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Compatibilization of inorganic particles for polymeric nanocomposites. Optimization of the size and the compatibility of ZnO particles

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Summary

The synthesis of in-situ hydrophobic functionalized ZnO nanoparticles via an emulsion process is systematically investigated. Different parameters are varied, such as precursor salt concentration and ultrasonification, to optimize the size and the size distribution of the ZnO particles. Particles with a size below 25 nm and surrounded by a hydrophobic polymer shell can be easily obtained. The influence of the polymeric shell on the compatibility with different polymeric matrices is described. Due to the small size of the inorganic particles and the excellent hydrophobization, highly transparent inorganic/organic nanocomposites can be obtained by spin-coating and extrusion.

Introduction

In recent years the design and synthesis of new polymer nanocomposites has gained increasing attention in polymer and material science. Combining the properties of two or more materials allows the preparation of new high performance polymer based materials. Depending on the required properties and fields of application, a wide spectrum of nanocomposites to suit each need are known. [1-12] The incorporation of a small amount of inorganic nanoparticles can dramatically change the bulk properties of a polymer such as stiffness, impact toughness [13], gas (vapor) permeability [14], adsorption spectrum or refractive index. [15]

Since polymer composite materials are multiphase systems, there is a need to achieve a full compatibility between the components. While preparing a polymer organic/ inorganic nanocomposite, it was found to be advantageous if the inorganic phase possessed a polymer layer, which was able to entangle with the chains of the given polymer matrix. [16-18] Inherently many polymer blends are incompatible, while only a few binary systems of compatible polymers are known. Statistical copolymers on the other hand, may be tuned to be miscible with various polymers or other statistical copolymers. [19] Well known examples are the blends of poly(styrene-*stat*-acrylonitrile) and poly(styrene-*stat*-maleic anhydride) [20] or blends of poly(methyl methacrylate) and poly(styrene-*stat*-acrylonitrile) [21]. In these examples the basic homopolymers are not compatible with the other components. Statistical copolymers can also be applied for functionalization on the surface of inorganic nanoparticles, which are used for the preparation of polymer nanocomposites, and provide better compatibility with a polymer matrix. We have shown that in the presence of statistical amphiphilic copolymers, ZnO nanoparticles can be obtained in inverse emulsion from zinc acetate and NaOH. [22] Our investigations have demonstrated that such a method is also applicable for the preparation of other surface functionalized inorganic nanoparticles. [23] The obtained particles were completely hydrophobic and could be redispersed in organic media. It was demonstrated that for achieving full redispersability of the particles molecular weight of the copolymers should not exceed 15 000 Da. The objectives of these contributions was the demonstration of the applicability of such a technique for an in-situ particle functionalization, as well as the utilization of such particles for nanocomposite preparation.

In the following we report a systematic study of the parameters that influence particle size of ZnO nanoparticles, prepared with amphiphilic statistical coloymers via an inverse emulsion technique. The influence of the precursor concentration as well as the power of ultrasound, which was used in the emulsion preparation, on the particle size and distribution is investigated. Also the influence of the surface bound polymer layer on the compatibility of the synthesized ZnO nanoparticles with various polymers is described. A comparative study between different methods for nanocomposite preparation, spin coating from a dispersion of the ZnO particles in a polymer solution and an extrusion process, is additionally presented.

Experimental part

Materials and methods

Ethylhexyl methacrylate (95% purity), dimethylaminoethyl methacrylate (97% purity), toluene, chloroform, AIBN, 1,3-propanesultone (97% purity) were purchased from Aldrich. Monomers were distilled in vacuo ($5*10^{-1}$ mbar) before polymerization. AIBN, 1,3-propanesultone and inorganic compounds were used as received.

UV/Vis spectra were recorded on a UV/Vis spectrophotometer Perkin-Elmer Lambda 15. GPC measurements were obtained on a chromatograph, equipped with a set of SD+ columns (MZ-Analysentechnik Mainz, Germany). THF was used as eluent. Molecular weights were calculated in respect to PMMA standards. For the preparation of the emulsions a Brandson-250D sonifier, operating at a frequency of 20kHz, was used. Thermogravimetric analysis was carried out on a Mettler TGA851e apparatus. The measurements were carried out under nitrogen and a heating rate of 10K/min. The particle size was determined by means of dynamic light scattering on a Zetasizer Malvern 3000. Nanocomposite films were investigated by electron microscopy on a scanning electron microscope LEO 1530 Gemini. Ultramicrotomed composites were studied on a transmission electron microscope Zeiss EM-912 Omega. Nanocomposite films were prepared with a spin coater from Headway Research Inc. A Haake MiniLab twin blade extruder was used for the preparation of the extrudates.

Preparation of amphiphilic copolymer

The detailed description of the synthesis of the statistical copolymer of ethylhexyl methacrylate (HexMA) and the functionalisized dimethyaminoethyl methacrylate (DMAEMA) **1** (Figure 1) can be found elsewhere. [22,24] According to our previous

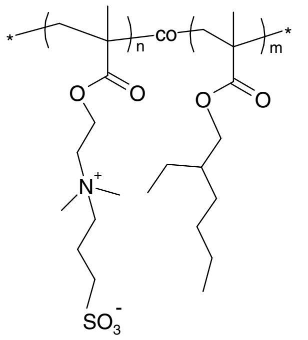


Figure 1. Chemical structure of the amphiphilic copolymer **1**.

studies a polymer with a molecular weight of Mn = 9500 Da and Mw = 15700 Da was synthesized. It contained 16 % of charged sulfobetain groups.[22]

Particle preparation

From two solutions, each containing 100 mg of the copolymer **1** in 13.6 ml of toluene, two emulsions (Emulsion 1 and Emulsion 2) were obtained by adding of the corresponding aqueous phases to the toluene solution (see Table 1). Emulsion 1 contained zinc acetate, which is the precursor to the inorganic solid being generated. Emulsion 2 comprised the sodium hydroxide, which is necessary for the precipitation. The biphasic mixtures were stirred for 30 minutes at 1000 rpm, followed by sonication for three minutes. Afterwards, both emulsions were combined and again treated with ultrasound for three minutes. The solvents, water and toluene, were evaporated at 60°C under reduced pressure (100-150 mbar). The obtained solid was dried *in vacuo* ($1 \cdot 10^{-2}$ mbar), washed with water to remove side products and other possible impurities and dried *in vacuo* again. The hydrophobic ZnO particles were redispersed by refluxing the dried particles in toluene for 1 day. [22]

Table 1. Compositions of the emulsions and characteristics of the prepared inorganic particles.

Sample	Aqueous phase of emulsion 1		Aqueous phase of emulsion 2		ZnO content, w/w%[a]	Power, W	Particle size, D[1,0]± σ nm [b]
	aq. phase, g	$Zn(Ac)_2$, mol/l	aq. phase, g	NaOH mol/l			
ZnO(1)	0,5	0,3	0,5	0,6	5,8	70	22±14
ZnO(2)		0,6		1,2	9,6	70	32±24
ZnO(3)		1,2		2,4	22.4	70	37±30
ZnO(4)		1,2		2,4	21.2	60	45±35
ZnO(5)		1,2		2,4	20.8	50	61±45
ZnO(6)		1,2		2,4	21.6	40	82±60

a) determined by TGA b) determined by Dynamic Light Scattering, Toluene, 90°

Preparation of nanocomposites

Formation of nanocomposite films

0.2 g of ZnO (Table 1, Sample 3) particles were mixed with 0.2 g of the corresponding polymer matrix, followed by the addition of 3 g of toluene. After refluxing this mixture for 1 day, it was used for film preparation. Prior to film casting, which was accomplished by spin coating, the dispersion of ZnO in the polymer solution was filtered through a 5µ Millipore filter.

Incorporation of the particles by extrusion

Extrudates were prepared by means of melt compounding at 190°C, using a Haake MiniLab twin blade extruder. Before extrusion, a mixture of 95% (w/w) of the corresponding polymer matrix and 5% (w/w) of modified ZnO particles was mixed in a ball mill. (Table 2)

Table 2. Conditions for composite preparation by extrusion.

Sample	Polymer matrix	ZnO Sample	Extrusion temperature, °C	Extrusion time, min	Extrusion speed, min^{-1}
ZnO/PMMA	PMMA	ZnO(3)	220	10	210
ZnO/PP	PP	ZnO(3)	145	10	210
ZnO/PS	PS	ZnO(3)	220	10	210

Results and discussion

Influence of the precursor concentration on ZnO particle size

During the preparation of inorganic particles in inverse emulsions using conventional surfactants, the ionic strength of the aqueous solution plays an important role. [13] It was shown that with growing ionic strength (i.e. salt concentration), the size of the droplets and of the resulting inorganic nanoparticles increased drastically as the emulsions became unstable and aggregation occurred. [25,26] If amphiphilic statistical copolymers were used, a stable emulsion could be obtained. As long as the ratio between aqueous phase, oil phase and emulsifier was constant the size of the resulting droplets remained independent from the salt concentration (typically in the herein described experiments 120 nm). The influence of ionic strength could be seen for the size of the nanoparticles. (Figure 2) In this case an increase of the particle size was observed (between 22 to 37 nm (Table 1)). The emulsions were stable with higher salt concentrations, which can be attributed to the higher amount of salt in one droplet. One may conclude that contrary to conventional low molecular surfactants, the salt concentration (or ionic strength respectively) has practically no influence on the emulsifier properties of the polymer, i.e. the emulsion stability, and as consequence, on the size of the emulsion droplets. The fact that the particles grow in size is obvious, since more of the precursor is emulsified in one droplet.

Influence of the ultrasound power

As mentioned earlier, the size of the inorganic particles prepared in inverse emulsions is directly related to the diameter of the emulsion droplets. [27,28] The

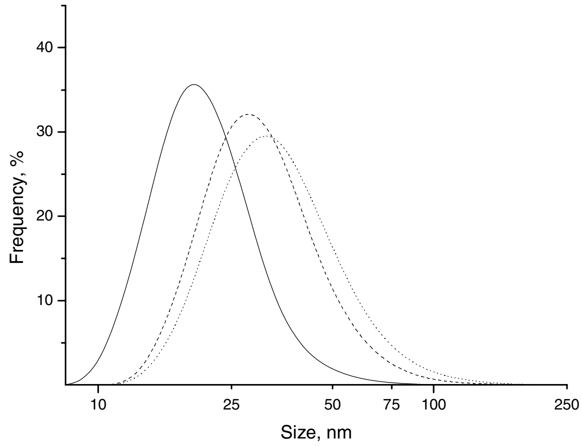


Figure 2. Number distribution of ZnO particles in toluene, prepared with various precursor concentrations. Samples — ZnO(1), – – – ZnO(2), ……… ZnO(3). Particle size distributions, obtained by DLS.

energy, which was consumed during emulsion preparation, also defines the size of the water droplets in the oil phase. [29-31] In the case of thermodynamically stable emulsions (microemulsions), this influence is not profound, because the system tends to relax into the most thermodynamically stable state after the energy source has been switched off. [32] It is also known that during formation of an emulsion the total surface area is directly related to the consumed energy, while the created surface is reciprocally related to the size of the emulsion droplets. [27,33] Thus, if the relaxation processes in the freshly prepared emulsion occur on a much longer time scale than the experiment, one can expect that the amount of consumed energy can determine the emulsion droplet size and the size of inorganic particles. In Figure 3a the particle size distributions of the ZnO nanoparticles prepared with different power of the ultrasound are presented.

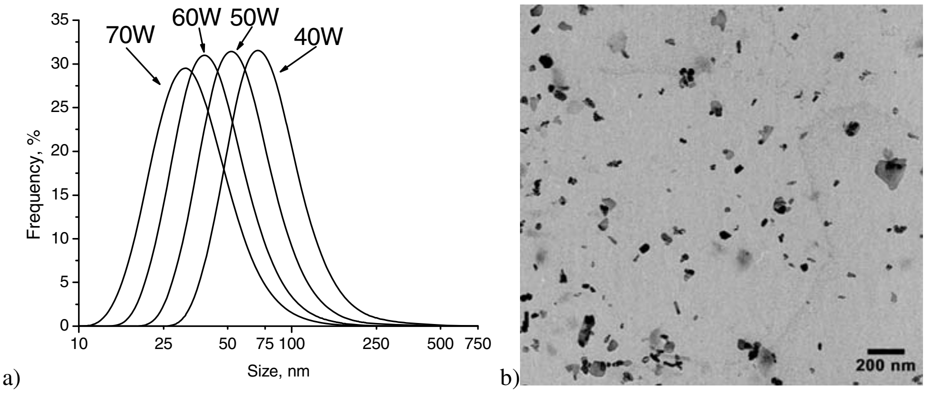


Figure 3. a) Size distributions (number average) of ZnO nanoparticles prepared with various power of ultrasound. Particle size distributions were determined by dynamic light scattering. Samples ZnO(3) (70W), ZnO(4) (60W), ZnO(5) (50W), ZnO(6) (40W). b) TEM image of the ZnO dispersion in toluene. Sample ZnO(3).

It can be seen that decreasing the power of the ultrasound results in an increase in the particle size and the particle size distribution. The observed behaviour can be well explained in terms of kinetic stability of the obtained emulsions. It can be assumed that the mobility of amphiphilic copolymers, which are adsorbed on the emulsion droplet surface, is very low. Thus, once an emulsion droplet is formed, the polymer becomes kinetically frozen and keeps its dimensions after the ultrasound has been switched off. Consequently, the size of the emulsion droplets is defined by the amount of energy which was introduced into the system during the ultrasonication.

Nanocomposite films with ZnO nanoparticles prepared by spin coating

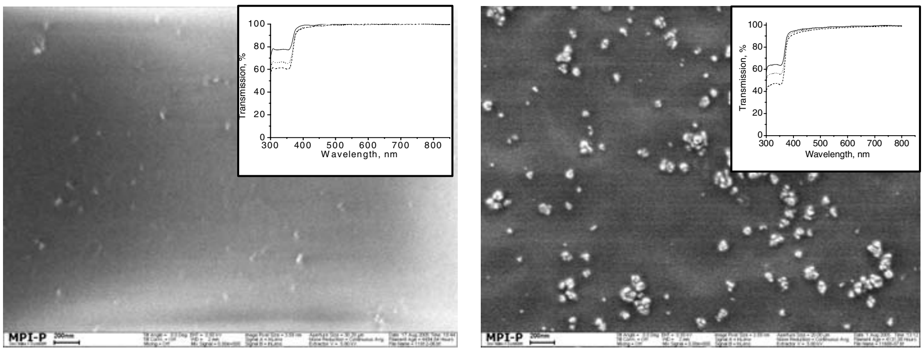
In the preparation of a nanocomposite, the compatibility between its components is the central issue. Upon the surface hydrophobizing of an inorganic particle, one eliminates the obvious incompatibility between hydrophilic particle and hydrophobic polymer matrix. However, such simple hydrophobization of the particle surface is often non-sufficient. [12] One should take into account the compatibility between the given polymer matrix and the polymer layer adsorbed on the particle surface. As mentioned previously, some polymers are inherently incompatible with each other. The compatibility was found to depend on the molecular weight, or in other words, on the number of segments of interacting polymers. Modification of the inorganic surfaces by means of adsorption of statistical copolymers can benefit nanocomposite preparation. Due to the specifics of the copolymer adsorption (formation of loops and tails), the length of copolymer segments, which interact with the polymer matrix, is comparatively low. One can expect that particles with the statistical copolymer on the surface are compatible with a larger number of polymers in comparison with particles which have a long surface bound polymer chain.

The compatibility of statistical copolymer (**1**)-functionalized ZnO nanoparticles with the matrix was studied by preparing nanocompoite coatings and subsequent investigation by scanning electron microscopy (SEM) and UV-vis spectroscopy.

Poly(2-ethylhexyl methacrylate) – PHexEMA, polymethylmethacrylate – PMMA and polystyrene – PS were chosen as polymer matrices. In the case of PHexEMA, good component compatibility was expected. When the surfaces of the nanocomposite films between functionalized ZnO and PHexEMA were investigated by SEM, a homogeneous and aggregate free particle distribution through the polymer matrix was observed (Figure 4a). The obtained nanocomposite films were highly transparent and demonstrated a good UV absorption.

When PMMA was used as a matrix, a slight particle aggregation was observed. As can be seen from the figure 4b, particles are homogeneously dispersed, but as well as primary particles, a few secondary particles are also present. Such small aggregates consist of several primary particles and do not exceed 200 nm in diameter. Polystyrene was found to be an inappropriate polymer matrix for the ZnO particles modified by the statistical copolymer **1**. The obtained films were quite turbid. UV-Vis Spectroscopy reveals strong scattering of the light. (Figure 5)

A study of the films by scanning electron microscopy demonstrates the coexistence of big aggregated particles along with primary ZnO particles of an average diameter of 50-60 nm. (Figure 5).



a) b)

Figure 4. a) Scanning electron microscopy image of ZnO/poly(2-ethylhexyl methacrylate) nanocomposite films. Inset: UV-VIS spectra of the obtained nanocomposite films. Film thickness (—) 0.82μm; (·····) 1.37μm; (‒‒‒) 1.68μm. b) Scanning electron microscopy image of ZnO/poly(methyl methacrylate) nanocomposite films. Film thickness (—) 0.92μm; (·····) 1.45μm; (‒‒‒) 1,.9μ. Inset: UV-VIS spectra of the obtained nanocomposite films.

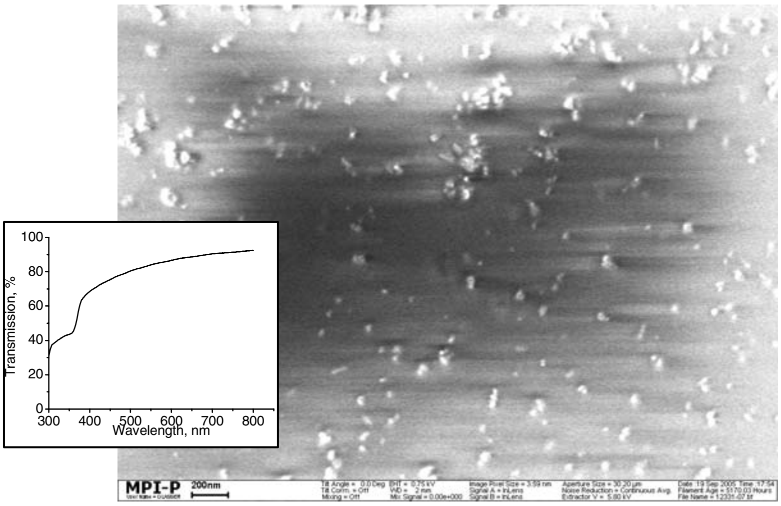


Figure 5. Scanning electron microscopy image of ZnO/polystyrene nanocomposite films. Inset: UV-VIS spectrum of a ZnO/polystyrene composite film. Film thickness 1.52μm

Nanocomposites with ZnO nanoparticles prepared by extrusion

Preparation of nanocomposite films by spin coating is very important for preparation of coatings, but extrusion is a conventional process for the preparation of bulk materials. We have also investigated the ZnO nanoparticles, which are functionalized with the statistical copolymer **1**, in an extrusion process. PMMA, PP and PS were chosen as the corresponding polymer matrices. The Figure 6 represents the TEM images of ultramicrotomed polymer nanocomposites.

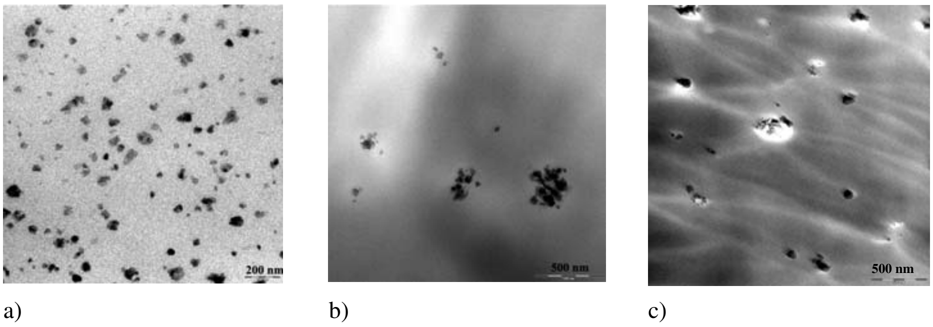


Figure 6. TEM images of ultramicrotomed composites, prepared by extrusion of surface modified ZnO nanoparticles by extrusion in melt. Samples: a) ZnO/PMMA; b) ZnO/PP; c) ZnO/PS.

In contrast to the spin coating process, the ZnO particles were found to be homogeneously distributed in PMMA and aggregate-free, which is probably due to the high shear forces occurring during processing. In the case of PP or PS, particle aggregation occurs because of the poor compatibility between the polymer matrix and the polymer layer of the particle surface. Results from the film formation, as well as from the extrusion processing, demonstrate that the hydrophobic 2-ethylhexyl methylmethacrylate is not a suitable compatibilizer for a polymer matrix such as styrene or PP. It is assumed that amphiphilic copolymers containing styrenes as hydrophobic monomer should improve the compatibility and so the particle distribution in the matrix.

Summary

Regarding the preparation of ZnO nanoparticles, we have systematically investigated parameters that can influence the size characteristics during the particle preparation. Contrary to conventional low molecular weight surfactants, high precursor concentrations in the emulsion process could be successfully stabilized for particle preparation. The size of the water droplets in the oil phase did not vary with different salt concentrations, which means that in a given system the size of the resulting inorganic particles can be controlled just by the variation of the concentration of the inorganic precursor salt. In a simple way, the size can also be controlled by the power of the ultrasound applied during emulsion preparation. With increasing power, the droplets get smaller and so smaller ZnO particles can be obtained.

Good surface functionalization of the ZnO with the statistical copolymer **1** facilitates the incorporation of these particles into various polymer matrices. High quality transparent nanocomposite films with PHexEMA could be obtained by spin coating, and with PMMA as the matrix polymer, transparent films were obtained. The incorporation of the surface modified inorganic nanoparticles into polymer matrices by means of an extrusion procedure were undertaken. While utilizing PMMA as the matrix polymer, a homogenous and almost aggregate-free composite was obtained. In the case of PP and PS, the particles tend to agglomerate as a consequence of the poor compatibility of the surface layer with the polymer matrix. In order to be completely compatible, amphiphilic statistical copolymers containing as the hydrophobic part the monomer units of the polymeric matrix have to be synthesized. As our surfactants are prepared by radical polymerization, this can be easily achieved by using styrene or MMA as comonomer in the polymerization of the DMAEMA. Such copolymers are currently being synthesized and used in nanoparticle formation. A comparative study of material properties (transparency, mechanical stability, flame retardance) of the nanocomposite materials, prepared with these particles, will be presented in the future.

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