

Optical and Thermomechanical Investigations on Thermoplastic Nanocomposites with Surface Modified Silica Nanoparticles

C. Becker, P. Mueller, H. Schmidt

Institut fuer Neue Materialien, Im Stadtwald, Geb. 43, D-66123 Saarbruecken, Germany

ABSTRACT

Dynamic mechanical thermal analysis (DMTA) and UV/VIS spectroscopy were applied to investigate the thermomechanical and optical properties of thermoplastic nanocomposites. The thermoplastic matrix material used was a copolymer derived from methylmethacrylate (MMA) and 2-hydroxyethylmethacrylate (HEMA). To improve the mechanical properties, especially in the high temperature region above the glass transition temperature (T_g) of the matrix, the copolymer was filled with spherical 10 nm silica particles (filler content 2, 5, and 10 vol.% respectively). The particles were introduced in the polymer matrix after appropriate surface coating to control the filler dispersion in the matrix and the filler/matrix adhesion. The coating was performed using acetoxypolytrimethoxysilane (APTS) to achieve higher filler/matrix compatibility compared to unmodified silica particles dispersed in the polymer matrix. Methacryloxypropyltrimethoxysilane (MPTS) was used to improve filler/matrix adhesion by covalent bonding between the filler surface and polymer matrix. The appearance of the poly(MMA-co-HEMA) nanocomposites (denoted: PMH nanocomposites) changes from translucent for the systems containing uncoated silica to more transparent for the compositions containing silane coated silica. This is indicated by a decrease in scattering/absorbance losses from 1.48 dB/cm to 1.06 dB/cm at $\lambda = 650$ nm. Investigations of the morphology of the same nanocomposites using transmission electron microscopy (TEM) showed that by coating the particles with silane an almost perfect dispersion of the fillers in the matrix can be realised. The more homogeneous dispersion of the silane coated particles in the polymer matrix compared to the uncoated silica is responsible for the increase in transparency of the systems. However, the composition dependence of the refractive index is in accordance with the expected behaviour and shows a decrease with increasing amounts of silica (0 % silica: $n_e = 1.5085$, 10 % silica $n_e = 1.4965$) whereas, the Abbe number remains almost constant at $v_e = 58$ for all compositions. In addition, the fortyfold increase in the value for the storage modulus E' at $T = 170$ °C (derived from dynamic mechanical thermal analysis (DMTA)) for the system with 9.5 vol.% MPTS coated particles compared to the unfilled matrix indicates an increased thermomechanical stability of the nanocomposites.

Keywords: nanocomposite, hybrid material, surface modification, scattering/absorbance losses, dynamic mechanical thermal analysis

1. INTRODUCTION

Organic-inorganic materials produced by combination of inorganic networks and organic polymers, so-called nanocomposites, have opened a wide field of investigations in materials science in the last decade [1- 15]. In the field of ophthalmic applications, thermosetting as well as thermoplastic materials have been developed from pourable reactive monomer mixtures using moulding techniques because of easy shaping and processing [16-18]. Some combinations of organic polymers and inorganic network structures showed very good optical performance such as high transparency, adjustable refractive index and low scattering/absorbance losses. Additionally also an improvement of the mechanical properties such as fracture toughness and stiffness at temperatures above the glass transition temperature is a strong requirement for the use of these for eye glass lenses or laser diode bar lenses. In general amorphous thermoplastics, e.g. polymethylmethacrylate, or special thermosettings, e.g. CR 39, possess some of the required properties such as high transparency and excellent fracture toughness. Additionally an improvement of the stiffness at higher temperature and an increase in heat distortion temperature of these materials would be of interest because the field of applications could be extended over a wider temperature range. Incorporation of inorganic particles in the thermoplastics usually represents a solution to increase the thermal stability of such systems. In particular thermoplastic polymers filled with inorganic spherical particles in the nanoscale range are expected to show, in addition to transparency, new interesting thermal and mechanical properties compared to thermoplastics usually filled with microparticles. According to Wu [19-21], the interparticulate distance i (or matrix ligament thickness) in a composite is dependent on the filler volume fraction ϕ and on the particle diameter d . It can be calculated by the following equation (1) assuming that monodisperse filler particles are arranged in a simple cubic packing:

$$i = ((\pi / 6 \phi)^{1/3} - 1) \cdot d \quad (1)$$

In general, the properties of composites filled with microparticles mainly depend on the filler volume fraction and only slightly on any interfacial phase existing between filler and matrix. The reason for this is the unfavourable surface to volume ratio of the microparticles. Polymer segments adsorbed on the filler surface in a definite layer thickness (for example layer thickness 1 nm, as is shown in the literature [22]) in general possess structures different from the bulk structure. The interfacial phase volume percentage (A) can be calculated by equation (2)

$$A = F / (v(1-F)) \cdot (V-v) \cdot 100 \quad (2)$$

where F is the filler volume fraction, v is the volume of one particle without interfacial layer and V the volume of one particle having an interfacial layer of definite thickness. According to equation (2), (A) is approximately 8 vol.% for a nanocomposite with 10 vol.% 10 nm particles assuming a layer thickness of 1 nm. From this point of view it can be expected that nanoparticles influence the mechanical and thermal properties of the resulting composites by the interfacial phase in addition to the pure "filling" effect. In order to observe the predicted effects, an almost perfect dispersion of the nanoparticles in the matrix is required. For this reason, the particle surface and the matrix have to be "compatibilised", which means the interfacial free energy has to be decreased.

Determination of the viscoelastic properties especially above the glass transition temperature (T_g) of the polymer matrix gives a lot of information about the filler reinforcement ability in composite systems. According to the theory of Guth-Gold Smallwood (G-G-S) [23] the increase in modulus by introducing increasing amounts of rigid filler particles in a thermoplastic matrix may be described as being equivalent to an increase in viscosity of dispersion systems containing spherical particles. The increase in E' value is described as an extended Einstein equation (equation 3):

$$E'_c = E'_M (1 + 2.5\phi + 14.1\phi^2) \quad (3)$$

with E'_c: storage modulus of the composite, E'_M: storage modulus of the unfilled polymer, φ: filler volume fraction.

Following the concept of matrix immobilisation on the surface of the filler particles, forming a more rigid polymer structure near the particle/matrix interface, the modulus increase may be even higher for nanoparticulate fillers as predicted by the G-G-S theory. On the other hand, the mechanical damping, i.e. the indicator for the viscous behaviour of the samples, can also serve as an important tool for obtaining information about polymer adsorbed on the filler surface. Usually the damping should decrease with increasing filler content in the samples because the inorganic filler particles do not pass through a phase transition in the glass transition region of the polymer matrix and therefore do not contribute to the mechanical damping. The theory of Lee and Nielsen [24] describes the damping of a composite system expressed as damping coming only from the polymer matrix and being reduced in value by the volume fraction of the incorporated filler particles (equation 4).

$$\Delta = \Delta_M \phi_M \quad (4)$$

Δ: damping of the composite, Δ_M: damping of the polymer matrix, φ_M: volume fraction of the polymer matrix.

If the damping of the composites is increased compared to the predictions of the theory, then additional damping mechanisms may be assumed such as interparticulate friction arising from points of contact between filler particles caused by incomplete mixing of the components or by statistical reasons. On the other hand if the damping decreased faster than the theoretical values this behaviour may indicate matrix immobilisation.

The aim of the present study was to elucidate whether it is possible to combine appropriate optical performance with enhancement of the mechanical and thermal properties of thermoplastic materials such as increase in glass transition temperature and stiffness at temperatures above T_g. In fact the approach was to try to increase the thermal stability of polymethacrylate polymers using the concept of nanocomposite formation, while conserving the good optical features of this class of materials. Furthermore, the experiments were evaluated with respect to special effects in addition to the pure „filling“ effect arising from the nanoparticulate structure in the systems.

2. EXPERIMENTAL

Monodisperse silica particles (supplied by Nissan, mean diameter: $d = 10$ nm) were coated with methacryloxypropyltrimethoxysilane (MPTS) and acetoxypopyltrimethoxysilane (APTS) in a methanolic dispersion containing approximately 1 vol.% of silica. MPTS was used to achieve covalent bonding between filler and matrix by fixation of the polymerisable methacrylate end group along the polymer backbone. APTS was used to realise compatibilisation without covalent bonding. The coating reaction was performed using equimolar amounts of silane compared to the calculated amount of silanol groups (Si-OH). The concentration of silanol groups was calculated assuming a surface density of 8 Si-OH groups / nm² as given by Iler [25]. The dispersions were used without further centrifugation.

In order to remove impurities the monomers methylmethacrylate (MMA) and 2-hydroxyethylmethacrylate (HEMA) were distilled under vacuum prior to use. Equal amounts of both monomers were mixed with calculated amounts of the methanolic silica dispersions. The monomer mixtures were calculated to contain 2, 5 and 10 vol.% silica respectively after removal of methanol. These mixtures were cured in a temperature program up to 120°C by free radical polymerisation using azobisisobutyronitril (AIBN) as initiator. The curing was performed in special reaction containers under exclusion of oxygen, resulting in plate like poly(MMA-co-HEMA) (denoted: PMH) nanocomposites with a thickness of 4 mm. The unfilled PMH copolymer matrix was synthesised as a reference system.

For the investigation of the morphology by transmission electron microscopy (TEM), the nanocomposites were ultramicrotomed in a Reichert ultracut using a diamond knife. The resulting slices with an approximate thickness of 100 nm floated on a water surface were prepared on copper grid 400 mesh. The TEM experiments were performed on the thin sections using a JEOL JEM 200 CX (JEOL Ltd., Tokyo, Japan) with an accelerating voltage of 200 kV. The dispersion of the filler particles was directly visible without further staining because of the intrinsic scattering contrast between carbon and silicon. Refractive indices and Abbe numbers were determined using a Pulfrich refractometer PR 2 (Zeiss Jena). UV/VIS transmittance spectra were recorded with a Bruins Instruments Omega 20 spectrometer from 250 nm to 1200 nm with a resolution of 1 nm. Dynamic mechanical thermal analysis (DMTA) was performed on a Rheometric Scientific MK III dynamic mechanical analyser using samples with rectangular cross section. The samples were measured in single cantilever bending mode at 1 Hz with a deflection of ± 8 μ m from 40°C up to 240°C (heating rate 0.5 K/min).

3. RESULTS AND DISCUSSION

The PMH nanocomposites containing 2, 5 and 10 vol.% filler, based on pure silica, were synthesised by curing via thermal free radical polymerisation reaction of the monomer mixture in the presence of the silica particles. Because of weighing errors and shrinkage during polymerisation an exact predetermination of the filler content can not be achieved. Therefore the real filler content values have to be determined by independent measurements after complete curing. For this reason, the exact filler volume fractions were calculated from density measurements according to the Archimedes buoyancy method of the completely cured nanocomposites in comparison to the density of the unfilled PMH matrix. The results of these calculations are shown in table 1 together with the denotations used for the nanocomposites under investigation.

Table 1: Denotation of the PMH nanocomposites containing 10 nm SiO₂ particles with different surface coating and comparison of the expected filler concentration with the SiO₂ filler content obtained from density measurements (Archimedes buoyancy method) on the completely cured PMH systems; skeletal density of the 10 nm SiO₂ particles: 2.15 g/cm³ (skeletal density of bulk solid silica: 2.2 g/cm³ [26, 27]).

denotation of the sample	filler coating	expected SiO ₂ filler content [vol. %]	measured density composite [g/cm ³]	SiO ₂ filler content from density measurements [vol. %]
PMH	-	0	1.244	0
PMH 10/2	uncoated	2	1.268	2.6 ± 0.2
PMH 10/5		5	1.298	5.9 ± 0.3
PMH 10/10		10	1.353	12.0 ± 0.5
PMH 10A/2	APTS	2	1.262	1.9 ± 0.1
PMH 10A/5		5	1.292	5.3 ± 0.3
PMH 10A/10		10	1.336	10.1 ± 0.5
PMH 10M/2	MPTS	2	1.261	1.8 ± 0.1
PMH 10M/5		5	1.294	5.5 ± 0.3
PMH 10M/10		10	1.330	9.5 ± 0.5

As can be seen from table 1 the silica filler contents lie in the expected range. The differences to the expected values mainly arise from errors in volumetric measurements of the silica dispersions during preparation of the nanocomposites.

In the case of uncoated 10 nm SiO₂ particles, translucent thermoplastic nanocomposites could be obtained. In contrast to this, the composites with silane coated 10 nm silica particles were almost transparent independent of the type of silane used. This behaviour can be quantified by UV/VIS transmittance spectroscopy. For this purpose transmittance spectra were recorded using polished, planparallel nanocomposite samples with a thickness of 2 mm. The spectra were corrected for transmittance losses due to reflection by the Fresnel equation (equation 5).

$$\text{Fresnel-equation: } R = \left(\frac{n_\lambda - 1}{n_\lambda + 1} \right)^2 * 100 \quad (5)$$

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

The most significant values for the transmittance in dependence on the particle surface modification, could be expected for the nanocomposites containing the highest silica concentration. Therefore the corrected UV/VIS spectra of the PMH nanocomposites containing 10 vol.% 10 nm silica particles with different surface modifications are shown in figure 1 in comparison to the unfilled PMH matrix.

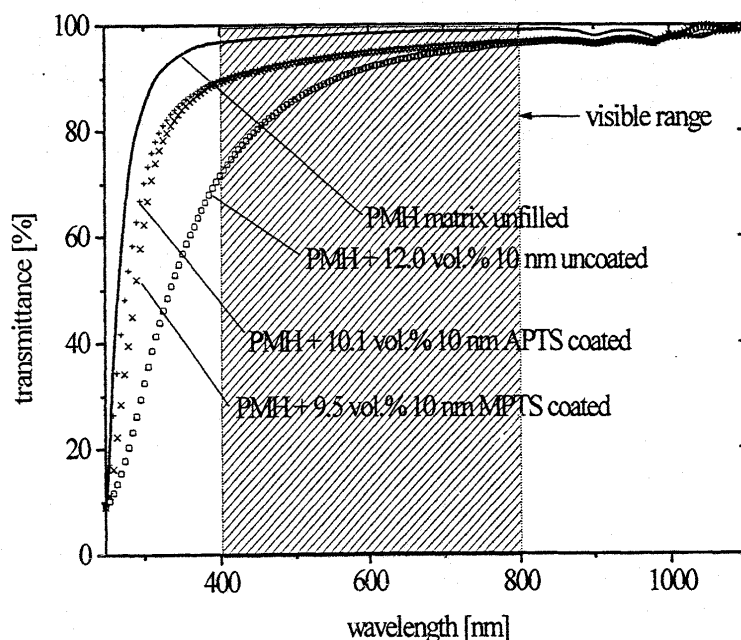


Figure 1: UV/VIS transmittance spectra for PMH nanocomposites containing approx. 10 vol.% 10 nm SiO₂ particles with different surface coating in comparison to the pure unfilled PMH copolymer matrix, sample thickness: 2 mm, spectra corrected for transmittance losses due to reflection by the Fresnel equation (equation 5).

Figure 1 shows that incorporation of uncoated 10 nm SiO₂ particles in the PMH copolymer matrix results in a loss of transparency in the wavelength range from the near UV region up to a wavelength (λ) of 600 nm compared to the unfilled PMH copolymer matrix. This behaviour may be attributed to the formation of larger scaled particle aggregates in the composite containing uncoated particles which cause light scattering because of the mismatch in refractive indices between the PMH polymer matrix and the SiO₂ particles. The upper limit in particle size above which light scattering occurs is approximately λ/20 for SiO₂ in a polymethacrylate matrix.

For this reason the transparency of the composite systems, built up from two phases having different refractive indices, should be a function of the degree of filler dispersion in the matrix. An almost homogeneous dispersion of the 10 nm SiO₂ primary particles in the PMH matrix should result in a high transparency of the nanocomposites because the scattering of light in the visible range is minimised. On the other hand if aggregates of the primary particles are present in the systems,

remarkable light scattering should occur, resulting in a loss of transparency. The homogeneity of the particle distribution can be visualised by transmission electron microscopy (TEM) on ultrathin specimens of 100-150 nm thickness. The SiO₂ nanoparticles are visible in TEM because of intrinsic scattering contrast between silicon and carbon coming from the particles and the polymer matrix respectively. Because the particle size of the SiO₂ primary particles $d = 10$ nm is much smaller than the thickness of the microtomed sections with 100 - 150 nm, the distribution of the particles in the PMH matrix can be best visualised with the nanocomposites having the lowest silica content of 2 vol.%. For the higher filler loadings the superposition of many layers of primary particles having a higher particle density in each layer causes a loss in scattering contrast. Fig. 2 therefore shows the TEM micrographs from ultramicrotomed sections of the nanocomposites filled with 2 vol.% 10 nm SiO₂ particles having different particle coatings.

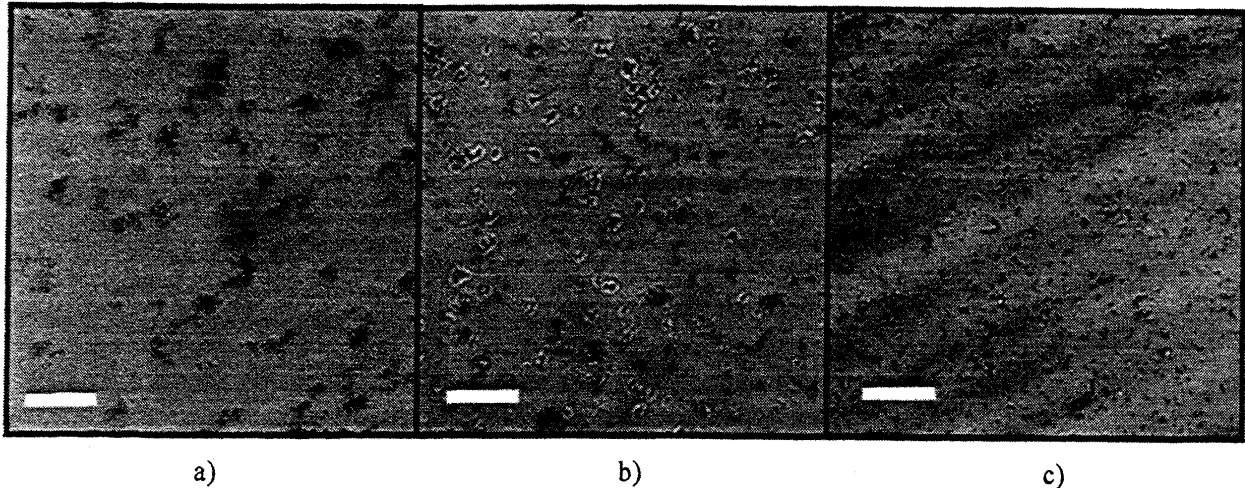


Figure 2: TEM micrographs of PMH nanocomposites with a) 2.6 vol.% uncoated, b) 1.9 vol.% APTS coated and c) 1.8 vol.% MPTS coated 10 nm SiO₂ particles, scale bar = 100 nm.

In figure 2a), large aggregates of nearly 100 nm in diameter are visible in the case of uncoated particles, whereas for particles with silane coating (figure 2b) and c)), a more homogeneous filler distribution in the polymer matrix can be observed with the primary particles forming only small aggregates. The particle aggregates of larger scale in the PMH systems containing uncoated silica arise from poor compatibility because of the mismatch in polarity between particle surface and PMH matrix induced by the tendency of the system to minimise the interfacial free energy. On the other hand it is obvious, that the surface modification of the filler particles by compatibilisation agents such as APTS and MPTS is an essential step to produce well dispersed agglomeration free composites. This is evident especially for the MPTS coated particles, which have the same methacrylate functionality on the surface as the matrix material along the polymer backbone (match of polarity). Additionally, the TEM results show a very strong correlation to the UV/VIS spectra of the same samples. The incorporation of silane coated particles led to a higher transparency in the systems compared to the nanocomposites filled with uncoated SiO₂ as was shown in figure 1. The loss in transparency of the nanocomposites with uncoated 10 nm silica therefore can now be attributed to the existence of large filler aggregates in the size range of 100 nm which cause light scattering and therefore transmittance losses. Furthermore the transparency of the systems increases when the size of the inclusions in the polymer matrix decreases, because the primary filler particles are dispersed more homogeneously in the PMH matrix thereby avoiding light scattering.

Besides this, refractive index and Abbe number are essential data for materials for optical components such as focussing lenses for cameras or lasers in order to enable an optical design to be performed. 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 2×10^{-5}). The Abbe number itself gives information about the dispersion in the systems and can be calculated as follows:

$$\text{Abbe number: } v_e = \frac{n_e - 1}{n_F - n_C} \quad (6)$$

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)

The results from the Pulfrich refractometer measurements showed that the refractive index decreases with increasing silica content independent of the filler surface coating as can be expected for the incorporation of increasing amounts of low refractive index particles. The values range from $n_e = 1.5085$ for the unfilled PMH matrix to $n_e = 1.4965$ for the systems containing 10 vol.% silica. The Abbe number, i.e. the dispersion, remains almost unchanged at $v_e = 58$. From the UV/VIS spectra shown in figure 1 one can directly calculate values for the scattering/absorbance losses in the systems, which show the transmittance quality of the PMH nanocomposites containing particles with different surface coating. Table 2 shows the scattering/absorbance losses of the PMH systems from figure 1 at a wavelength of $\lambda = 650$ nm.

Table 2: Scattering/absorbance losses (dB/cm) at $\lambda = 650$ nm for PMH nanocomposites with different composition derived from the UV/VIS transmittance spectra (figure 1), values corrected for transmittance losses due to reflection by the Fresnel equation.

sample	filler coating	SiO ₂ filler content [vol.%]	scattering/absorbance losses [dB/cm] ($\lambda = 650$ nm)
PMH	-	0	0.33 ± 0.02
PMH 10/10	uncoated	12.0	1.48 ± 0.05
PMH 10A/10	APTS	10.1	1.06 ± 0.03
PMH 10M/10	MPTS	9.5	1.13 ± 0.04

In accordance to the UV/VIS spectra the scattering/absorbance losses show that the unfilled PMH matrix has the highest transparency in the series presented in table 2. The addition of uncoated silica to the PMH matrix results in remarkable losses which arise from light scattering on larger particle aggregates. The incorporation of silane coated particles reduces the scattering losses compared to the sample with uncoated silica but the excellent value of the unfilled matrix was no more achievable. Besides this values for the scattering/absorbance losses higher than 1 dB/cm indicate that the optical quality of these materials is not sufficient for their use as optical components e.g. such as laser diode bar lenses. For this reason additional optimisation of the optical quality and therefore mainly of the dispersion of the coated particles of the PMH nanocomposites is required and will be the aim of further investigations.

Furthermore it was of interest to prove, if the nanocomposite formation has led to an increased thermal stability of the systems. However, an improved thermal stability of such materials is important for their use in industrial applications. Optical components often require a high glass transition temperature, a high heat distortion temperature and high stiffness at elevated temperatures since they have to be used under various environmental loadings depending on the field of application. The distribution of the filler particles in the polymer matrix and especially the filler/matrix adhesion should have an influence on the thermal and the mechanical properties of the resulting nanocomposites. A large amount of information in this field can be drawn from dynamic mechanical thermal analysis (DMTA) experiments covering a temperature range from the glassy state below the glass transition temperature (T_g) of the polymer matrix up to temperatures far above the T_g of the polymer in the region of viscous flow. The viscoelastic behaviour of the PMH nanocomposites can be directly investigated by DMTA measurements. The storage modulus E' gives information about the elastic properties of the samples. In addition the viscous parts in the nanocomposites, coming from the polymer matrix, lead to a phase shift δ between the applied oscillation and the corresponding response of the sample. The phase shift is expressed as damping $\tan \delta$ and serves as a measure of the viscous properties of the samples. Most information about the viscoelastic behaviour can be obtained from the samples containing the higher filler concentrations since the volume fraction of any interfacial phase may not be negligible in these systems. For this reason these nanocomposites may show the most pronounced effects in addition to the pure „filling“ effect. The temperature dependence of the storage modulus E' , thus the elastic behaviour, is shown in figure 3 for nanocomposites with 10 vol.% filler, having different surface coating respectively.

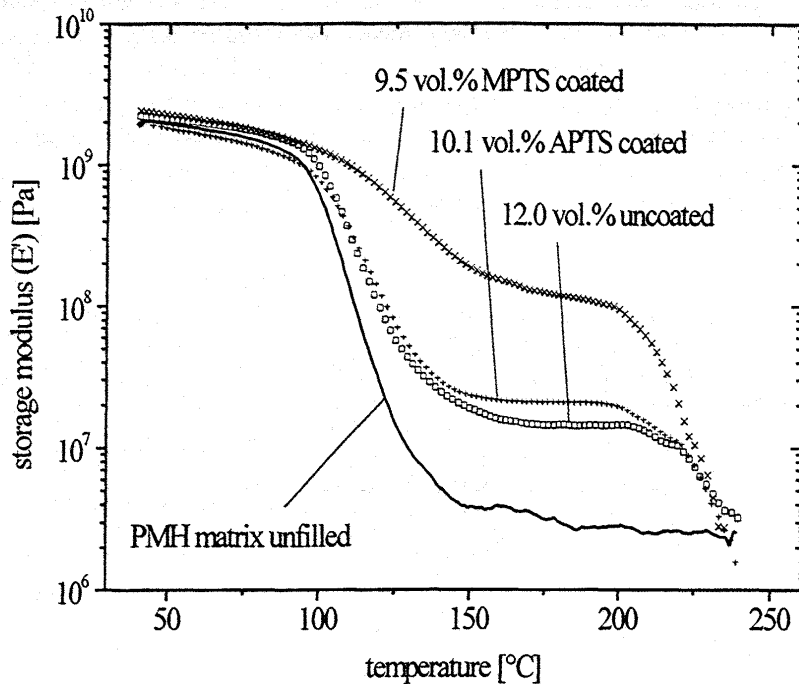


Figure 3: Temperature dependence of the storage modulus E' from DMTA measurements for PMH nanocomposites containing 10 vol.% 10 nm SiO_2 particles with different surface coatings in comparison to the pure unfilled PMH copolymer.

The storage modulus E' shows a decrease with increasing temperature by about three decades for all PMH nanocomposites as well as for the unfilled PMH matrix. This behaviour is well known for thermoplastic polymers. The temperature regime where the E' decreases in value represents the glass transition region of the polymer matrix. Below the glass transition temperature (T_g) the polymer is in the glassy state and appears very stiff. Passing through the T_g region the polymer shows increasingly leathery behaviour with increasing temperature. For the temperature range between 150 °C and 200 °C, E' reaches a plateau for all samples shown in figure 3. This is the so-called rubbery plateau region where the samples are in the rubbery state, as indicated by an approximately constant E' value. As one can observe, the E' value in the plateau region increases for the composites with different filler surface coatings in the series uncoated, APTS coated and MPTS coated silica indicating an increasing stiffness of the samples at temperatures above T_g . This behaviour will be discussed in detail in the next section. In the temperature regime above 200 °C, an additional decrease in the E' value can be observed with increasing temperature, especially for the filled samples, indicating the beginning of viscous flow in the samples. This observation may be attributed to the thermal decomposition of the polymer matrix above 200 °C, which causes destruction of the rubbery network and results in an overall instability of the samples. The thermal decomposition of the polymer matrix above 200 °C was confirmed by thermogravimetric analysis showing a significant weight loss of the samples in this temperature range.

In particular the value of the storage modulus in the rubbery plateau region (150 °C - 200 °C) gives significant information about the filler/matrix interaction in addition to the pure filling effect. The enhanced resolution on this feature comes from the fact, that the polymer matrix has a much lower modulus above T_g than at temperatures below T_g . For this reason any special effect of the polymer chains near the particle surface, e.g. having a hindered mobility, should be more pronounced. If the filler/matrix interaction is increased then the value of the storage modulus should also increase in comparison to the unfilled PMH matrix and the PMH nanocomposites with uncoated silica particles. To evaluate this influence E' values for all systems under investigation have to be compared at one temperature, which should lie neither in the glass transition region nor in the temperature range above 200 °C where thermal matrix degradation occurs. For this reason 170 °C was chosen as the so-called reference temperature. The composition dependence of the storage modulus at 170 °C is shown in figure 4 for PMH nanocomposites with filler particles of different surface coatings in comparison to the unfilled PMH copolymer and the theoretical values derived from the Guth-Gold-Smallwood (G-G-S) equation. According to the G-G-S

theory the increase in modulus can be estimated as if it were an increase in viscosity for the dispersion of spherical particles in a solvent.

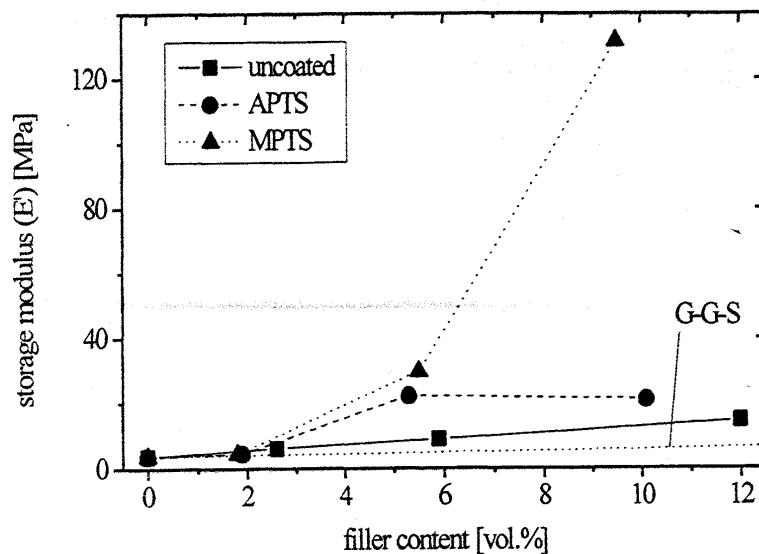


Figure 4: Storage modulus E' from DMTA measurements for PMH nanocomposites containing 10 nm silica particles with different surface coatings in dependence on the filler content; G-G-S: E' increase according to Guth-Gold-Smallwood theory.

The composition dependence of the storage modulus at 170 °C shows significant differences in the increase of the E' value with increasing filler content for the systems with uncoated, APTS coated and MPTS coated SiO_2 nanoparticles. The PMH system with uncoated particles shows an increase in E' , which is only slightly higher than the values predicted by the G-G-S theory. As shown by TEM analysis these nanocomposites contain particle aggregates in the size range of 100 nm. Since it is well known that dispersions containing aggregated particles usually show higher viscosity compared to those with well separated particles of the same filler content the behaviour of the storage modulus seems to be reasonable for the PMH nanocomposites filled with uncoated particles. In contrast to this the PMH nanocomposites with APTS coated particles show even higher E' values compared to the systems with uncoated particles because of the better distribution of the APTS coated particles in the PMH matrix, as could be shown by TEM analysis. This behaviour suggests that particle aggregation can not be the only reason for the enhancement in modulus compared to the theory. The observed behaviour rather implies that a certain portion of the polymer matrix may be immobilised on the filler surface forming an interfacial layer of slightly higher stiffness compared to the surrounding bulk matrix. These immobilised polymer segments might increase the apparent filler volume fraction and therefore lead to an increase in modulus, which is more pronounced than is expected from the theory or from the assumption that larger particle aggregates may be responsible for the observed behaviour. According to the proposed model a higher amount of polymer segments can be immobilised in the systems with APTS particles to those with uncoated silica because there is more filler surface available in the former systems assuming equal filler volume fraction and particle size. On the other hand, the strong increase in the E' value is evident for the PMH nanocomposites containing MPTS coated particles. The covalent phase adhesion between filler and matrix through the MPTS coupling agent in these systems leads to somewhat crosslinked nanocomposites with a higher crosslinking density especially for the higher filler content.

The filler/matrix adhesion can also be evaluated from the mechanical damping behaviour derived from the DMTA experiments. The peak area under the $\tan \delta$ curve (denoted: Δ) may be directly correlated to parts of the polymer matrix which contribute to the glass transition. According to the theory of Lee and Nielsen (see above) the damping gives direct information about the existence of additional damping mechanisms or polymer immobilisation on the surface of the filler particles. The corresponding results for the PMH nanocomposites with 10 vol.% silica having different surface modification are shown in figure 5.

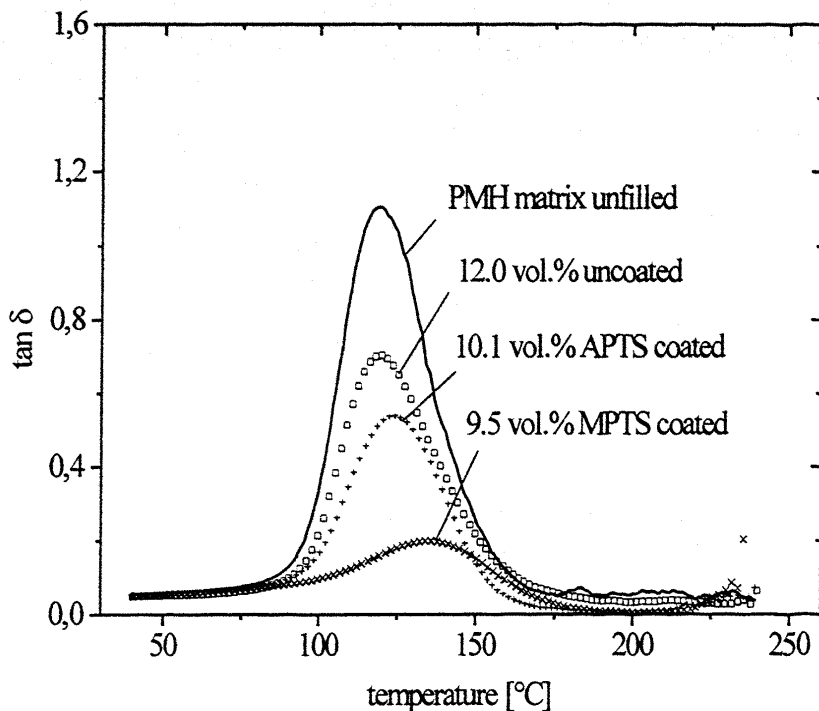


Figure 5: Temperature dependence of the damping $\tan \delta$ from DMTA measurements for PMH nanocomposites containing 10 vol.% 10 nm SiO_2 particles with different surface coatings in comparison to the pure unfilled PMH copolymer.

The results of the mechanical damping are in agreement with the observations made for the behaviour of the storage modulus. The peak area under the $\tan \delta$ curve is decreasing with increasing filler matrix adhesion in the series uncoated, APTS coated and MPTS coated silica particles. Almost the same molecular mechanisms may be responsible for the observed behaviour. While the damping decreases in value the glass transition temperature, represented by the temperature coinciding with the $\tan \delta$ maximum, increases at the same time. To obtain more quantitative data about the shift of glass transition temperature and the dependence of the mechanical damping on the composition figure 6 and 7 show the T_g values and peak areas for all nanocomposites under investigation.

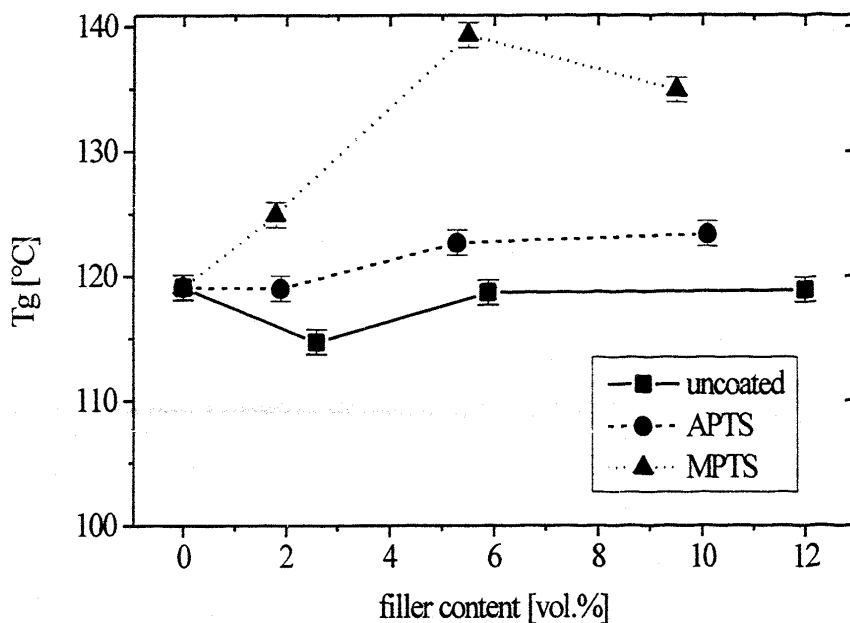


Figure 6: Glass transition temperatures (T_g) from DMTA measurements for PMH nanocomposites containing 10 nm silica particles with different surface coating in dependence on the SiO_2 filler content.

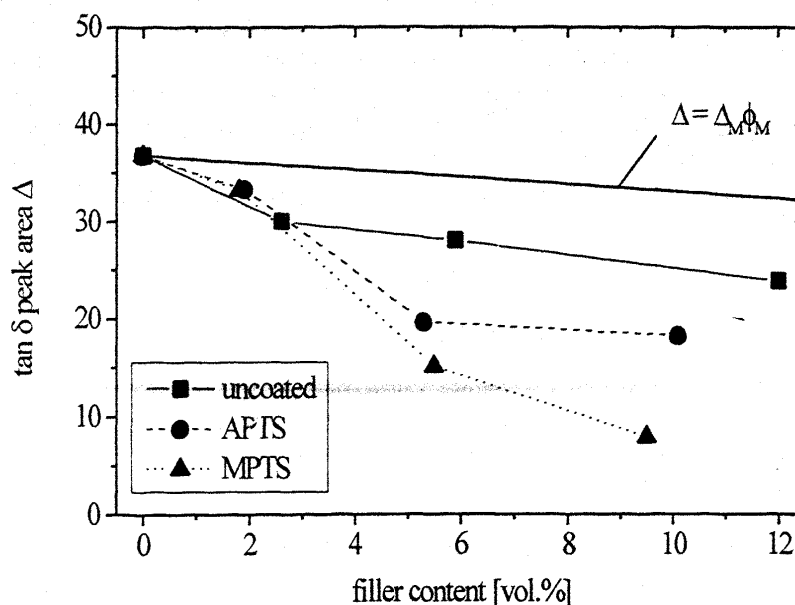


Figure 7: Peak area under the $\tan \delta$ curve from DMTA for PMH systems containing 10 nm silica particles with different surface coating in dependence on the SiO_2 filler content; $\Delta = \Delta_M \phi_M$: theory of Lee and Nielsen, Δ_M : damping matrix, ϕ_M : volume fraction matrix.

The evolution of the T_g values shown in figure 6 reveals significant increases in glass transition temperature only for the PMH systems containing MPTS coated particles. For all other nanocomposites the T_g remains almost unchanged in comparison to the unfilled PMH matrix. The T_g increase of the former systems indicates immobilisation of polymer chains on the filler surface, which arises from the covalent phase adhesion via MPTS as coupling agent. The mechanical damping on the other hand (figure 7) decreases more than predicted by the theory of Lee and Nielsen for all systems. This behaviour may be attributed once again to strongly hindered mobility of the polymer chains in the nanocomposites. The effect is more pronounced for the silane coated particles. As mentioned above the APTS coating leads to an increase in available surface area in the systems resulting in an increased number of polymer/particle contact points. The incorporation of MPTS coated particles leads to covalent bonding between filler and matrix resulting in an increased network density and a shorter polymer chain length between the network points. These phenomena cause a strongly hindered polymer mobility in the systems with MPTS coated particles, which causes both decrease in mechanical damping and increase in T_g value.

4. CONCLUSIONS

Thermoplastic organic-inorganic nanocomposite materials derived from polymerisable methacrylate monomers and nanoscaled silica particles could be prepared possessing high thermal stability and good optical performance. The improved thermal stability, especially of the systems containing the nanoparticulate phase covalently bonded to the polymer via methacrylic silane, arises from the formation of a semi-interpenetrating network like structure together with strong immobilisation of polymer chain segments on the surface of the inorganic nanoparticles. This immobilisation phenomenon led to an improvement of the thermomechanical properties in addition to the pure „filling“ effect. Besides this these nanocomposites also showed increased transparency compared to the systems filled with silica having no surface modification. The increase in transparency could be related to the more homogeneous dispersion of the SiO_2 nanofillers in the systems with MPTS coated particles compared to those with uncoated silica as revealed by TEM.

The nanoscaled filler particles itself have shown to strongly influence the properties of polymer derived nanocomposites in the sense of synergistic effects and therefore are of high interest for future investigations to design new materials for optical applications. The results presented here also indicate that the concept of nanocomposite formation can be very useful to improve the overall performance of materials as possible candidates for different focussing lenses, e.g. laser diode bar lenses or camera lenses.

New thermoplastic materials with improved thermomechanical properties and good optical performance offer the possibility to produce optical elements for enhanced requirements by low cost processes like injection moulding. Despite good thermomechanical behaviour the optical losses of the presented nanocomposites require further improvement which may be achieved by establishing a totally perfect dispersion of the nanoscaled primary particles in the polymer matrix. In summary the experiences made in these investigations may serve as an important basis for the creation of new interesting optical materials which may have the potential for being a substitute for inorganic glasses or thermosets.

5. REFERENCES

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