

SYSTEMATIC APPROACH TO THE SYNTHESIS OF ORGANIC-INORGANIC NANOCOMPOSITES BASED ON DMTA MEASUREMENTS AND IR SPECTROSCOPY

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ABSTRACT

Sol-gel derived organic-inorganic hybrid materials with potential fields of application as refractive optical components for example laser diode bars and ophthalmic lenses are presented. The main components of the hybrid materials under investigation are precondensed methacryloxypropyltrimethoxysilane (MPTS, denoted: M) with an organically polymerisable methacrylic functionality and tetraethyleneglycoldimethacrylate (TEGDMA, denoted: T) as crosslinking organic monomer with two polymerisable double bonds. The molar ratios of the components ranged from M/T 10/90 up to M/T 70/30. The polymer derived from pure TEGDMA (M/T 0/100) served as a reference material. In addition to this nanoscaled TiO₂ particles (5 wt.% and 10 wt.%) were incorporated in the organic-inorganic M/T 30/70 matrix to increase the refractive index of the resulting nanocomposites. For the preparation of the different systems, precondensed MPTS was mixed with TEGDMA, the nanoparticulate titania sol (when used), an appropriate photoinitiator and a thermoinitiator. The reaction mixtures were polymerised photochemically and/or thermally. The propagation of the free radical polymerisation reaction after photopolymerisation and subsequent thermal curing was followed by IR-spectroscopy, showing that the degree of double bond conversion is strongly increased by the thermal curing step. Incorporation of increasing amounts of TiO₂ nanoparticles resulted in reduction of the double bond conversion compared to the corresponding unfilled system. The homogeneous dispersion of the titania particles in the completely cured M/T 30/70 matrix could be manifested by high resolution transmission electron microscopy (HTEM). The thermomechanical properties of the completely cured nanocomposites were monitored by dynamic mechanical thermal analysis (DMTA) showing a strong dependence on composition.

INTRODUCTION

Organic-inorganic hybrid materials derived from sol-gel process with oxide nanoparticles incorporated in the hybrid matrix open a new wide field of investigation in materials science and offer the possibility to advance in many potential fields of application such as optical components [1-4], adhesives [5], coatings [6] and bulk composites [7, 8]. To create new materials with special functions it is necessary to have detailed information about the structure-property relationships in the systems. Most information about the morphology in the nanoscale range is available from transmission electron microscopy (TEM) [9, 10] and small angle x-ray scattering (SAXS) [11-16]. In addition spectroscopic methods such as infrared (IR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy have shown to be very useful in gaining insight into structural relations or structural changes in nanocomposites [17-21]. In combination with mechanical testing such as stress strain experiments or flexural impact testing as well as thermomechanical probe techniques such as dynamic mechanical thermal analysis (DMTA) or thermomechanical analysis (TMA) the above spectroscopic and microscopic methods allow appropriate models to be developed, which serve to give a better understanding of the dependence of the materials' end properties on the morphology [17, 22-26]. This is an important point for designing materials with

well adjusted properties, so that they may be used in industrial applications with very specific requirements. To improve the optical performance of composite materials, disperse inorganic nanoparticles with special properties may be very effective in changing the refractive index or the non linear optical behaviour. Titania nanoparticles with high refractive index have already been incorporated in hybrid matrices to increase the refractive index of the resulting composites [27, 28]. In the majority, the authors were mainly interested in the production of composites with good optical performance. Besides this the inorganic nanoparticles also may influence the mechanical and thermal properties. Excellent mechanical properties are often strong requirements to use those materials as refractive optical components, e.g. ophthalmic lenses. This work presents IR spectroscopic investigations and DMTA experiments on organic-inorganic hybrid materials filled with different amounts of TiO_2 nanoparticles. The aim was to estimate the extent of conversion depending on curing conditions and the amount of nanosized filler particles. In addition, the resulting influence on the thermomechanical damping behaviour was evaluated.

EXPERIMENT

The nanosized TiO_2 particles were prepared as follows: Titanium tetraisopropoxide was mixed as received with isopropanol p.a. in a concentration 0.37 mole/l and hydrolysed at 25 °C with HCl/ H_2O in the ratios H_2O :alkoxide 6:1 and HCl:alkoxide 1.35:1. MPTS (denoted: M) was distilled under vacuum ($p = 0.1$ mbar) at 100°C prior to use and then stirred 24h at 40 °C with 0.1 mole/l HCl/ H_2O in the molar ratio 1.5 to MPTS based on mole H_2O to mole MPTS. Residual amounts of solvent were removed by vacuum distillation at 40°C ($p = 10$ mbar). TEGDMA (denoted: T) was used without further purification. For the preparation of the nanocomposites TEGDMA and prehydrolysed MPTS were mixed homogenously in various molar ratios of MPTS to TEGDMA thus: M/T 10/90, 30/70, 50/50 and 70/30. Pure TEGDMA was used as reference material. To introduce the TiO_2 nanoparticles, the sol was mixed with the monomers in calculated amounts to obtain 5 wt.% and 10 wt.% titania in the final nanocomposites. Azobisisobutyronitrile (AIBN) as thermoinitiator as well as Irgacure 184 (Ciba Geigy) as photoinitiator were added in a concentration of 0.001 mole per mole methacrylate endgroups in the reaction mixture. The photopolymerisation reaction was performed in special reaction vessels by several UV light exposure cycles under exclusion of oxygen using a Beltron apparatus. For the thermal curing reaction the samples were removed from the reaction container and heated from 20 °C to 130 °C over 4 h under a nitrogen atmosphere. IR spectra were accumulated with a FT-IR spectrometer (Bruker). HTEM analysis was performed on ground thin pieces of the nanocomposites with a high transmission electron microscope (Philips). The DMTA measurements were carried out with a Rheometric Scientific dynamic mechanical thermal analyser MKIII using the single cantilever bending mode. Samples with rectangular cross-section (annealed 12 h at 80 °C at 10 mbar prior to measurement) were heated from -50°C to 200°C at a heating rate of 1 K/min (strain: ± 8 μm , frequency: 1 Hz).

RESULTS

To reveal structure-property relationships in nanocomposites one has to obtain information about the degree of double bond conversion in each system. Additionally the conversion is important for the end properties of the nanocomposites. The conversion was determined by IR spectroscopy. Each methacrylic group in the systems has one polymerisable C=C double bond and one carbonyl function (C=O). The C=O function can be used as an internal standard because its concentration during the polymerisation reaction does not change and corresponds to the C=C dou-

ble bond concentration of the initial monomer mixture. This means that the C=C/C=O ratio should be the same for systems with the same extent of double bond conversion. Since the nanocomposites investigated here are crosslinked thermosetting systems the maximum conversion obtainable is in the range of 80 % [29]. To determine the influence of the TiO₂ nanoparticles on the polymerisation reaction one has to investigate first the unfilled organic inorganic systems for comparison. The progress of the conversion after photochemical and subsequent thermal curing can be derived from the IR spectra in the carbonyl region and is shown in figure 1 for the composition M/T 30/70 as an example for all unfilled systems. This system has been chosen because it is a composition having a medium MPTS content and therefore combining properties coming from both the organic and the inorganic components respectively.

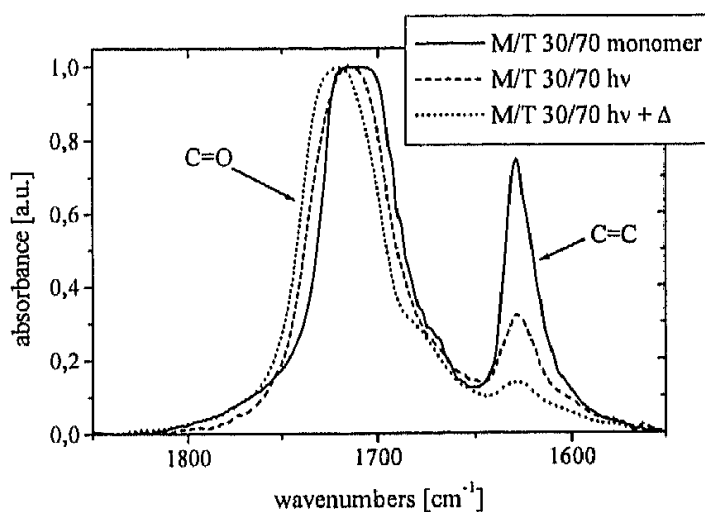


Figure 1: IR spectra of the system M/T 30/70 in the carbonyl region as a function of the curing conditions (monomer: reaction mixture before curing, hv: photochemical curing, Δ : additional thermal curing up to 130 °C).

Photochemical curing of the M/T 30/70 monomer mixture leads to an increase in double bond conversion indicated by a decrease of the corresponding C=C signal relatively to the carbonyl signal as can be seen from figure 1. A fur-

ther increase of the double bond conversion can be achieved by additional thermal curing up to 130 °C. The thermal postcuring causes a higher mobility of the remaining reactive species in the system and induces the thermal decomposition of the thermoinitiator AIBN. The combination of both processes leads to a proceeding of the free radical polymerisation reaction resulting in a further increased double bond conversion. Now the influence of titania nanoparticles on the conversion should be evaluated. TiO₂ fillers when used in polymeric matrices may interact with the matrix as a radical transfer agent and therefore might change the course of the free radical polymerisation reaction [30]. However free radical species are known to play a role in reactions where TiO₂ is involved, and therefore also the thermal free radical polymerisation reaction might be influenced by the titania nanoparticles. This was also investigated by IR spectroscopy. To avoid UV light induced matrix destruction in the titania filled nanocomposites, these systems were cured only thermally. The influence of an increasing titania filler content on the double bond conversion after complete thermal curing of the M/T 30/70 system in comparison to the corresponding uncured M/T 30/70 monomer mixture containing 5 wt.% TiO₂ nanoparticles is shown in the IR spectra in figure 2. The corresponding unfilled M/T 30/70 system is also shown for comparison.

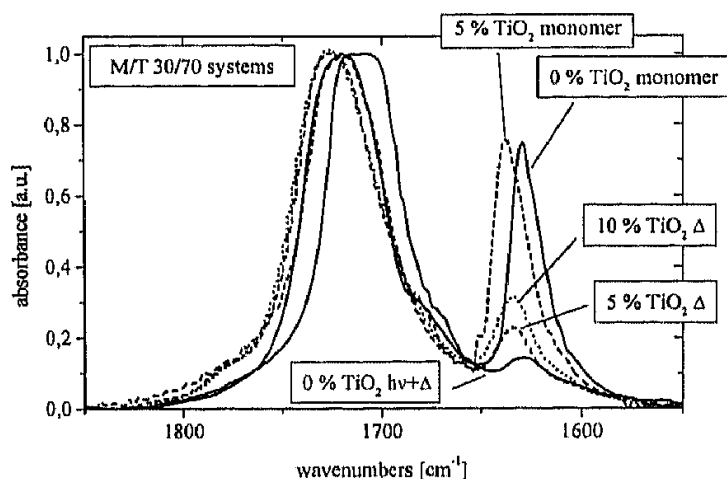


Figure 2: IR spectra of M/T 30/70 systems containing different amounts of TiO₂ particles in the carbonyl region after different curing steps; (monomer: reaction mixture before curing for comparison, hv: photochemical curing, Δ: thermal curing (temperature program up to 130 °C).

Incorporation of 5 wt.% TiO₂ nanoparticles in the M/T 30/70 system results in a higher am-

ount of remaining unreacted double bonds after complete curing up to 130 °C. This can be deduced from the comparison of the IR spectra of the completely cured M/T 30/70 system containing 5 wt.% TiO₂ nanoparticles with the corresponding unfilled system. Further increase in the titania concentration up to 10 wt.% causes further reduction of the double bond conversion. An explanation for this behaviour may be that the incorporation of TiO₂ nanoparticles in the composites influences the kinetics of the free radical thermal polymerisation in such a way that the rate of the propagating reaction is reduced via chain transfer reactions to the TiO₂ nanoparticles. The lifetime of the radical species on the TiO₂ particles may be sufficiently long so that some kind of inhibition of the reaction occurs. Nevertheless the remaining unreacted double bonds may also appear as chain ends because of the bifunctionality of the TEGDMA. This fact must be taken into consideration when interpreting the thermomechanical behaviour of the systems because a decrease in double bond conversion would lead to a lower molecular weight of the organic polymethacrylate backbone. This may cause increased chain mobility and higher overall flexibility in the composite systems. Completely cured transparent nanocomposites could be obtained for every composition employing the synthesis described above. In the case of nanocomposites with dispersed TiO₂ nanoparticles a homogeneous distribution of the particles in the matrix is an important requirement for obtaining transparent systems by minimising scattering losses. The homogeneous distribution can be visualised by HTEM on ultrathin specimens because of the scattering contrast between titanium in the particles, and silicon and carbon in the matrix. The distribution of the titania nanoparticles in the M/T 30/70 composite matrix with 5 wt.% TiO₂ nanoparticles is shown in figure 3.

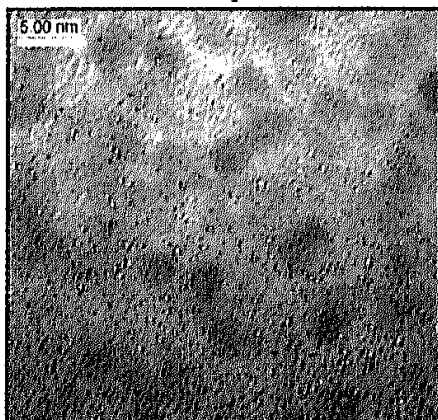


Figure 3: TEM micrograph of the completely cured M/T 30/70 nanocomposite containing 5 wt.% TiO₂ nanoparticles visible as dark spots.

Figure 3 shows that an almost homogeneous distribution of the titania nanoparticles in an organic-inorganic matrix can be achieved by transferring the particles from the sol to the monomer mixture and subsequent curing. The TiO₂ filler particles are visible as dark spots.

Furthermore dynamic mechanical thermal analysis was performed to obtain information about the temperature stability and the viscoelastic behaviour.

The glass transition temperature and the damping behaviour of the nanocomposites were of particular interest. The values for the mechanical damping $\tan \delta$ give qualitative evidence about the degree of network formation and the position of the glass transition temperature [13, 16]. The $\tan \delta$ of the completely cured unfilled M/T systems as a function of the temperature, is shown in figure 4. The mechanical damping behaviour is not only related to the organic backbone and its network density, but also to the formation of the inorganic Si-O-Si network. To demonstrate the inorganic network formation the IR spectra in the Si-O region are shown in figure 5.

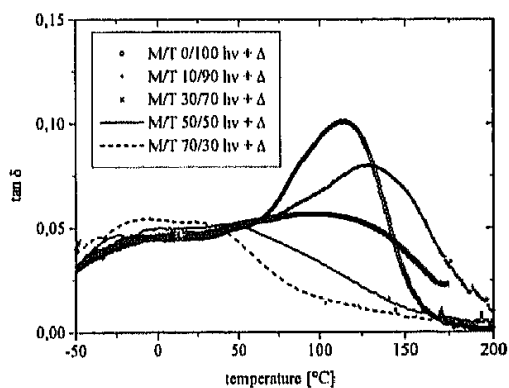


Figure 4: Damping $\tan \delta$ from DMTA measurements as a function of temperature for completely cured M/T systems of different compositions in comparison to the pure polymer M/T 0/100 (hv: photochemical curing, Δ : thermal curing).

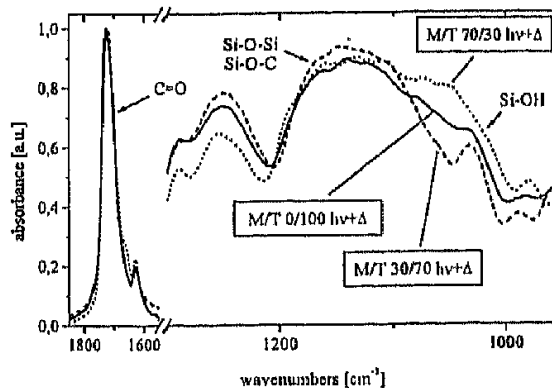


Figure 5: IR spectra in the SiO region showing the inorganic network formation for completely cured M/T systems of different compositions in comparison to the pure polymer M/T 0/100 (hv: photochemical curing, Δ : thermal curing).

Figure 4 shows that the damping value in the temperature region around 120 °C decreases with increasing MPTS content in the samples. A decreasing damping value indicates an increasing crosslinking density. This behaviour is reasonable because the precondensed MPTS species are connected to linear oligomers by their inorganic functionality and therefore may act as very effective three dimensional crosslinking agents if their methacrylic endgroup is incorporated into the growing radical chain during free radical polymerisation reaction. This process leads to the formation of an organic-inorganic interpenetrating network. The growth of the inorganic network to oligomers may be indicated in figure 5 by the disappearance of the Si-OH band as the MPTS content is increased from 30 mol.% to 70 mol.%. On the other hand the Si-O-Si band is broadened indicating Si-O-Si bond formation. The change in network density may also be deduced from the evolution of the glass transition temperature (T_g) with increasing silane content in the systems. Replacement of 10 mol.% TEGDMA by prehydrolysed MPTS results in an increase of the T_g value from 114 °C to 128 °C indicating an increased immobilisation of the created polymer chains by stronger network formation. Further increase of the MPTS content in addition leads to a significant decrease in the damping values and an exact determination of the T_g value is no longer possible because of the broadening of the $\tan \delta$ signal. On replacement of 50 mol.% of the TEGDMA by MPTS the glass transition is suppressed completely. The reason for the disappearance of the glass transition may be that the increasing inorganic network density results in an overall chain length between the network points which is too short to show a glass transition. Polymer chains with molecular weights between the network points which are lower than the required chain length for the collective crankshaft motion of the chain segments (e.g. 1000 g/mole for methacrylate polymers) are expected to show no glass transition. The systems M/T 50/50 and M/T 70/30 therefore show pure duroplastic behaviour because the distance be-

tween the network points is too short for the polymer segments for their collective movement by means of crankshaft motion. Furthermore the influence of the titania filler particles on the thermomechanical damping behaviour was of particular interest. The temperature dependence of the $\tan \delta$ for the TiO_2 filled M/T 30/70 nanocomposites is shown in figure 6 in combination with the corresponding IR spectra in the Si-O region (figure 7).

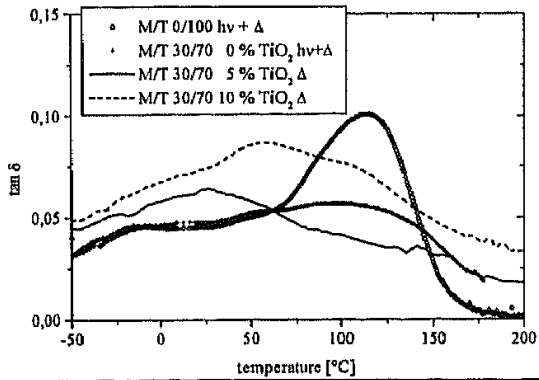


Figure 6: $\tan \delta$ from DMTA measurements as a function of temperature for completely cured M/T 30/70 nanocomposites with different amounts of TiO_2 nanoparticles in comparison to the pure polymer derived from TEGDMA M/T 0/100 (hv: photochemical curing, Δ : thermal curing).

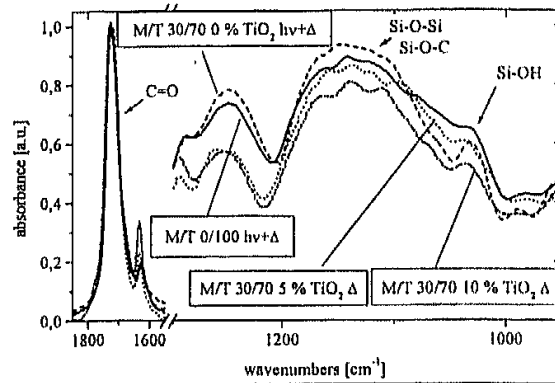


Figure 7: IR spectra in the SiO region showing the inorganic network formation for completely cured M/T 30/70 nanocomposites with different amounts of TiO_2 nanoparticles in comparison to the pure polymer M/T 0/100 (hv: photochemical curing, Δ : thermal curing).

Incorporation of TiO_2 nanoparticles in the M/T 30/70 matrix (figure 6) causes immobilisation of the polymer main chains on the filler surface compared to the pure M/T 30/70 system as can be detected from the reduction of a damping peak in the range of 114 °C. The disappearance of the Si-OH band in the IR spectra (figure 7) indicates the formation of an inorganic network, with crosslinking density increasing with increasing filler content. The TiO_2 particles may act as additional inorganic network points by covalent bonding between filler and matrix. On the other hand the influence of an increasing amount of polymer chain ends caused by an increasing amount of remaining C=C double bonds as detected by IR spectroscopy becomes visible. This is indicated by an increased damping on the lower temperature part of the curves in the range of 50 °C. All systems under investigation especially with the higher silane content are of practical interest. The system M/T 50/50 combines excellent thermomechanical properties with the absence of a glass transition, and good processability. It can be used to fabricate optical components e.g. laser diode bars which are shown in figure 8.

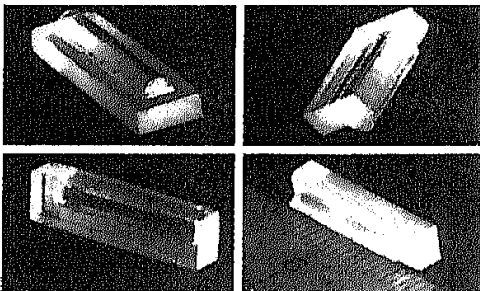


Figure 8: Laser diode bars fabricated using the system M/T 50/50 with the complete photochemical and thermal curing program.

The example shows that transparent components of almost any shape can be fabricated from the materials described above.

CONCLUSIONS

Transparent organic-inorganic nanocomposites containing different amounts of highly dispersed TiO₂ nanoparticles (d = 5 nm) could be produced using precondensed MPTS and TEGDMA as organically polymerisable comonomers. The hardening procedure, photo- and subsequent thermal radical polymerisation, could be followed by IR spectroscopy. It could be shown that the double bond conversion can be maximised by an additional thermal curing step after completion of the photopolymerisation. Incorporation of increasing amounts of titania nanoparticles in the hybrid matrices led to an increased amount of residual C=C double bonds. This result indicates a direct involvement of the TiO₂ nanoparticles in the mechanism of free radical polymerisation by radical transfer from the growing chains to the oxide nanoparticles. In addition the IR results were consistent with the DMTA measurements after complete curing of the nanocomposites. From the DMTA results it could be concluded that the TiO₂ particles reduce the crosslinking density on the organic polymerisable parts and act themselves as newly created inorganic crosslinking points. Appropriate analysis of IR spectra in combination with dynamic mechanical testing, in dependence of composition and curing conditions, serves as an important tool for gaining an initial insight into structure-property relations of nanocomposite materials. Optical components of almost any shape may be fabricated using these nanocomposite systems.

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