

TAILORING OF THERMOMECHANICAL PROPERTIES OF THERMOPLASTIC NANOCOMPOSITES BY SURFACE MODIFICATION OF NANOSCALE SILICA PARTICLES

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Abstract

Thermoplastic nanocomposites based on linear polymethacrylates as matrix materials and spherical silica particles as fillers have been synthesized using the in situ free radical polymerization technique of methacrylate monomers in presence of specially functionalized SiO₂ nanoparticulate fillers. Uncoated monodisperse silica particles with particle sizes 100 nm and 10 nm were used as reference fillers. For surface modification, the alcoholic dispersions of the fillers were treated with appropriate amounts of methacryloxypropyltrimethoxysilane (MPTS) and acetoxypolytrimethoxysilane (APTS). Transmission electron microscopy (TEM) was used to investigate dispersion behaviour in dependence on surface modification. Dynamic mechanical properties were measured by dynamic mechanical thermal analysis (DMTA).

1. Introduction

Thermoplastic polymers filled with inorganic spherical particles in the nanoscale range, so called nanocomposites, are expected to show new interesting thermal and mechanical properties compared to thermoplastics filled with microparticles. According to Wu^{1,2,3}, 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:

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

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 microparticles. Polymer segments adsorbed on the filler surface in a definite layer thickness (layer thickness 2 nm for example as shown in the literature⁴) in general possess structures different from the bulk structure. The interfacial phase volume percentage (A) can be calculated by equation (2)

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

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 30 vol.% for a nanocomposite with 15 vol.% 10 nm particles assuming a layer thickness of 2 nm. From this point of view it can be expected that nanoparticles influence the mechanical and thermal properties of the resulting composites by the in-

terfacial 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 “compatibilized”, which means the interfacial free energy has to be decreased.

2. Experiment

Monodisperse 10 nm (Nissan) and 100 nm (Merck) Stöber silica particles were coated with methacryloxypropyltrimethoxysilane (MPTS) and acetoxypopyltrimethoxysilane (APTS) in a methanolic dispersion containing approximately 1 vol.% silica. MPTS was used to achieve covalent bonding between filler and matrix by fixation of the polymerizable methacrylate end group along the polymer backbone. APTS was used to realize compatibilization without covalent bonding because of the absence of the polymerizable double bond. The 100 nm particles were used as reference systems for bigger particles with a less favorable surface to volume ratio. Butylamine was used as catalyst to accelerate the coating reaction. In the case of 100 nm particles, the silanes were added in twofold excess compared to the calculated amount of silanole groups. After reaction at 50°C for 12 h the unreacted silane was removed from the silica by centrifugation and subsequent washing with methanol. In the case of 10 nm particles the coating reaction was performed using equal molar amounts of silane compared to the calculated amount of silanole groups. The dispersions with 10 nm particles were used without further centrifugation.

The monomers methylmethacrylate (MMA) and 2-hydroxyethylmethacrylate (HEMA) were distilled in vacuum prior to use. Equal amounts of both monomers were mixed with calculated amounts of the methanolic silica dispersions. After removal of methanole the monomer mixtures contained 2, 5 and 10 vol.% silica. These mixtures were cured in a temperature program until 120°C by free radical polymerization using azobisisobutyronitrile (AIBN) as initiator. The curing was performed in special reaction containers under exclusion of oxygen, resulting in plate like poly(MMA-co-HEMA) nanocomposites with a thickness of 4 mm. The nanocomposites were ultramicrotomed using a Reichert ultracut and their morphology was investigated in a transmission electron microscope (TEM). Dynamic mechanical thermal analysis (DMTA) was performed using samples with rectangular cross section. The samples were measured in single cantilever bending mode at 1 Hz with a deflection of $\pm 8 \mu\text{m}$ between 40°C and 240°C (heating rate 0,5 K/min).

3. Results and Discussion

For the preparation of hydrophilic polymer matrices, HEMA was added to MMA. The poly(MMA-co-HEMA) nanocomposites containing 2, 5 and 10 vol.% filler, based on pure silica, were synthesized by free radical polymerization in the presence of the silica particles. In the case of 10 nm particles, transparent thermoplastic nanocomposites could be obtained. In contrast to this, the composites with 100 nm silica particles were only translucent. Fig 1 shows the transmission electron micrographs from ultramicrotomed sections of the nanocomposites filled with 2 vol.% 10 nm SiO₂ particles with different particle coatings.

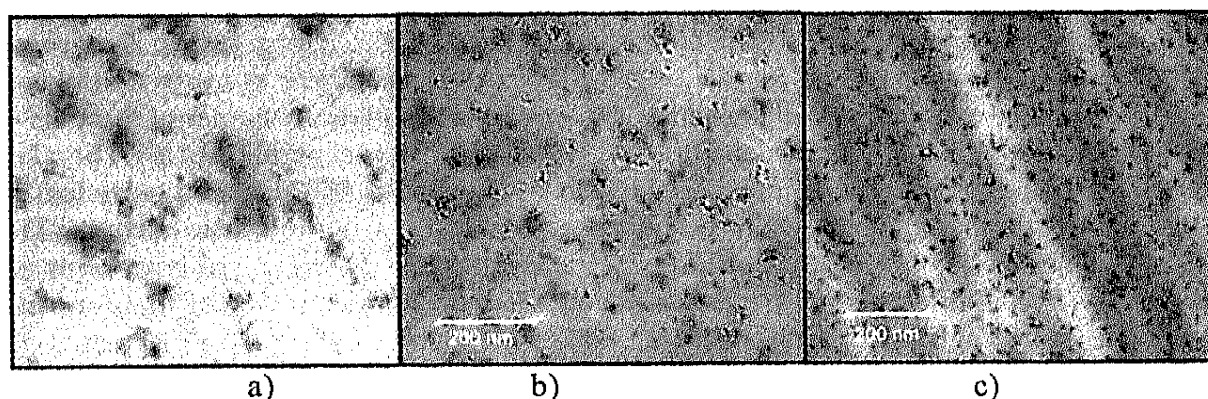


Fig.1: TEM micrographs of poly(MMA-co-HEMA) nanocomposites with 2 vol.% of a) uncoated, b) APTS coated and c) MPTS coated 10 nm SiO₂ particles.

In figure 1, large aggregates of nearly 100 nm in size are visible in the case of uncoated particles, whereas in the case of particles with APTS coating, small aggregates are visible and in case of MPTS coating the particles are nearly homogeneously distributed in the polymer matrix. It is obvious, that the surface modification of the filler particles by compatibilization agents is an essential step to produce well dispersed agglomeration free composites. This is evident especially for the MPTS-coated particles, which have the same functionality on the surface as the matrix material along the polymer backbone.

Dynamic mechanical thermal analysis (DMTA) was performed in order to investigate the rheological properties, because it offers much information about the influence of the particle coating and the state of particle agglomeration on the thermomechanical behaviour of the resulting composites^{5,6,7,8}. The storage modulus E' is equal to the elastic response, in fact the reversible part of the resistance against the applied dynamic strain (stiffness). As shown in literature, especially above the glass transition temperature (T_g), E' will be increased compared to the unfilled matrix by increased filler volume content, by increased phase adhesion between filler and matrix and, in the presence of particle aggregates, by particle/particle friction at the points of contact between the primary filler particles^{9,10}. Figure 2 shows the storage modulus E' at 170°C, in the rubbery plateau region above the glass temperature, for poly(MMA-co-HEMA) nanocomposites in dependence on the filler volume content for different filler surface coatings.

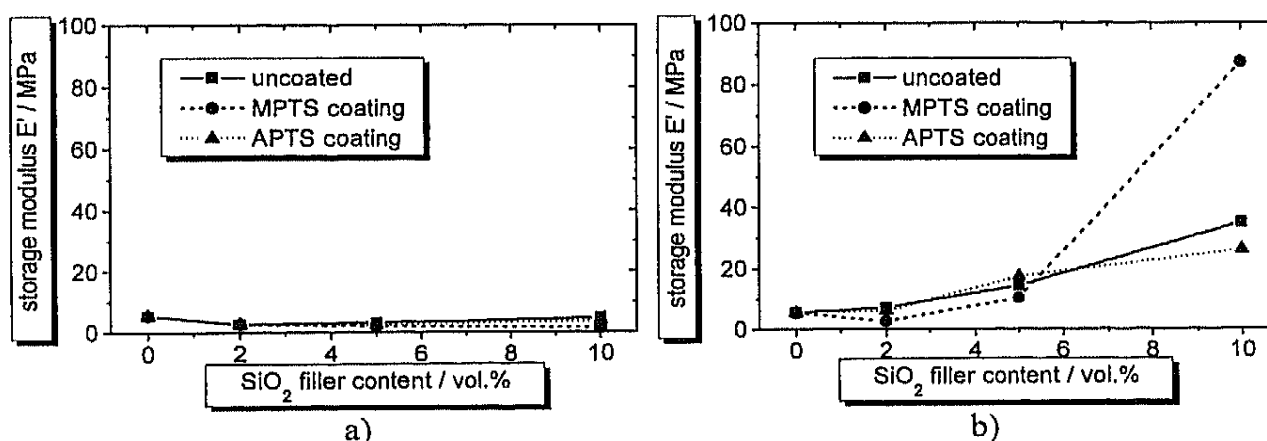


Fig.2: Dependence of the storage modulus E' for poly(MMA-co-HEMA) nanocomposites on the filler volume fraction for different surface coatings of the a) 100 nm and b) 10 nm silica particles; $T = 170$ °C.

Figure 2 shows, that in the case of 100 nm particles there is no influence of filler volume fraction and filler/matrix adhesion on the storage modulus at 170°C compared to the systems filled with 10 nm silica particles. In the case of 10 nm particles the storage modulus E' increases with filler content for all systems. Up to 5 vol.% particle content, there is no significant influence by the particle coating. At 10 vol.% filler content the MPTS coated particles cause a large increase in E' compared to the uncoated and APTS coated particles. The MPTS coating of the particles allows covalent adhesion of polymer molecules near the filler surface during composite synthesis, resulting in immobilization of these polymer segments. The immobilized shell like polymer increases the apparent particle diameter of the pure silica particles obtained by TEM and therefore increases the filler volume fraction. The result is an increase in melt viscosity, in fact an increase in E' caused by an increased resistance of the greater particles against the applied dynamic strain.

Polymers in general are viscoelastic materials. Usually the applied dynamic deformation and the response of the sample are out of phase. The phase shift δ in a DMTA experiment is expressed as damping $\tan \delta$. The peak area under the $\tan \delta$ curve at the glass transition for example, is a measure of the energy dissipated during the dynamic experiment and gives information about the viscous parts of the sample. The glass transition temperature (T_g) itself is defined as the temperature corresponding to the maximum in the $\tan \delta$ curve. Changes in T_g can be classified as significant if they show differences of more than $\pm 5^\circ\text{C}$ compared to the T_g of the pure matrix. The T_g is expected to increase compared to the T_g of the pure matrix in the case of covalent filler adhesion, because for the part of polymer segments near the filler surface the chain mobility is restricted¹¹. Figure 3 shows the glass transition temperature for all composites with 100 nm and 10 nm particles in dependence on the silica filler content.

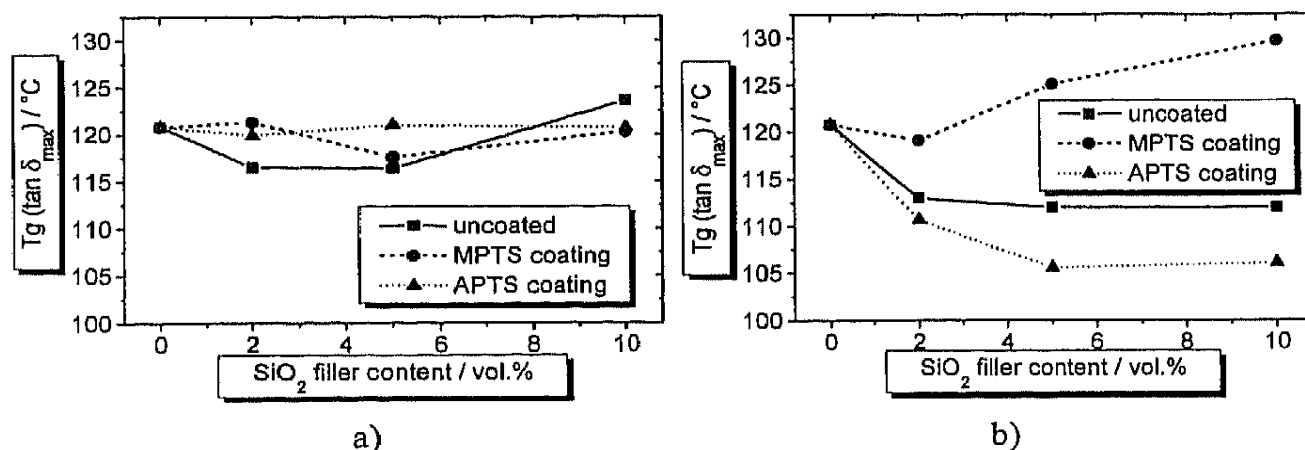


Fig.3: Dependence of the glass transition temperature from $\tan \delta$ maximum for poly(MMA-co-HEMA) nanocomposites on the filler volume fraction for different surface coatings of the a) 100 nm and b) 10 nm silica particles.

For 100 nm particles (fig. 3a)), there is no significant T_g change in dependence on the filler content and the filler coating. In contrast to this, the T_g is changing to a marked extent in the case of 10 nm particles (fig 3b)). The MPTS coating causes immobilization of polymer chains near the filler surface by covalent adhesion with resulting restricted chain mobility. The APTS coating leads to a decrease in T_g compared to the unfilled polymer. It can be assumed, that the covalent bonding of MPTS-coated particles results in a rigid polymer morphology at the

particle surface and Tg increases. Although the APTS-coated particles are less agglomerated in comparison to the uncoated particles by compatibilization, the polymer morphology at the surface is “softened” by APTS-molecules and Tg decreases caused by increased chain mobility.

According to the above results, the nanocomposites with 10 vol.% 10 nm silica seem to be the interesting ones to be compared over the whole investigated temperature range. Figure 4 shows the temperature dependence of the storage modulus and the $\tan \delta$ between 40°C and 240°C for all these nanocomposites compared to the unfilled matrix.

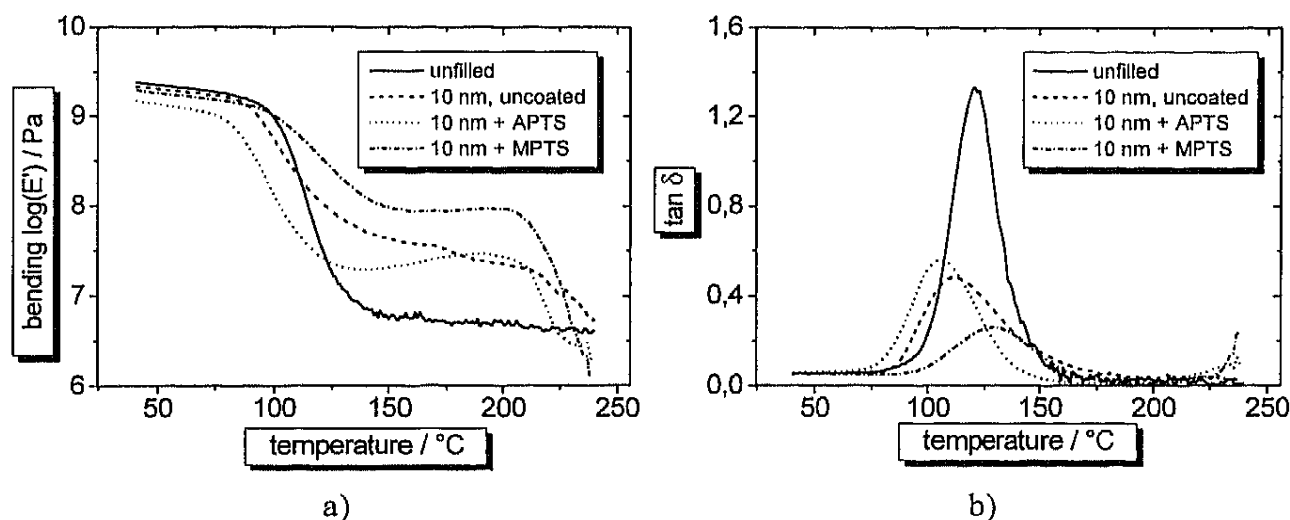


Fig.4: Temperature dependence of a) the storage modulus E' and b) the damping $\tan \delta$ of poly(MMA-co-HEMA) nanocomposites filled with 10 vol.% 10 nm SiO_2 particles with different coatings compared to the unfilled matrix.

The plateau-like behaviour of the storage modulus between 120°C and 220°C for the unfilled poly(MMA-co-HEMA) shown in figure 4a), indicates that the pure bulk matrix is built up by high molecular weight polymer species ($M_n > 10^6$ g/mol) with a large number of entanglements. The system with 10 vol.% uncoated 10 nm particles therefore shows the expected enhancement in E' value in the same temperature range caused by the filler loading. However, there is a faster decrease in E' value with increasing temperature compared to the pure matrix system, indicating a faster destruction of entanglements between the polymer chains. In comparison with this, the storage modulus shows a maximum with MPTS and APTS coated particles after going through a minimum at a higher level compared to the unfilled system with increasing temperature. It is generally expected, that the storage modulus decreases with increasing temperature. This phenomenon cannot be attributed to residual monomers and additional curing effects, since IR-measurements proved that the residual monomer content is only about 1 %. An explanation for the effect could be that the particle to polymer bond is strengthened by temperature, leading to less flexible interfacial structures. At temperatures above 210°C an additional flow process starts in the systems with APTS and MPTS coated particles, visible in a sharp decrease in E' . This indicates the presence of lower molecular weight polymer chains with less amounts of entanglements, which tend to flow at lower temperatures.

Figure 4b) shows that there is a large decrease in the peak area under the $\tan \delta$ curve for all filled systems compared to the unfilled polymer. The damping is not only reduced by the pres-

ence of 10 vol.% filler but also by covalent filler/matrix adhesion in the case of MPTS coating. The polymer segments near the filler surface are covalently bound and do not seem to contribute to the glass transition of the matrix. Besides this it should also be noted that the particles in a composite normally contribute to the damping behaviour too, especially by particle/particle and particle/matrix friction as indicated by Nielsen⁹, a fact which can not be quantified here.

In fact it can be concluded for the system with 10 vol.% MPTS coated 10 nm particles that the interparticulate distance in the nanocomposites, which lies in the range of the silica particle diameter, is just too small to be treated as a material in which the filler particles are well separated from each other. The MPTS coated 10 nm silica fillers in the nanocomposite with 10 vol.% seem to be interconnected by their outer covalently fixed polymer shell, resulting in a more network like structure.

4. Conclusions

Thermoplastic nanocomposites based on methylmethacrylate (MMA) and 2-hydroxyethyl-methacrylate (HEMA) as comonomers could be prepared using monodisperse uncoated as well as MPTS and APTS coated 10 nm and 100 nm SiO₂ particles. High dispersity was achievable by increased compatibilization between filler and matrix as shown by transmission electron microscopy. The nanocomposites with MPTS coated 10 nm particles showed the most pronounced effects in rheological and thermal properties. For these systems also an increase in glass transition temperature of about 10°C was detectable compared to the unfilled polymer. In both cases the behaviour could be interpreted by covalent fixation of polymer chain segments at the filler surface produced while synthesis. The results indicate interconnection between the filler particles by entanglements via their outer covalently bound polymer shell.

Acknowledgements

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5. References

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