Fabrication of monolithic refractive optical lenses with organic-inorganic nanocomposites: Relations between composition and mechanical and optical properties

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ABSTRACT

Sol-gel derived organic-inorganic hybrid materials and their potential for the production of refractive optical elements are presented. The main components of the investigated compositions are precondensed silanes with polymerizable double bonds (e.g. methacryloxypropyltrimethoxysilane (MPTS)) and co-condensates thereof. Dimethacrylates like tetraethyleneglycoldimethacrylate (TEGDMA) were employed as organic monomers. Molar ratios of silanes to organic monomers between 10:90 and 90:10 were investigated. Nanoscaled titania was incorporated in the homogeneous mixture of silanes and organic monomers. The combination of different molecular hybrid matrices and inorganic nanoparticles allows the adjustment of material properties, for example: impact strength between 2 and 15 kJ/m^2, Youngs moduli between 0.8 and 3.7 GPa and universal hardness in the range from 40 to 170 N/mm^2. Phase separation could be kept in the nanometer range to minimize optical losses due to scattering effects. Depending on composition, n_e could be varied between 1.50 and 1.54, whereby the corresponding Abbe numbers ranged from 57 to 45. Ophthalmic lenses were prepared in less than 10 hours by simple mould techniques and by applying a combination of photochemical and thermal curing processes.

Keywords: NANOMERS, sol-gel, ophthalmic lens, monoliths

1. INTRODUCTION

Organic-inorganic composite materials, processed by sol-gel-techniques, received much attention in the last decade[1] for optical applications. They represent a new material group with an attractive combination of the properties of glasses (e.g. scratch resistance and environmental durability) and plastics (e.g. simple, low-cost processing and low density). Moreover, the combination of an inorganic network with an organic polymer matrix, with the addition of nanoscaled particles, allows the tailoring of properties of the final material via the type and concentration of each educt[2]. Transparent sol-gel-materials are used as protective coatings for plastics, such as eye glass-lenses[3] or magnification lenses[4] for example. Furthermore it has been shown, that controlled conversion of C=C double bonds in combination with patterning techniques such as direct laser writing, maskaligner techniques, holography or embossing techniques allow the production of diffractive optical elements[5] such as diffraction gratings[6], Fresnel lenses[7], microlens arrays[8] or thin and thick diffractive volume gratings of high efficiencies[9].

Despite these promising results there are only a few publications[10-16] dealing with the fabrication of bulk materials (shaped articles with volume > 1 cm^3) produced from composites with covalent bonds between the inorganic and the organic components for optical applications. This may be related to the long synthesis times[13,15] or problems to obtain crack-free monoliths[14]. Indeed, systematic approaches concerning the influence of varying the different components with respect to the mechanical properties (e.g. hardness, impact strength, Youngs modulus, flexural strength), optical properties (e.g. transparency, refractive index, Abbe-number) or thermal properties (e.g. glass transition temperature, thermal expansion coefficient) are rare. Coltrain et al.[14] studied the influence of minor amounts of methacryl functionalized trialkoxysilanes (<10 mol%) on the morphology and mechanical properties of mixtures of poly(meth)acrylates and tetraalkoxysilanes. These observations indicate, that an optimization of mechanical properties may be possible, using trialkoxysilane-functionalization. Wei[13] et al. investigated copolymers made from 3-(trimethoxysilyl) propyl methacrylate (MPTS) and methyl methacrylate (MMA) in different ratios and the effect of added and co-condensed amounts of tetraethyl orthosilicate (TEOS) with respect to hardness and the onset of decomposition. They concluded that the polymer composition did not significantly influence the hardness or the thermal stability. A significant increase in both properties is observable, on increasing the amount of TEOS co-condensed. As was shown by Philipp and Schmidt[10] the combination of functionalized alkoxysilanes with organic monomers and metal alkoxides allows the properties of the final monolithic products such as tensile strength, Mohs' hardness or refractive index to be adjusted.

Since the influence of changes in the structure on the mechanical and optical data of monolithic composites are at the moment not well investigated, the approach presented here deals with different materials with systematic changes in the composition. For this reason the following procedure was established: precondensed MPTS (or MPTS co-condensed with an arylalkoxysilane) is mixed with dimethacrylates to give a homogenous pourable solution. After the addition of initiators a photopolymerizing step is employed to give a cured prepolymer; this is then thermally postcured to give the final transparent monolith. Mechanical and optical properties were investigated in dependence on the molar ratio of organic to inorganic compound. In addition the influence of the change of the structure of the inorganic backbone and the organic monomers is considered. Furthermore, nanoparticles were incorporated (which yields the so called NANOMERS) to investigate their effect on optical and mechanical properties. The aim of these investigations is to elucidate the influence of different changes of the composition (and therewith of the molecular structure of the network) on optical properties (as transmittance or refractive index) and mechanical properties (Youngs modulus, hardness and impact strength). In addition a synthesis way to refractive bulk lenses with these materials is shown, employing simple mould techniques.

2. EXPERIMENTAL

Methacryloxypropyltrimethoxysilane (MPTS) was distilled under reduced pressure at 40°C, prior to use, and then stirred 24h at 40 °C with HCl (aq.) in an amount corresponding to 1.5 mole H_2O per mole MPTS. Residual amounts of solvent and produced methanol were removed by destillation at 40°C and 5 mbar. Molar mass per repeat unit of the condensed MPTS was determined to be 188 g/mole (by measuring the residual weight of the condensate and correlating with the initial mols of silanes). For preparing co-condensates of MPTS and diphenyledimethoxysilane (DPDMS) almost the same procedure was applied. The co-condensate of 60 mol% MPTS and 40 mol% DPDMS has a medium molar mass of 198 g/mole. Tetraethyleneglycoledimethacrylate (TEGDMA) was destabilised by caustic washing to remove the inhibitor, dried and mixed homogeneously with the prehydrolysed MPTS in various molar ratios of MPTS based on monomer units to TEGDMA equal to 10/90, 30/70, 50/50, 70/30 and 90/10. Polyethyleneglycoledimethacrylate (PEG(400)DMA, molecular weight PEG: 400 g/mole) was introduced by replacing 50 mol % of the TEGDMA to investigate the influence on the fracture toughness of the composites. 50 mol % of the TEGDMA was replaced by 2,2-Bis[4(3'-methacryloyl-oxy-2'-hydroxy)propoxy-phenyl]propane (Bis-GMA) to investigate the influence of a species with higher molar fraction to the index of refraction of the composite.

For the synthesis of TiO_2 nanoparticles a tetraisopropylorthotitanate ($Ti(OiPr)_4$) solution in isopropanol was stirred 1h at 23 °C with HCl (aq.) in an amount corresponding to 6 mole H_2O per mole $Ti(OiPr)_4$. To avoid photocatalytic degradation of the composite matrix material, the TiO_2 particles were coated at 100 °C in an isopropanolic dispersion with MPTS prior to use. The effectiveness of particle coating was revealed by addition of $H_2O_2(aq)$, which leads to an intensive yellow complex with insufficient coated TiO_2-sols. This synthesis route allows particles to be produced with diameters in the range of 4 nm, with a narrow particle size distibution as determined by photon correlation spectroscopy with an ALV/SP-125 (ALV-Laser-Vertriebsgesellschaft mbH). For the choosen particle concentrations in the matrix, titania particles with diameters less than 10 nm are necessary in order to avoid light losses in the visible range due to scattering effects. The thus coated TiO_2 particles in isopropanolic dispersion were mixed with MPTS and TEGDMA in such an amount that after removal of the solvent under reduced pressure the titania contents in the resulting nanocomposite were 4 and 10 wt.% respectively and the MPTS:TEGDMA molar ratio was equal to 50:50.

For the preparation of composites and Nanomers, azobisisobutyronitrile (AIBN) as thermoinitiator and Irgacure 184 as photoinitiator were added to the reaction mixture. The reaction mixtures were filled in glass moulds as closed reaction containers or open teflon moulds respectively. The photopolymerisation reaction was performed in a Beltron UV conveyor belt. After photocuring the samples were removed from the moulds and processed in a temperature controlled furnace under nitrogen atmosphere using a temperature program with 130 °C as maximum temperature. To avoid stress cracking of the composites the samples were cooled down from 130 °C to room temperature over 4 hours.

Reduced modulus values and hardness were obtained from micro hardness measurements using a Fischerscope H100 equipped with a HCU100 controller and a Vickers diamond as indentor according to VDI instructions[14]. Impact resistance on unnotched samples was measured with a Zwick pendulum apparatus according to DIN 53453[15] (Normkleinstab). Refractive indices and Abbe numbers were determined using a Pulfrich refractometer PR 2 (Zeiss Jena). UV/Vis spectra were recorded with a Bruins Instruments Omega 20 between wavelength 250 nm and 1000 nm.

3. RESULTS

The following composites were considered for their mechanical and optical properties, since they display an overview of the different possibilities for changing the composition (table 1). The first five samples display a variation of the amounts of MPTS and TEGDMA without other components. The next two examples show a change of the organic component with fixed silane-concentration (30 mol%), in which 50 mol% of the TEGDMA is substituted by either Bis-GMA (#6) or PEGDMA (#7). In composition #8 the silane-content is also fixed, but a co-condensate of MPTS and a non-polymerizable silane (DPDMS) was used. Compositions #9 and #10 are nanocomposites with the same ratio of organic to inorganic parts as was used in compositions #3. These samples display an overview of the possibilities for varying the composition: organic component, inorganic component and additional nanoparticles.

Table 1: systems under consideration- concentrations given as molar ratios unless otherwise stated. Molar mass of the repeat unit of the condensed MPTS was measured to be 188 g/mole and for the co-condensate with DPMS 198 g/mole.

no.	abbreviation	MPTS	DPDMS	TEGDMA	other methacrylate	titania [wt%]
1	M/T 10	10	/	90	/	/
2	M/T 30	30	/	70	/	/
3	M/T 50	50	/	50	/	/
4	M/T 70	70	/	30	/	/
5	M/T 90	90	/	10	/	/
6	M/T/G	30	/	35	Bis-GMA 35	/
7	M/T/P	30	/	35	PEGDMA 35	/
8	M/T/D	18	12	70	/	/
9	M/T-Ti 4	50	/	50	/	4
10	M/T-Ti 10	50	/	50	/	10

For the further characterization the transparent and crackfree bulks were used as produced or post treated with well known processes such as grinding, drilling and polishing.

With the exception of the two NANOMERS (M/T-Ti 4 and M/T-Ti 10) which were slightly yellow, the composites were colourless, as is shown by UV-Vis-spectroscopy (fig.2). For most optical applications absence of colour is necessary, not only for aesthetic reasons but also because absorption of light leads to a heating-up of the material and thus the complete optical module.

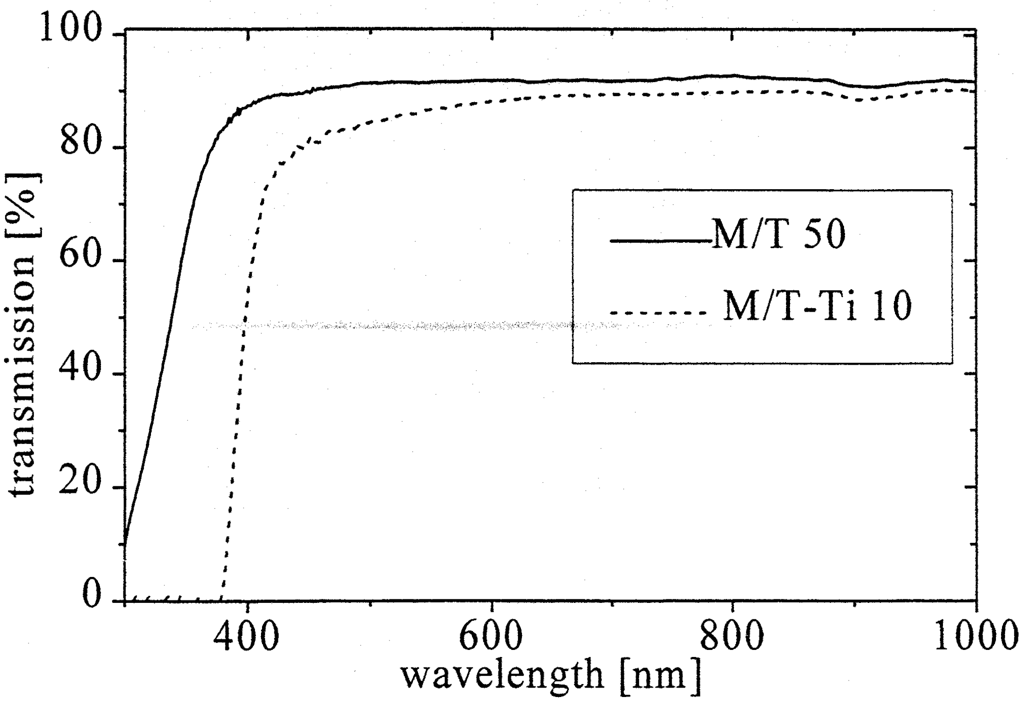

Figure 1: UV-Vis-spectrum of M/T 50 as an example of a bulk material and for M/T-Ti 10 as an example of a titania-nanocomposite (thickness of samples: 3 mm)

Under consideration of transmission losses due to reflexion by the simple fresnel-equation (see eq. 1) for sample M/T 30 from fig. 2 the values for transmittance are 98.1 % (450 nm; n_{450nm}=1,51689), 100.0 % (600 nm; n_{600nm}=1,50682) and 100.0 % (750 nm; n_{750nm}=1,50208) respectively.

Fresnel-equation: $R = \left(\frac{n_\lambda - 1}{n_\lambda + 1}\right)^2 *100$ (eq. 1);

R: reflexion [%] per surface; n_λ: refractive index at wavelength λ

The homogenity of the composites were tested visually and microscopically. No bubbles or strias are present in any of the samples. The characterization of the birefringence of planar composite-discs between crossed polarizers showed just small bright areas at the edge of the planar discs (thickness 2 mm; see fig. 3). In comparison to commercially available plastics (polymethylmethacrylate (birefringence: 80±20 nm)[22] or polycarbonate (2400±300 nm)[22] -plates) the intensity is significantly lower for the different composite materials (< 20 nm (estimated value)). Investigations for obtaining exact numerical values for the birefringence are in preparation.

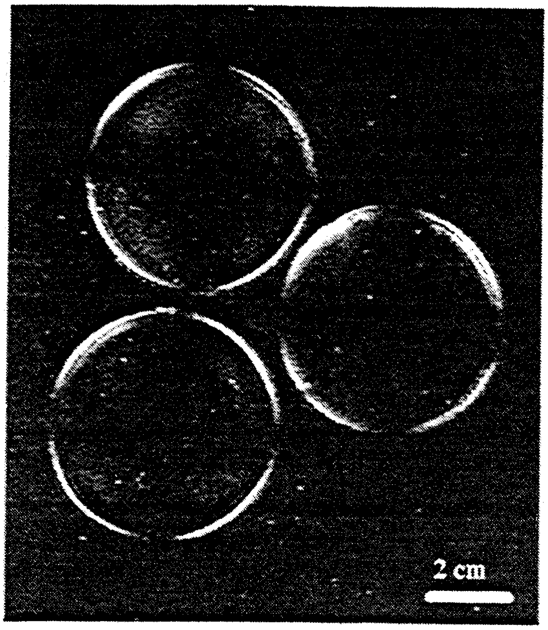

Figure 2: planar discs of M/T 30; M/T 50 und M/T/D with a thickness of 2 mm between crossed polarizers

Refractive index and Abbe-number are elemental data for materials used in optical applications. The values were collected with a Pulfrich refractometer, which allows the refractive index of bulk materials to be determined with high accuracy (the standard deviation is in the range of 2 x 10^{-5}). The point is to show, that the presented materials allow the refractive index to be matched over a wide range. The results of the measurement of the refractive index of the different composites (table 2) displays the expected[19] increase of this value with increasing amounts of aromatic compounds. Moreover, the incorporation of nanoscaled titania particles led also to an increase of the refractive index. This effect is in both cases accompanied by a decrease in the Abbe-number (equation 2) which is equivalent to an increase in the dispersion.

Abbe-number: $\nu_e = \frac{n_e - 1}{n_{F'} - n_{C'}}$ (eq. 2);

n_e, $n_{F'}$, $n_{C'}$: refractive indices at 546 nm, 480 nm and 644 nm respectively (corresponding to the green mercury line, blue cadmium line and red cadmium line)

Table 2: refractive indices and Abbe-numbers for the composites under investigation (n_d: refractive index at 588 nm (yellow helium line))

used abbreviation	n_d	n_e	$n_{C'}$	$n_{F'}$	ν_e
M/T 10	1.50695	1.50905	1.50475	1.51366	57.1
M/T 30	1.50742	1.50951	1.50509	1.51414	56.3
M/T 50	1.50389	1.50621	1.50179	1.51092	55.4
M/T 70	1.50057	1.50323	1.49854	1.50799	53.3
M/T 90	1.49726	1.49951	1.49487	1.50433	52.8
M/T/G	1.53302	1.53593	1.53007	1.54224	44.0
M/T/P	1.50390	1.50606	1.50168	1.51073	55.9
M/T/D	1.51431	1.51664	1.51174	1.52193	50.7
M/T-Ti 4	1.51748	1.51761	1.51282	1.52301	50.8
M/T-Ti 10	1.52877	1.52895	1.52311	1.53468	45.7

The mechanical properties of a material are important for the selection of potential application fields. As the flexibility of composition for the presented composites allows one to change these properties it is important to evaluate the region of attainable values. Impact strength, hardness and Youngs modulus were taken into account as mechanical properties, since a significant dependence on the composition is expected (compare table 3). For the Youngs modulus and the hardness measurements planar, polished examples were used and examined at five different locations. The impact strength was monitored in accordance with DIN 53453 with a standard bar of the dimensions 80 mm x 6 mm x 4 mm.

Table 3: hardness, Youngs modulus and impact strength of the materials under consideration

used abbreviation	hardness [N/mm^2]	Youngs modulus [GPa]	impact strength [kJ/m^2]
M/T 10	107	2.4	4.6
M/T 30	105	2.4	4.3
M/T 50	103	2.3	2.9
M/T 70	84	1.9	3.9
M/T 90	46	1.1	2.0
M/T/G	147	3.2	2.9
M/T/P	37	0.8	6.1
M/T/D	83	1.9	3.7
M/T-Ti 4	156	3.2	3.7
M/T-Ti 10	173	3.7	2.6

(with a combination of a silane-cocondensate, TEGDMA and PEGDMA(400) values for the impact strength of up to 15 kJ/m^2 were obtained).

The change of composition leads to a strong change of the mechanical properties. In the investigated systems the values for the hardness vary between 40 and 170 N/mm^2, for the Youngs modulus between 0.8 and 3.7 and for the impact strength between 2 and 6 kJ/m^2.

The results show, that the organic-inorganic composites allow the optical and mechanical properties to be adjusted by the chosen composition. The resulting materials show excellent optical properties and may be shaped by curing in moulds in nearly any required geometry. If necessary a post treatment by grinding and polishing can be used. Examples for moulded articles in different geometries (some of them post-treated in the descibed manner) prepared with the new composite materials are given in figure 3.

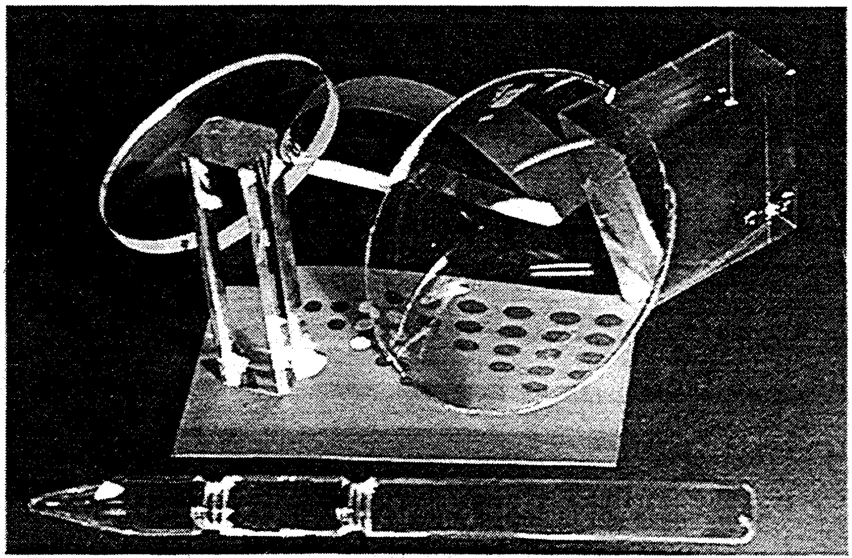

Figure 3: examples for shaped articles made with composite-material under description (some ground and polished, some shown as polymerized)

4. DISCUSSION

It could be shown, that with organic-inorganic composites transparent articles with good optical quality can be obtained. The curing times for producing stress free bulks is less than 10 hours. Since curing times for inorganic-organic composites presented in the literature are often in the range of weeks[14, 15] or months[13], a significant shortening of synthesis times may result in a greater interest for technical applications. Transparent, nearly birefringence free bulk materials with volumes of up to 150 cm^3 are produced with changes in the composition on the inorganic part, as well as on the organic part. Moreover with the addition of nanoscaled particles another degree of freedom for varying the final properties is obtained, whereby the slight yellow appearance of the titania nanomers has to be removed. A promising approach is the further optimization of the particle coating, to avoid direct contact between titania and organic compounds of the matrix.

With respect to distinct optical properties, like the index of refraction, a tailoring by an easy adjustment of the educts is possible. For the investigated systems the values for the index of refraction (n_e) ranges from 1.50 up to 1.54. Values up to 1.59 are attainable[20] with titania nanocomposites having an high amount of copolymerized aromatic compounds (e.g. 50 mol%). With increasing index of refraction the Abbe-number decreases. This well known effect[21] is found to be present for the added titania, as well as for the aromatic compounds in the same magnitude. However for the simple MPTS/TEGDMA-composites an slight reverse effect is obtained (i. e. an increase in the refractive index leads to a slightly higher Abbe-number). The low observable birefringence may be important for some optical applications with high demands on the performance of the used material. Transparent plastics like polymethylmethacrylate or polycarbonate show significantly poorer results concerning the birefringence[22].

Mechanical properties do not appear to be sensitive to changes in molecular ratios between inorganic component (MPTS) and organic component (TEGDMA), when the organic compound is used in amounts higher than 50 mol%. This leads to the conclusion, that the mechanical properties in this concentration range are dominated by the organic part. With higher amounts of MPTS hardness and Youngs modulus decreased, indicating the presence of small plasticiser molecules in the samples resulting from residual water or partially condensed silane species. On the other hand introduction of titania nanoparticles leads to an increased hardness and Youngs modulus as is expected from the literature according to a simple mixing of rigid particles in a soft matrix[23,24].

A stronger dependence is observable when the basic components (that means MPTS and TEGDMA) are partly exchanged by other monomers. The use of Bis-GMA leads to an increased hardness and Youngs modulus, indicating an higher stiffness of the molecular structure. Since the Bis-GMA-molecule possesses a higher stiffness than the TEGDMA-molecule this is in accordance with structural considerations. Surprisingly the higher stiffness is combined with an increased impact strength. The reason for this behaviour is still under investigation and may be related to a change in the copolymer-type accompanied by an increased ability of the matrix to dissipate mechanical energy. When exchanging 50 mol % of the TEGDMA with PEGDMA(400), from a structural point of view very similar molecules, hardness and Youngs modulus are strongly reduced and the impact strength rises significantly. However, the organic network with PEGDMA(400) has a bigger „mesh width", due to the higher number of ethylene-oxide-units per monomer molecule, which forms to a more soft and elastic material. For the same reason, on the inorganic side, the use of a co-condensate of MPTS and DPDMS, which is ineffective for the organic polymerization, leads to a decrease of hardness and Youngs modulus. A significant influence on the impact strength with the investigated concentration was not observed. Further investigations will show the concentration dependence of these quantities in correlation.

5. CONCLUSION

Organic-inorganic composites could be developed with promising properties, with respect to optical and mechanical data, for optical applications. The investigations generally show the possibility of preparing monolitic materials by simple curing techniques, such as moulding. Relations between composition and properties were obtained, displaying the option of tailoring special material properties by varying the kind and amount of the educts. The farbrication of stress free bulk materials with small birefringency in relatively short times may be the key to commercial applications. The incorporation of nanoscaled particles strongly effects the investigated properties and leads to an interesting prospect for new materials.

A objective for the future work is to establish a modular design for achieving desired combinations of optical, mechanical and thermal properties.

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