

Mechanical Properties of Copolymers from Methacrylate Functionalized Silanes and Bifunctional Methacrylate Monomers

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Abstract. Sol gel derived composite materials were prepared from methacryloxypropyltrimethoxysilane (MPTS) and tetraethyleneoxidedimethacrylate (TEGDMA). The amount of MPTS in the composites was varied from 0 to 50 mole%. MPTS was prehydrolyzed at room temperature with 0,1 mole/l HCl/H₂O. After complete removal of solvent calculated amounts of TEGDMA were added to the reaction mixture of the prehydrolyzed MPTS. Thermically initiated free radical copolymerization of the methacrylate endgroups was performed in the resulting mixture under nitrogen atmosphere using azobisisobutyronitril (AIBN) as initiator. The composites were investigated by high resolution transmission electronmicroscopy in order to investigate the morphology. The thermomechanical properties as storage, loss modulus, tan δ – as well as the glass transition temperature (T_g) of the composites were estimated by dynamic mechanical thermal analysis (DMTA).

Keywords: composite materials, sol-gel-process, methacrylate copolymers, dynamic-mechanical-analysis, electron microscopy

1. Introduction

Composite materials of high optical purity synthesized by the sol gel process in combination with radical polymerization are of wide interest for optical applications [1, 2]. The synthesis of bulk materials with high quality end properties requires exact knowledge of the parameters which determine the processing procedure [3, 4]. Important properties of the composites are the morphology, the mechanical and thermomechanical behaviour which also have an influence on the availability of materials for optical uses because long time stability is required in this field too. The aim of this work is therefore to investigate basically the synthesis and the mechanical end properties of such composites in order to make the first step in developing new composite materials with new interesting properties.

2. Experimental

MPTS was distilled under vacuum at 40°C prior to use and then stirred 24 h at room temperature with 0,1 mole/l HCl/H₂O in the molar ratio 0,5 to MPTS

based on mole H₂O to mole MPTS. Residual amounts of solvent were removed by distillation at 40°C and 0,5 mbar). TEGDMA (destabilized to remove the inhibitor) and the prehydrolyzed MPTS were mixed homogeneously in various molar ratios of MPTS (methacrylate endgroups) to TEGDMA equal to 10/90, 25/75, 40/60 and 50/50. Pure TEGDMA was used as reference material. AIBN was added as initiator in a concentration of 0,1 mole% based on methacrylate endgroups in the reaction mixture. The polymerization reaction was performed in a temperature controlled furnace under nitrogen atmosphere using 4 day temperature program with slow heating rate from 20°C to 90°C. For H-TEM sample fabrication a Reichert Ultracut with a diamond knife was used to cut 100–150 nm thick samples. The slices (prepared on 3 mm copper grid 400 mesh) were analyzed in a high resolution transmission electron microscope (Philips). The DMTA measurements were performed with a Rheometric Scientific Dynamic mechanical analyzer MKIII using the single cantilever bending mode. Samples with rectangular cross-section were heated from 0°C to 250°C with a heating rate of 0,5 K/min (strain: $\leq 16 \mu\text{m}$, frequencies: 1 Hz, 5 Hz, 10 Hz).

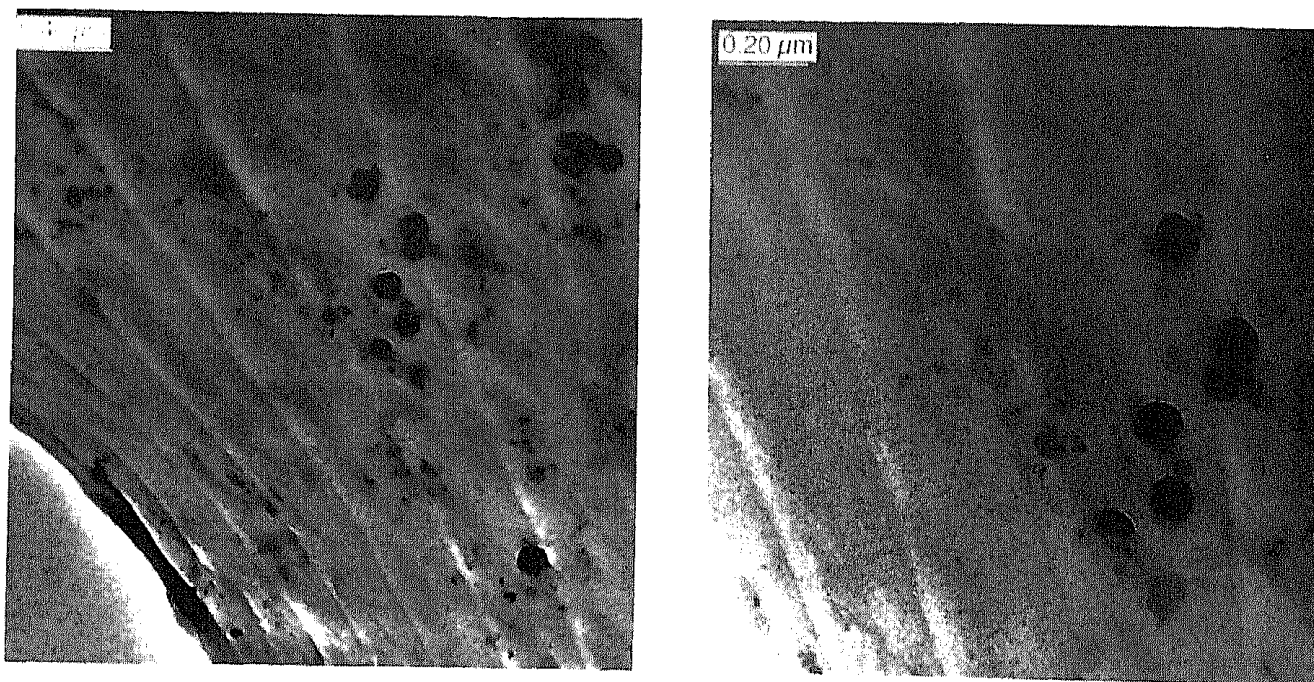


Figure 1. H-TEM micrographs from composite MPTS/TEGDMA 10/90, ultramicrotomed sections on Cu-grid 400 mesh.

3. Results and Discussion

Highly transparent bulk materials (6 cm \times 1 cm \times 0,5 cm) could be prepared by this experimental method. High resolution transmission electron microscopy (H-TEM) was used to investigate the morphology of the MPTS/TEGDMA composites. Figure 1 shows two H-TEM micrographs of ultramicrotomed sections from the composite with 10 mole% MPTS. As one can see from Fig. 1 the composite MPTS/TEGDMA 10/90 has a particulate morphology with a broad particle size distribution ranging from approximately 20 nm with a few particles to 200 nm in particle size. The composites with higher MPTS content are still under investigation. Their morphology will be presented in further publications. EDX-analysis showed that in the region of the particles the silicon/carbon ratio is 0,33 whereas in the brighter areas of the picture it is only 0,07. So the particles contain mainly silica structures from prehydrolyzed MPTS which are visible because of the scattering contrast between carbon and silicon.

DMTA was used to investigate the thermomechanical behaviour of the MPTS/TEGDMA composites. Most information about the network density is given by the damping behaviour. Figure 2 shows therefore the $\tan \delta$ of the different composites in dependence of the temperature.

As can be seen from Fig. 2 an increase in MPTS content has a great influence on the damping behaviour. The $\tan \delta$ - peak height and the values for the glass transition temperature which correspond to the $\tan \delta$ - peak maximum decreases continuously with increasing MPTS content. The small visible peaks in the curves above 100°C are caused by moving of the sample during the measurement. The condensation process of the MPTS species is not finished at 90°C (polymerization end temperature) and its proceeding results in an instability of the sample during the measurement. Table 1 shows the T_g behaviour and the $\tan \delta$ - peak height for the different MPTS/TEGDMA composites.

A decrease in peak height with increasing MPTS content indicates the formation of a higher crosslinked

Table 1. Glass transition temperatures and $\tan \delta$ - peak heights from DMTA measurements of the MPTS/TEGDMA composites with different amounts of MPTS.

Sample	MPTS mole%	TEGDMA mole%	Peak height $\tan \delta$ - (arb. units)	T_g (tan δ - max., 1 Hz)/°C
1	0	100	1,00	117,7
2	10	90	0,74	114,9
3	25	75	0,60	109,9
4	40	60	0,30	104,2
5	50	50	0,07	—

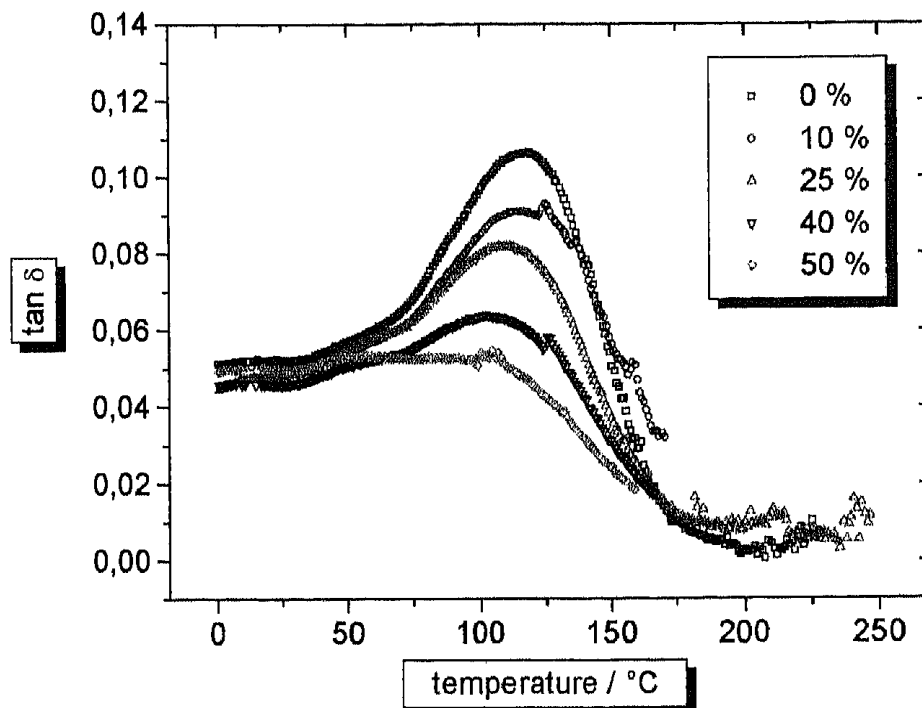


Figure 2. Damping behaviour of the MPTS/TEGDMA composites with 0, 10, 25, 40 and 50 mole% MPTS from DMTA single cantilever bending measurements at 1 Hz.

network, because the chain length between two network points of silicon is smaller than chain length of a TEGDMA unit resulting in a decreased mobility for the chains between two network points. The amount of polymer chains which can move at T_g is therefore decreased. On the other hand a decrease in T_g with increasing MPTS content indicates the presence of smaller oligomeric species however from prehydrolyzed MPTS which act as plasticizers for the polymer chains. Furthermore the post condensation reaction and the resulting change in thermomechanical and mechanical properties will be the aim of further investigations.

4. Conclusions

Transparent bulk composite materials could be prepared from prehydrolyzed MPTS and TEGDMA as comonomer with different amounts of MPTS. The H-TEM analysis showed a particulate morphology with MPTS forming silica particles which were crosslinked with TEGDMA to networks of different densities by radical polymerization of the methacrylate endgroups. The extent of crosslinking can be seen qualitatively in the damping behaviour of the composites in DMTA

measurements. The height of the tan δ - peak decreases with increasing MPTS content because the network becomes more stiff and the amount of chains which are mobile in the T_g region decreases. This behaviour is accompanied by a decrease in T_g with increasing MPTS content, a phenomenon which can be explained by the fact that there might be some oligomeric silica species from MPTS which act as plasticizers for the remaining mobile polymer chains.

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