Preparation and Characterization of Organic/Inorganic Polymer Nanocomposites
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Preparation and Characterization of Organic/Inorganic Polymer Nanocomposites

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Abstract

Inorganic cores, consisting of silica and titania, have been prepared via basic Stoeber synthesis. Those cores have been functionalized, using trimethoxysilyl propylmethacrylate (MPTMS) and introduced into a miniemulsion copolymerization system. Separation of the physically and chemically adsorbed fractions of modified particles was achieved with Soxhlet extraction. By using thermo gravimetric analysis (TGA), the various fractions can be determined. The investigation shows that the MALDI-TOF analysis can only be used to detect the physically adsorbed fractions of modified surfaces.

The miniemulsion consisted of styrene (S) and 2-hydroxyethyl methacrylate (HEMA), styrene sulfonic acid (SSA) or aminoethyl methacrylate hydrochloride (AEMA) as comonomer in varying compositions. The morphology of the products has been investigated by SEM and dynamic light scattering (DLS) measurements. The composition of the products has been investigated by photoacoustic FTIR (PA-FTIR) spectroscopy and elemental analysis. Thermal properties have been determined by TGA and DSC analysis.

Keywords: core shell nanoparticle, composit materials, miniemulsion

1. Introduction

The combination of polymers with inorganic materials is a research field of steadily growing interest and importance. Especially, the synergism of polymeric properties such as elasticity and chemical resistance with organic quality like hardness, stability, electrical conductivity and other properties offer a vast potential concerning new materials and applications.

The preparation of polymer composites does not always lead to the desired synergetic effects. Due to the complementary properties of the components often phase separation occurs, giving rise to unsatisfactory material properties. This problem can be solved by linking organic and inorganic part covalently. Typical coupling agents for this purpose are substituted alkyl trialkoxysilanes and tetraalkoxysilanes.

Different styrene and acrylate based organic/inorganic polymer composites incorporating magnesium hydroxide were successfully synthesized using MPTMS as coupling agent and $MgCl_2$ as inorganic precursor [1, 2]. The polymer composites were prepared by free radical emulsion polymerization.

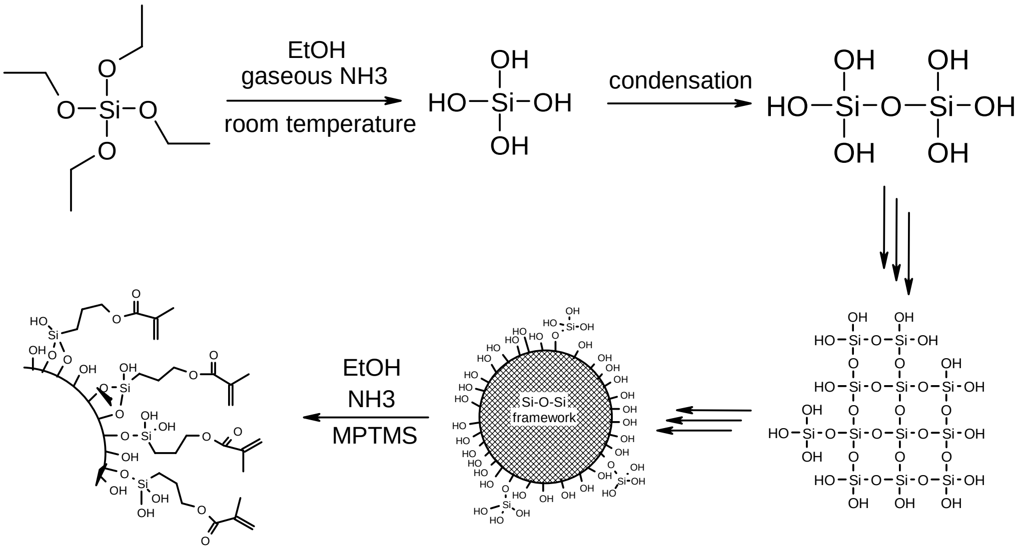
Another interesting field of research is devoted to the encapsulation of inorganic particles by polymers, the so called core-shell particles.

The main focus of our study are the preparation of functionalized hybrids. Therefore, inorganic cores were produced, varying from silica cores to Al_2O_3 - , ZrO_2 - and TiO_2 - cores with polymerizable functionalities. In our study, MALDI-TOF mass spectrometry was used to investigate the polysiloxane shell around modified particle. Those cores have been copolymerized in miniemulsion with functionally comonomers. This leads to functionalized emulsion core shell products. The comonomer concentration was varied to achieve different polymer compositions and thus different rates of functional groups at the surface. The received emulsions were investigated with respect to thermal stability, rate of functionalization at the surface and particle size distribution, using a dynamic light scattering machine, equipped with a cross correlation system which enables the investigation of emulsions in reaction-state concentration.

2. Results

Two different inorganic cores have been synthesized via basic Stoeber synthesis.[3,4]

Both inorganic cores, the SiO_2 core as well as the TiO_2 core, have been functionalized with MPTMS under condensation conditions. Scheme 1 shows a condensation and functionalization process exemplarily given on tetraethoxysilane (TEOS).



Scheme 1: Condensation and functionalization process exemplarily shown on silica, using MPTMS for in-situ functionalization

The nanoparticle functionalization using MPTMS follows in situ. Figure 1 shows the particle size distribution of silica and titania nanoparticles before and after functionalization. The mentioned polydispersity index (PDI) represents the quotient of X_{90} divided by X_{50}.

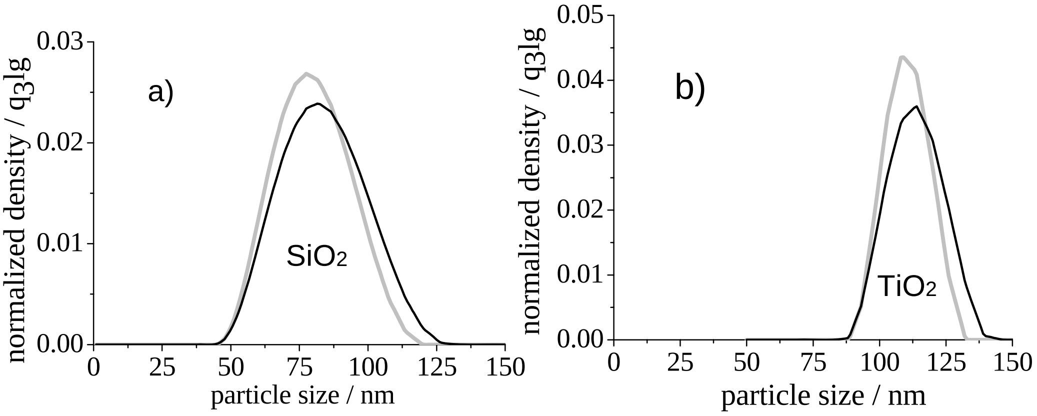
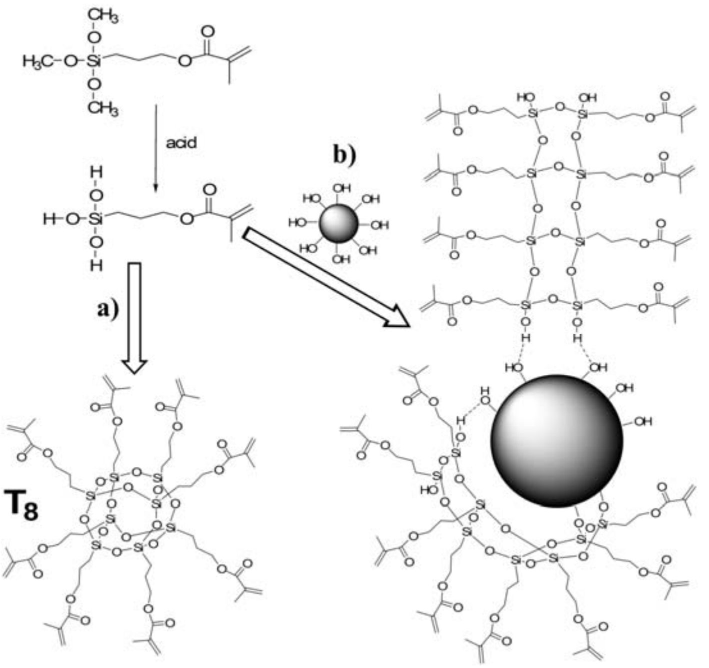


Figure 1: a) Particle size distribution of non modified silica (gray) with an average particle size of 77 nm (PDI=1.2) and MPTMS modified silica (black) with an average particle size of 79 nm (PDI=1.4);
b) Particle size distribution of non modified titania (gray) with an average particle size of 112 nm (PDI=1.1) and MPTMS modified titania (black) with an average particle size of 115 nm (PDI=1.4).

The average particle size increases in both cases by a few nm due to the attached methacryloyl groups. However, no aggregation is observed during particle formation or functionalization. Thermogravimetrical analysis of the washed and dried product indicates 9 wt.% of organic compound covalently bond onto the particle surface which can be calculated to a number of 200000 methacryloyl groups on the surface of a particle with a diameter of 100 nm or 0.47 mmol methacryloyl groups per gram inorganic compound.

Scheme 2 shows the modification reaction. MPTMS is hydrolyzed by acidic or basic catalysis. In the next step the resulting trihydroxysilane can homopolymerized to form silsesquioxane structures which can be expressed in generally formula $(RSiO_{3/2})_n$ (n = for even). Or they can interact with a free hydroxyl group of the nanoparticles. In this case there are two possibilities: either the formation of Si-O-Si bonds from the organosilane to the modified particle or an interaction via hydrogen bonds. This is the reason why the polysiloxane shell around the particle consists of physically and chemically adsorbed fractions. The organosilanes form three-dimensional siloxane structures which are either bound to the particle or cross-linked among each other.

The Separation of the physically and chemically adsorbed fractions of modified particles was achieved with a Soxhlet extraction. By using thermo gravimetric analysis, the various fractions can be determined.



Scheme 2: Scheme of hydrolysis/condensation reactions. First the trialkoxysilane (MPTMS) was hydrolyzed; a) homocondensation to form silsesquioxane structures like T_8 species $(RSiO_{3/2})_8$, b) silane modification of nanoparticle

The MALDI spectra (Fig. 2) of the particle before extraction and the Soxhlet extract show the same series like the MPTMS homo condensate.

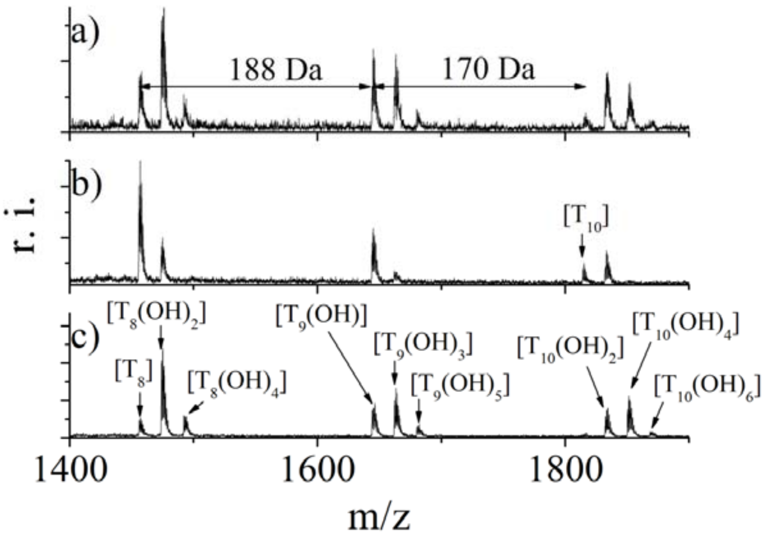


Figure 2: MALDI spectra of the fractions in the mass range of 1400 – 1900 Da;
a) MPTMS modified particle before extraction;
b) Soxhlet extract; c) MPTMS homocondensate as a cross check (all molecules were observed as sodium adducts)

Highly condensed oligomeric silsesquioxane structures which contain more than 20 repeat units could be observed. The investigation shows that the MALDI-TOF analysis can only be used to detect the physically adsorbed fractions of modified surfaces[5].

These cores have been copolymerized under miniemulsion conditions using sodium dodecyl sulphate (SDS) as surfactant and potassium persulphate (KPS) as initiator with styrene as matrix monomer and HEMA, SSA and AEMA (Fig. 3) as comonomer [5]. Apart from diffusion controlled effects in a swollen polymer shell, only these functional groups that are situated on the surface of the core shell particle are accessible for further reactions. To increase the specific surface area as well as the structural integrity of the core shell particle, the acrylate based crosslinker tetraethylene glycol diacrylate (TEGDA) has been introduced.

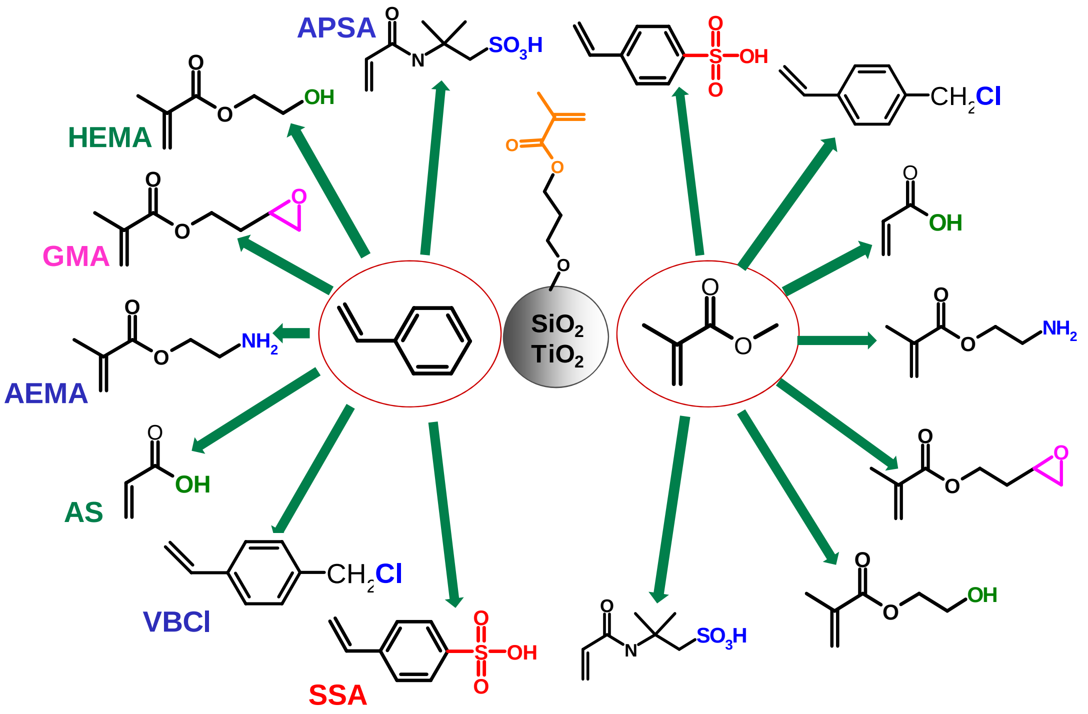


Figure 3: Composition of the comonomers

The used monomers for copolymerization were S or MMA with HEMA, AEMA , SSA and other see Fig. 3 in a variation of 5 mol% over 10 mol% to 20 mol% functional monomer related to S or MMA.

In the case of poly(S-*co*-HEMA) polymer composites with silica, the HEMA content could be varied from 8 mol% to 20 mol% which could be adjusted in the monomer feed. The morphology of the S-*co*-HEMA polymer composite exhibits a typical miniemulsion product of spherical particles with a narrow particle size distribution (Fig. 4).

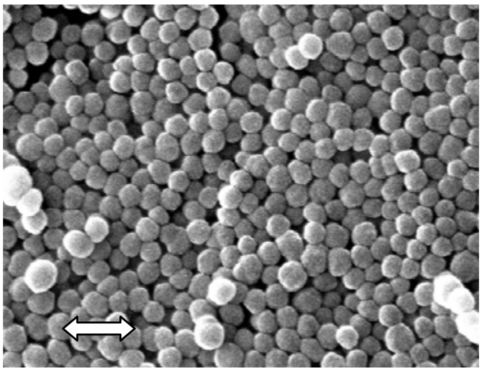


Figure 4: SEM image of S-*co*-HEMA polymer composite (HEMA content 19.8 mol%) with an average particle size of 150 nm. Arrow size is 500 nm.

However, higher incorporation rates than poly(S-*co*-HEMA) polymer composites could be achieved in the poly(S-*co*-AEMA) system with either silica or titania.

Dynamic light scattering measurements of the miniemulsion lattices prove the successful incorporation of the inorganic cores into the miniemulsion droplet. All silica based polymer composites show particle sizes between 120 nm and 150 nm with a low PDI, whereas the silica precursor itself showed an average particle size of 79 nm. Hence, all silica nanoparticles have been incorporated into the emulsion droplet and each droplet contains only one silica particle. This can be proved by the SEM image of the composite.

The titania based polymer composites with poly(S-*co*-SSA) show rather large particles with particle sizes of 300 nm to 500 nm. In this case, it is possible that two or more titania particles could have entered the emulsion droplet. Still the product remains stable and no aggregation has been observed.

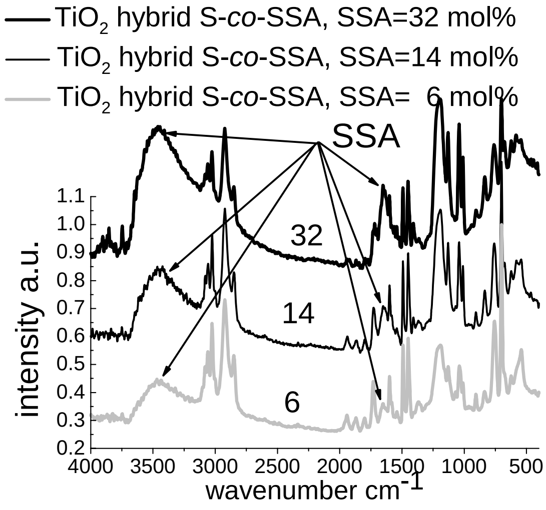


Figure 5: Photoacoustic infrared spectra of TiO_2 hybrid S-co-SSA core shell particle with different SSA content

However the IEC measurements confirm the integration of SSA into the polymer composite. The accessible SSA groups reach up to 75 % of the calculated maximum due to the fact that the added crosslinker TEGDA increases the specific surface area by forming porous and highly swellable shells around the inorganic core of this system.

4. Conclusion

The presented three step method of inorganic particle preparation, consequent functionalization and finally embedding into a miniemulsion copolymerization system offers an easy way to prepare core shell particles with a wide range of functionalities at the surface. These products have a high potential as reactive filler materials in advanced polymers composites or as reactive polymer films.
The investigation shows that the MALDI-TOF analysis can only be used to detect the physically adsorbed fractions of modified surfaces.

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