HCl content of the boehmite suspension as a catalyst. Nanocrystalline boehmite ($\text{AlO}(\text{OH})$) was chosen for reasons of its potential to catalyse the polymerisation of the epoxy function to polyethylene oxide (which is known from aluminium alkoxides) and to determine it by ^{13}C -NMR and to monitor the possible formation of Si-O-Al bonds in the sol by ^{27}Al -NMR. Furthermore, the reaction opens the chance, to suspend the $\text{AlO}(\text{OH})$ particles within the matrix and to prevent agglomeration.

First experiments using tetramethoxysilane (TMOS) together with the stabilized boehmite show that, due to the high reactivity of TMOS, gelation takes place after 2 hrs. Therefore,

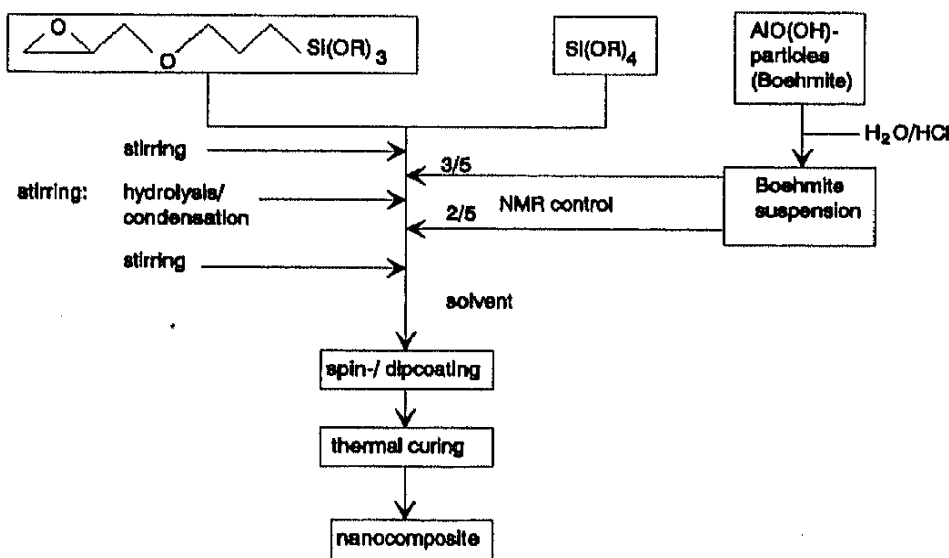


Fig. 1: Reaction scheme of the GPTS/ TEOS/ boehmite nano composite.

TEOS was chosen and the reaction was followed by ^{29}Si -NMR spectroscopy. Since the shelf life of the reaction mixture is important for coating application, the ratio between GPTS and TEOS was varied. It was found that an increased GPTS content reduces the shelf life, but too high a TEOS content leads to brittle materials and densification problems. Systematic variations of the GPTS/TEOS ratio in combination with ^{29}Si NMR studies show that materials with a ratio of 5:3 have an appropriate reactivity and shelf time (several weeks), respectively. Additionally, the sequence of the precursor addition has been investigated to ensure highly transparent coating liquids. In Fig. 1, the optimized process is shown schematically. The appropriate properties (high transparency) with the relatively high $\text{AlO}(\text{OH})$ content can only be achieved by the two-step hydrolysis process. This is interpreted by the fact that the incorporation mechanism of boehmite particles is a time-determining step, and too high concentrations lead to agglomeration.

A comparison of the ^{29}Si -NMR spectra of the reaction mixture with and without boehmite particles is shown in Fig. 2.

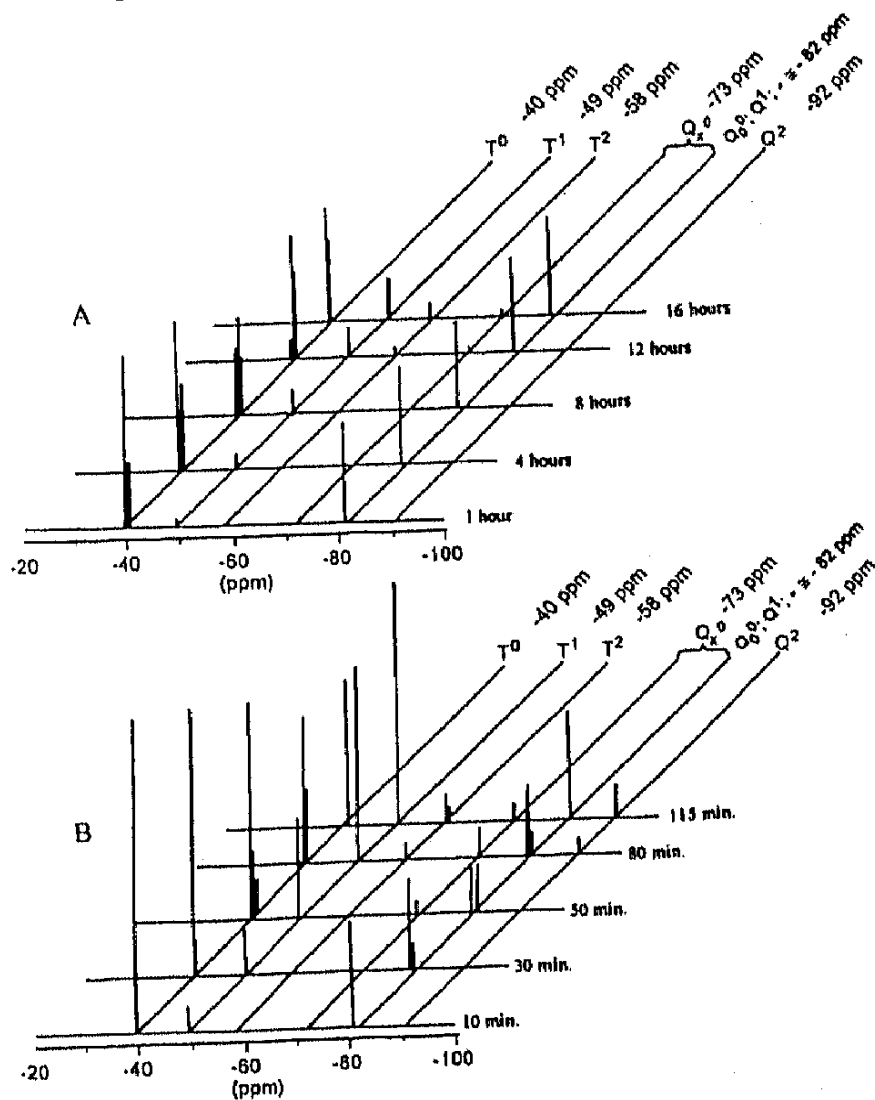


Fig.2: ^{29}Si NMR kinetic study of hydrolysis and condensation in the GPTS/TEOS/HCl system with (B) and without (A) boehmite (T^x , Q^y ; $x =$ number of siloxane bonds, $y =$ number of OH groups; Q^0 , Q^1 , and $\text{Si}^*\text{-O-Al}$ [15]: ≈ -82 ppm)

The ^{29}Si -NMR study of the system without boehmite shows a low reactivity of GPTS and an extremely low reactivity of TEOS. After 1 hour hydrolysis products of GPTS (T^0_x) and first condensation products (T^1_x) are formed. In the following 15 hours hydrolysis of GPTS is completed and the concentration of T^1_x species increases. Due to the low reactivity of TEOS, first reaction products of TEOS only can be detected after 12 hours. The comparison of the ^{29}Si -NMR study with boehmite clearly shows a strong catalytic effect of the boehmite. After 10 min reaction time hydrolysis products of GPTS (T^0_x) as well as first condensation products (T^1_x) are detected. 30 min after the start of the reaction first hydrolysis products of TEOS (Q^0_x) are formed. After 115 min only T^1_x and T^2_x signals (condensates of GPTS) and Q^1_x and Q^2_x (condensates of TEOS) are visible. It is assumed that heterocondensation of GPTS and TEOS takes place, but due to low concentrations and similar chemical shifts of homocondensates and heterocondensates of GPTS and TEOS a clear proof of heterocondensation is not achieved. The question arises how far Al-O-Si bonds are formed in addition to the formation of Si-O-Si bonds, which can be assumed because of the known high reaction rate of Al-OH with Si-O-R, forming Si-O-Al links. For this reason, ^{27}Al -NMR analysis has been carried out, as shown in Fig. 3. The results clearly demonstrate the formation of the Si-O-Al bonds [16] as can be seen from the deconvoluted curves.

The investigations of the catalytic influence of the boehmite particles on the polymerisation of the epoxy function were carried out by ^{13}C solid state NMR. Two materials starting with GPTS, TEOS, $\text{H}_2\text{O}/\text{HCl}$ with and without boehmite using the same reaction conditions (4 h curing/ 100°C) were prepared. The comparison of the ^{13}C solid-state NMR spectra (Fig. 4) shows that in the material with boehmite the epoxy groupings are completely polymerized to polyethylene oxide, and in the case of missing boehmite the major part of the epoxy functions are unchanged.

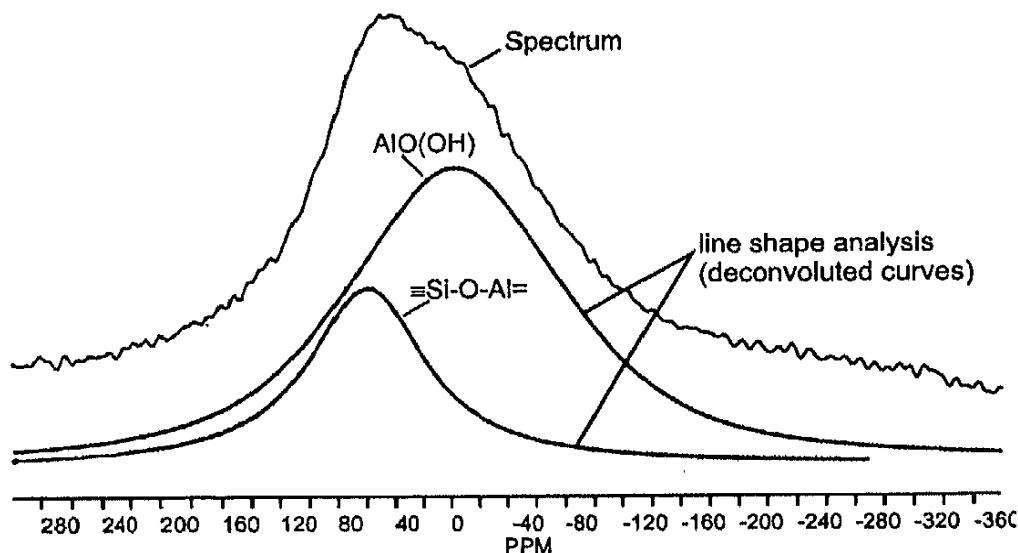


Fig. 3: ^{27}Al - NMR spectra of the GPTS/TEOS/boehmite sol.

Only small amounts are hydrolyzed to diols. This result is a proof for the catalytic activity of the boehmite on the polymerisation of the epoxy groups, which is so far unknown.

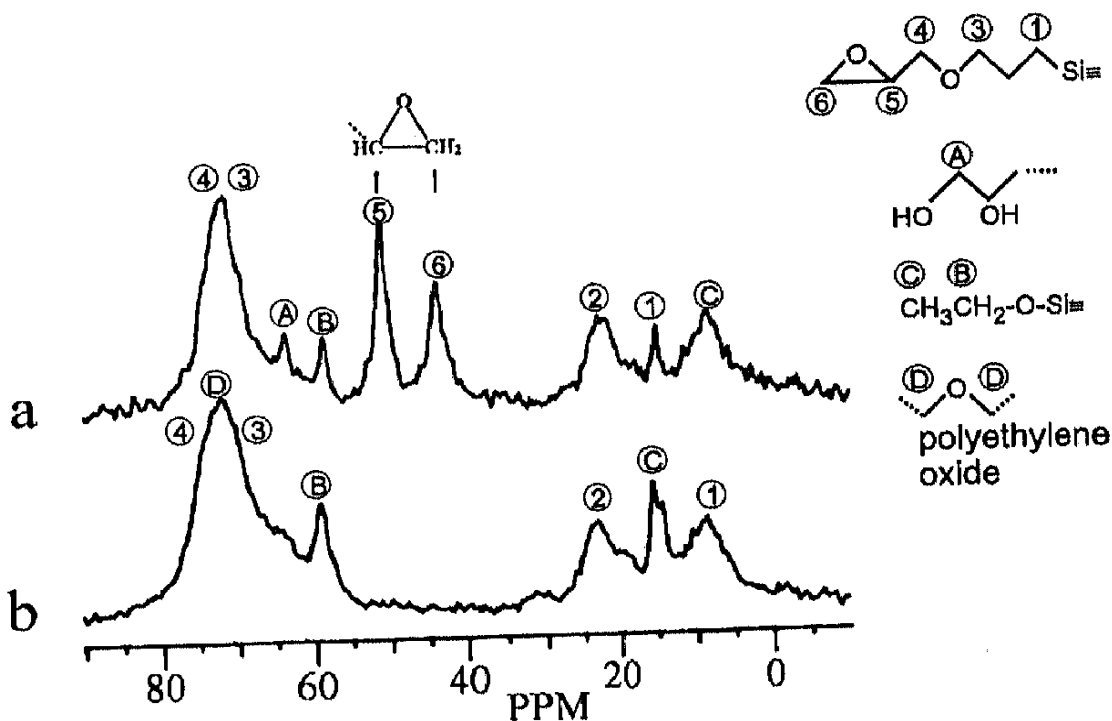


Fig. 4: ^{13}C -MAS NMR spectra of a GPTS/TEOS system with (b) and without (a) boehmite.

Since catalysis should take place preferably close to the particle surface, an increase of the concentration of polyethylene oxide (PEO) chains around the boehmite particles should take place, leading to the model of a „flexible suspension“ of the nano particles within the inorganic-organic matrix.

In the first reaction step an oligomeric system with unchanged epoxy groups is formed by hydrolysis and condensation of GPTS and TEOS, and at the same time, the formation of Si-O-Al links between the boehmite and sol components occurs. During curing, hydrolysis and condensation is completed, and boehmite catalyses the epoxy polymerisation to polyethylene oxide. Based on these investigations, a reaction and structural model can be proposed, including the formation of a Si-O-Si network, additionally connected by PEO chains surrounding the $\text{AlO}(\text{OH})$ particles which are chemically bonded to the Si-O-Si network by Si-O-Al bridges (Fig. 5).

Using standard coating techniques (spin-, dipcoating), polycarbonate substrates (CR39[®]) were coated and cured thermally. Due to the tailored phase dimensions ≤ 50 nm, the coatings are fully transparent and show excellent adhesion (cross-cut (DIN 53151) 0-1; tape test (ASTM D3359) 4-5). The determination of the hardness and the E-module of the new nano composite was investigated by microhardness measurements in comparison with an Ormocer coating, used commercially as hard coating for ophthalmic CR39[®] lenses. The microhardness value of the boehmite nano composite is 306 MPa (E- module 5.22 GPa) in comparison to 209 MPa (E- module 3.34 GPa) for the Ormocer. The scratch resistance, proven by a modified Erichsen test, strongly depends on the coating thickness (Fig. 6) and reached 120 g at a thickness of 30 μm , exceeding conventional Ormocer hard coatings by a factor of 6.

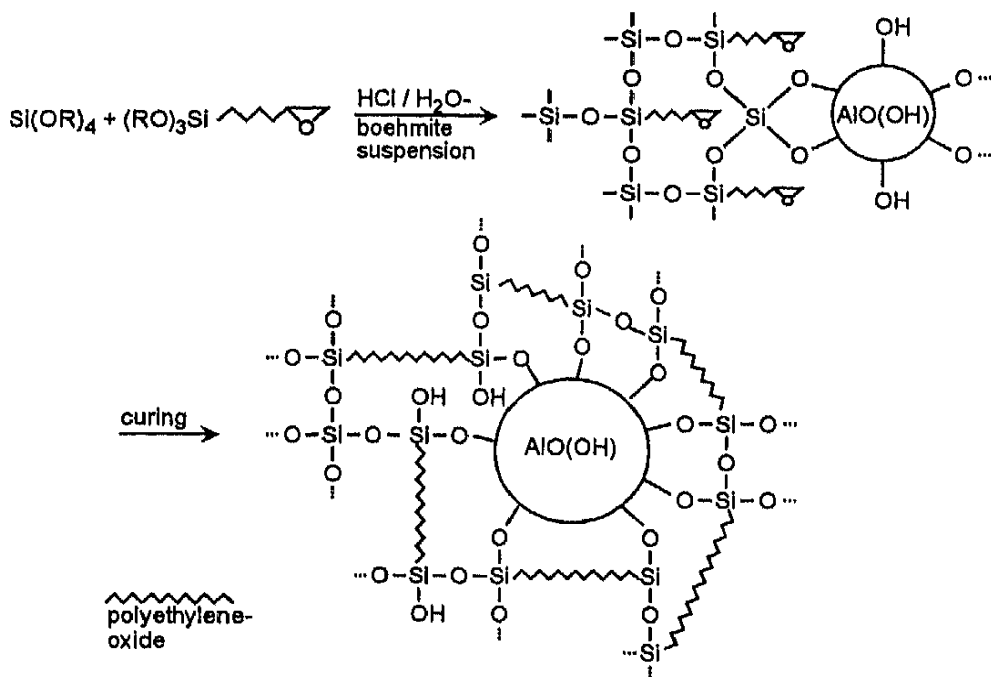


Fig. 5: Reaction scheme and structural model of the GPTS/TEOS/boehmite-based material.

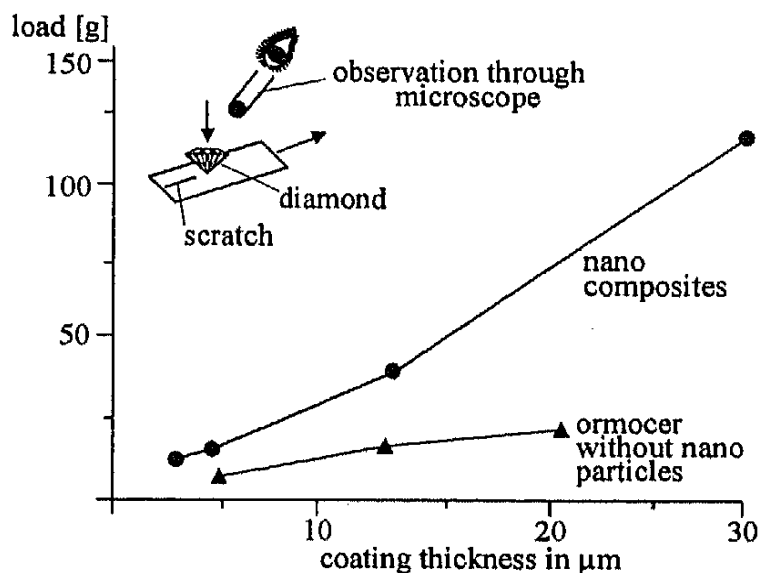


Fig. 6: Scratch resistance of the nano composite coating depending on the thickness in comparison to a conventional Ormocer coating.

These results cannot only be explained by simple "addition" of the properties of the inorganic particles and the matrix, since the diamond test shows on hard and brittle materials (e.g. glass) low values ($\approx 1\text{g}$ for glass). There is evidence for a special structure at the particle matrix interface formed by an enrichment of polyethylene oxide chains by the catalytic effect of boehmite on the epoxides. Structural investigations of the particle/matrix interface have to prove this hypothesis.

CONCLUSION

The described new concept of increasing the inorganic phase dimensions by incorporation of nano-scale metal oxide particles with tailored sizes for the synthesis of inorganic-organic nano composites leads to transparent materials with so far unknown mechanical properties. The concept of increased inorganic phase dimensions with tailored interfaces is a way to improve mechanical properties of sol-gel coatings for a variety of applications, not only restricted to hardcoatings for polymers.

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