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Silica/polyethylene nanocomposites from catalytic emulsion polymerization

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INTRODUCTION

Nanocomposites consisting of polymers and inorganic materials are of strong interest. Nanoscale inorganic particles can improve polymer properties such as thermal stability or mechanical strength or introduce new properties like enhanced scratch resistance, which can not be obtained by simple mixing of polymer with a bulk inorganic material. Among the various synthetic routes for the preparation of nanocomposite materials, heterophase polymerization offers a suitable way to obtain nanocomposites with controlled compositions, shapes, sizes and surface properties.[1] By performing heterophase polymerizations in aqueous systems (e.g. suspension, dispersion or emulsion polymerization) in the presence of inorganic particles, polymer-inorganic nanocomposite particles can be prepared.[1] In most of these synthetic routes, an appropriate modification of the surface of the inorganic material is a prerequisite to achieve sufficient compatibility of the inorganic particles with the polymer. This modification typically involves covalent attachment of hydrophobic groups or copolymerizable organic groups on the particle surface. Emulsion polymerization, especially miniemulsion polymerization allows for the synthesis of composite particles with various morphologies.[2-4]

We have previously reported the synthesis of nanocomposites of polyethylene with silica nanoparticles by catalytic polymerization in emulsion.[4] The polyethylene portion was either linear, semicrystalline or highly branched, amorphous, depending on the choice of catalyst. While only moderate to low degrees of crystallinity are desirable to enable film formation, in the case of the amorphous polymer molecular weight was also very low ($M_n \sim 10^3$ g·mol^{-1}; this is due to both branch formation and chain transfer being a result of enhanced β-hydride elimination) and the material was liquid. In this paper we present the synthesis of nanocomposite materials which consist of branched polyethylene with higher molecular weight ($M_n \geq 10^4$ g·mol^{-1}) and silica particles with different surface modifications.

EXPERIMENTAL

General procedures. All manipulations were carried out under argon of 99.998 % purity using standard Schlenk line techniques or in a glovebox under a nitrogen atmosphere. All glassware was dried at 70 ℃ overnight or treated with a heat gun under high vacuum prior to use. Solvents were dried and distilled under argon. Tetraethyl orthosilicate (TEOS) was purchased from Aldrich and vacuumtransferred prior to use. The organosilanes trimethoxy(7-octen-1-yl)silane (**1**), trimethoxy(octyl)silane (**2**) and trimethoxy-(phenyl)silane (**3**) were purchased from Aldrich. Molecular weights and molecular weight distributions of the polymers were determined with a Polymer Laboratories PL-GPC 220 instrument. 1,2,4-trichlorobenzene containing 3,5-di-tert-butyl-4-hydroxytoluene as a stabilizer was employed as the solvent at a flow rate of 1.0 mL min^{-1}. GPC was performed at 160 ℃ vs. linear polyethylene standards. Thermogravimetric analysis (TGA) was performed under an O_2 atmosphere on a Netzsch STA 429 at a heating rate of 5 K min^{-1}. The silicas and composites were investigated in the temperature range of 20-800 ℃. EF-TEM was carried out on a Carl Zeiss Libra 120 instrument at an acceleration voltage of 120 kV. Samples were prepared by spincoating a drop of the composite dispersion on a carbon-coated grid. Volume averaged particle sizes were determined by DLS using a Malvern Nano-ZS ZEN 3600 particle sizer. Volume averaged particle sizes were calculated from the autocorrelation function using the Malvern 3.30 software.

Preparation and modification of silica particles. Silica particles were prepared according to the Stöber method in ethanolic ammonia solution.[4,5] A volume average particle size of 50 nm with a polydispersity index of 0.06 was determined by DLS. The obtained silica dispersion was used without further purification for lipophilic modification. The surface of the silica nanoparticles was modified with one or two types of functionalities (Figure 1).

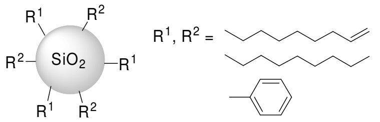

Figure 1. Surface modifications of the silica nanoparticles: The particle surface is modified either with one functionality type (R^1 and R^2 = octyl or 7-octen-1-yl) or with two types of functionalities (R^1 = octyl or 7-octen-1-yl; R^2 = phenyl).

Surface modification of the silica nanoparticles with a single type of functionality was performed according to [4]. Surface modification of the silica nanoparticles with two types of functionalities was achieved in a two step reaction. In the first step the silica dispersion from the Stöber-synthesis was mixed with 16 μmol m^{-2} of organosilane **1** or **2** and stirred for 24 h at room temperature. This corresponds to two fold the silanol concentration on the particle surface, which was estimated to be 8 μmol m^{-2}.[6] After a solvent transfer from ethanol to toluene by distillation the premodified silica particles were reacted in a second step with 16 μmol m^{-2} of organosilane **3** for 48 h at room temperature. The solution was concentrated under reduced pressure (to 1-1.5 g in 90 mL) and then purified from excess organosilane by a series of centrifugations (2 h at 6500 rpm). To remove remaining water the modified silicas were redispersed in 90 mL of toluene. The solvent was removed in vacuo and the silica particles were dried in vacuo for 3 h. Finally, the modified silica particles were redispersed in dry toluene.

Synthesis of SiO_2/polyethylene composite dispersions. The catalyst precursor [κ^2-*N*,*O*-3-[((2,6-Diisopropylphenyl)imine)methyl]-1,1,1,5,5,5-hexafluoropent-3-ene-2-one-4-olato]methyl(pyridine)-nickel(II) (**4**) was prepared according to [7]. To the catalyst solution in toluene was first added hexadecane (0.3 mL), then the silica dispersion (0.3 g silica in 3 mL of toluene) and one third of an aqueous solution of surfactant (1 g SDS in 95 mL of water). The resulting biphasic mixture was ultrasonicated to afford the "catalyst/silica miniemulsion". The remaining two-thirds of the SDS solution and the miniemulsion were then introduced into a mechanically stirred 250 mL steel reactor equipped with a heating/cooling jacket controlled by a temperature sensor dipping into the reaction mixture. The reactor was pressurized with ethylene (p = 40 bar) under stirring (1000 rpm), while rapidly heating to the polymerization temperature (50 ℃). The pressure was kept constant during the polymerization by feeding monomer. After 1 h the reaction was stopped by cooling and releasing the gas pressure. The obtained dispersions were filtered through a funnel with glass wool prior to further workup. The solids contents were determined using a moisture analyser and by precipitating the silica/polymer composites from the reaction mixtures by addition of methanol. The solid residue was separated by filtration, dried in vacuo at 50 ℃ for 12 h and analyzed by GPC, DSC and TGA.

DISCUSSION

Surface modification of the silica particles by covalent binding of the organosilanes is evident by the solubility of the resulting silica particles in toluene. TGA analysis of dry samples of the different silica particles afforded a total weight loss of 11.6 % for unmodified silica particles (due to the removal of residual ethoxy moieties from the Stöber-synthesis and calcination of the silica), 19.7 % for octyl modification, 19.4 % for octyl-phenyl modification and 19.3 % for octenyl-phenyl modification. Also, the efficiency of the method employed has been demonstrated by ^{13}C and ^{29}Si NMR previously.[4]

The electron-poor catalyst precursor employed is compatible with polymerization in the presence of silica particles. Colloidally stable dispersions are obtained. The polyethylene portion of these dispersions is branched with a moderate crystallinity, as is evident from the melting peaks observed (Table 1; linear polyethylene for comparison: T_m ca. 135 °C).

Table 1. Synthesis of silica/polyethylene nanocomposites

Entry	Silica modification	wt % SiO_2[b]	M_w[c] [$g \cdot mol^{-1}$]	M_w/M_n[c]	T_m[d] [°C]
1	octyl	19	23 400	3.4	94
2	octyl-phenyl	30	27 300	2.0	88
3	octenyl-phenyl	35	21 100	2.1	85
4	without silica		33 100	2.4	96

[a] Polymerization conditions: T = 50 °C; p(ethylene) = 40 bar; 1 g of SDS, 0.3 mL hexadecane, 0.3 g silica dispersed in 3 mL toluene, H_2O; catalyst: 20 μmol **4** in 2 mL toluene; total volume: 100 mL; reaction time = 2 h. [b] Wt % silica in composite (determined by TGA). [c] Determined by GPC vs. linear polyethylene standards. [d] Determined by DSC.

Molecular weights of the polymer portions in the composites are ≥ 10^4 g mol^{-1}. This similar to the molecular weight obtained in the absence of silica particles (Table 1; entry 4). The amount of SiO_2, as determined by TGA, in the composites ranges from 20 % to 35 % (vs. 80 % for modified silica particles before the polymerization). TEM images reveal the formation of a polymer film. The silica particles are non-aggregated, and homogeneously distributed in the polymer. Note that for non-surface modified silica aggregation would occur.[4] The nature of the organic moieties R^1, R^2 on the silica particles had no observable influence on the colloidal stability of the composite dispersion, or the morphology observed by TEM. A physical interaction, as is present in the case of the non-polymerizable octyl moieties, is sufficient for the homogeneous distribution of the silica particles observed (Figure 2).

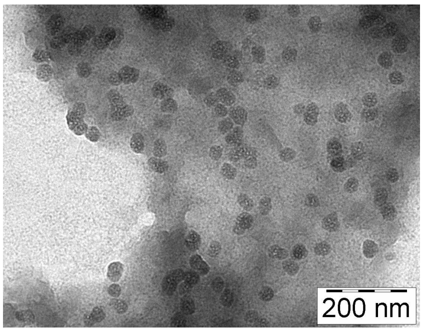

Figure 2. TEM image of a nanocomposite material consisting of octyl-modified silica particles and branched polyethylene.

SUMMARY AND CONCLUSIONS

With the employed catalyst precursor, colloidally stable dispersions of composites, consisting of branched polyethylene and surface modified silica nanoparticles, were obtained by catalytic emulsion polymerization. TEM images revealed the formation of a polymer film in which the silica particles are non-aggregated and homogeneously distributed.

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