New Polyolefin Nanocomposites and Catalyst Supports Based on Organophilic Boehmites

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Summary: PE-boehmite nanocomposites were prepared by means of metallocene-catalyzed in situ polymerization of ethylene in presence of dispersed boehmites which were rendered organophilic by modification with organic acids. Polymerization activity, filler dispersion and mechanical properties of the nanocomposites were investigated as a function of type and concentration of the organophilic boehmites. Sulfonate modified boehmites were used as supports for MAO-activated single site metallocene catalysts and nanocomposite formation via fragmentation of the self-assembled nanoparticles and redispersion during polymerization.

Keywords: boehmites; metallocene catalysts; nanocomposites; polyolefins; supports

Introduction

The dispersion of nanoparticles in polyolefin matrices leads to polyolefin nanocomposites. Compared to conventional fillers, low nanoparticle contents are already sufficient to obtain new or modified material charatacteristics, e.g. increased stiffness, strength and dimensional stability combined with barrier and flame-retardant properties.[1,2] In nanocomposites prepared by conventional melt compounding strong interactions between nanoparticles can cause formation of agglomerates and premature breakdown of the material. For this reason new *in situ* techniques are explored which employ the dispersion of a nano-scaled filler in the reaction medium before and during polymerization.[3] In addition, for large-scale applicability of those synthesis strategies heterogeneous polymerization conditions are a prerequisite in order to ensure good product morphology and to avoid reactor fouling.[4] Therefore it is necessary to immobilize catalyst on the nano-filler. An important objective of this research was to support MAO-activated single site catalysts on self-assembled nanoboehmites which undergo easy fragmentation during polymerization to produce simultaneously polyethylene with controlled morphology and nanocomposites containing uniformly dispersed nanofillers. Organophilic boehmite obtained by modification with *p*-hydroxybenzoic acid was reported by Barron and coworkers to produce boehmite-supported catalysts useful in olefin polymerization.[5]

Experimental

Materials

Cp_2ZrCl_2 (98%) was purchased from Aldrich, *rac*-$Me_2Si(2\text{-}Me\text{-}benz[e]\text{-}Ind)_2ZrCl_2$ from MCat GmbH, Konstanz, MAO (10 wt% solution in toluene) from Crompton GmbH, Bergkamen, heptane and toluene from Merck, ethylene from Gerling Holz u. Co. Handels-GmbH, Hamburg. All Disperal samples (Table 1) were generously provided by SASOL Germany, Hamburg. Solvents were dried by refluxing over Na/K alloy under inert gas and distilled prior to use. Disperal samples were dried under vacuum at 150 °C for 2 h.

Preparation of Heterogeneous Catalysts

0.25 g of the pre-dried support were stirred in 4.3 ml of a 10 wt% MAO solution at

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Table 1.
Properties of Disperal particles.

	modification reagent	modification [wt.%]	crystallite size [nm]
Disperal	none	0	10
DOS1	*p*-toluenesulfonic acid	7	10
DUA2	undecylenic acid	2	8
DSA2	stearic acid	2	6
DUA20	undecylenic acid	20	n.d.
DSA20	stearic aid	20	n.d.

room temperature for 30 min. After sedimentation, the supernatant liquid was removed with a pipette. The solid was then washed by slurring the particles two times in 10 mL heptane. Subsequently, the support was impregnated with the catalyst by addition of the desired amount of a Cp_2ZrCl_2 solution in toluene, and the particles were dried under vacuum. The desired amount of the catalyst particles was then dispersed in 20 mL heptane for injection into the reactor.

The amount of MAO supported on the carrier was determined by the weight increase after MAO treatment.

Ethylene Homopolymerizations

Polymerizations were carried out in a semi-automated double jacket metal reactor. The reactor was filled with heptane and flushed with ethylene until the solvent was saturated. For homogeneous polymerizations, the desired amount of particles was then added to the reactor, followed by one part of the MAO. The mixture was stirred for 30 min and the polymerization was started by addition of the catalyst which was pre-activated with the other part of the MAO. For heterogeneous polymerizations, the reaction was started by addition of the catalyst particle suspension. Ethylene pressure and reactor temperature were kept constant at 3 bar and 40 °C.

Polymer Characterization

Molecular weights and molecular weight distributions of the polymers were determined by SEC using a PL-220 chromatograph (Polymer Laboratories) at 140 °C. DSC Measurements were carried out on a Seiko 6200 thermal analysis system in the temperature range from -70 to 170 °C at a heating rate of 10 K/min. Environmental Scanning Electron Microscope pictures were recorded with an ESEM 2020, Electroscan, Wilmington, USA. TEM measurements were carried out with a LEO 912 Omega transmission electron microscope. DMA measurements were performed on a Rheometrics Solids Analyzer RSA III at 1 Hz and a heating rate of 2 K/min using a dual cantilever geometry applying a strain of 0.1%.

Organophilic Boehmites

Boehmites are composed of Al-O double-layers which are interconnected by hydrogen bonds between the hydroxyl groups (Fig. 1a). The boehmites used in this study are pseudo-crystalline (crystallite size <50 nm) and synthesized by a sol-gel route starting from aluminum alkoxides. This process ensures high purity and, in addition, allows for the chemical modification of the generated boehmites with organic acids such as carboxylic (Fig. 1b) and sulfonic acids (Fig. 1c), thus generating organophilic boehmites.[6] As a consequence of the modification, these boehmites are highly dispersible in organic media.

Polyolefin Nanocomposites *via* Polymerization Filling

Nanocomposites consisting of polyethylene and various boehmites have been prepared by in situ ethylene polymerization using MAO-activated *rac*-Me_2Si(2-Me-benz[e]-

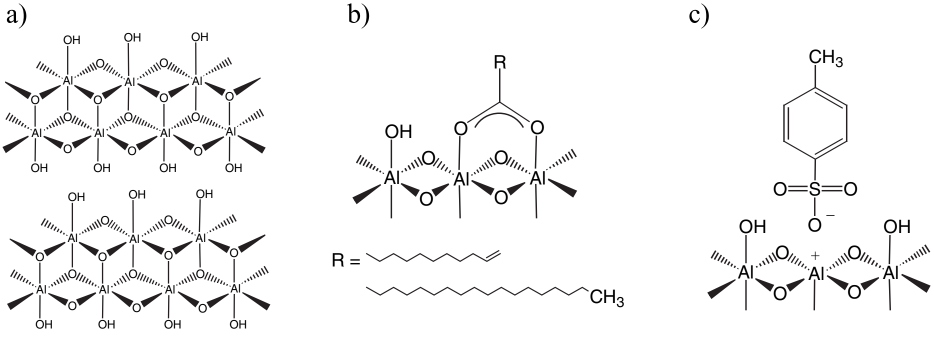

Figure 1.
Structures of (a) pure boehmite; (b) carboxylate modified boehmite; and (c) sulfonate modified boehmite.

Ind)$_2$ZrCl$_2$. Prior to the polymerization the fillers were dispersed in toluene. For the highly modified boehmites DUA20 and DSA20 stable dispersions are obtained due to their organophilicity, whereas the unmodified and low-modified boehmites form suspensions. MAO was added to the dispersions before catalyst injection in order to deactivate polar groups on the boehmite surface which might be detrimental to the catalyst.

Table 2 summarizes the polymerization activities in presence and absence of unmodified and modified boehmites and the resulting polymer properties. In presence of DUA2 the catalyst activity is doubled, in case of Disperal and DSA2 it is increased by 50% and 70% respectively. Instead, in presence of the boehmites with 20% organic modification (DUA20, DSA20) a pronounced decrease of catalyst activity is observed. Interestingly, the in situ formation of the PE nanocomposites leads to centimeter-sized PE particles and prevents reactor fouling which is observed for ethylene polymerization in absence of filler. Within the range of the prepared catalyst families, polymer molar masses and polydispersities were not affected by the presence of fillers during the polymerization.

Table 2.
In situ polymerisation in presence of various boehmites.

	activity [kg mol^{-1} h^{-1}]	M$_w$ [g/mol]	PDI	T$_m$ [°C]
—	33801	295424	5.7	137.3
Disperal	52234	290873	5.7	136.0
DUA2	76541	302297	6.2	136.0
DSA2	57689	296894	5.8	135.4
DUA20$^{*)}$	16072	n.d.	n.d.	135.4
DSA20$^{*)}$	8337	n.d.	n.d.	134.7

Conditions: [Zr] = 3 μmol/L; Al/Zr = 5000; [boehmite] = 5 g/L; ethylene pressure = 3 bar; T = 40 °C; t = 20 min.
$^{*)}$[Zr] = 6 μmol/L; [boehmite] = 3 g/L.

The dispersion of modified and unmodified boehmites in the polymer matrix was analyzed by TEM (Fig. 2). Composites with unmodified boehmite show large clusters of particles and inhomogeneous filler distribution. In case of organically modified boehmites, TEM analyses exhibit that increasing organic modification improves the dispersion of the boehmite in the PE matrix, in accordance with the observed dispersibilities in toluene. In case of DUA2, the distribution is slightly improved compared to Disperal. Increasing the organic modification to 20% (DUA20) results in a fine dispersion of nanoparticles and homogeneous filler distribution.

The mechanical properties of some nanocomposites were investigated by dynamic mechanical analysis (DMA; Fig. 3). The mechanical properties of PE nanocomposites containing 7% DSA20 are slightly improved in comparison to pure PE which can be seen by an increase of E' in the temperature range from −130 °C to +25 °C, indicating a reinforcement effect of DSA20.

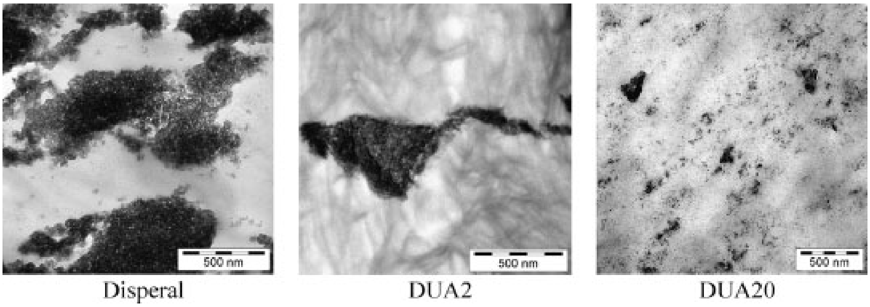

Figure 2.
TEM images of PE-boehmite nanocomposites with increasing organic modification.

This effect is even more pronounced at a filler content of 11% DSA20.

Organophilic Boehmites as Catalyst Supports

With respect to obtain polyolefin nanocomposites under heterogeneous polymerization conditions which are strongly favorable in view of product morphology and high bulk density, DOS1 was tested as support for MAO-activated Cp_2ZrCl_2 catalyst. Therefore, the particles were first treated with MAO followed by impregnation with the catalyst. The same procedure was applied for Sylopol 948, a commonly used silica support. Interestingly, the quantity of immobilized MAO cocatalyst on DOS1 (expressed as aluminum alkyl equivalents) is twice as high as that on conventional silica gel (Table 3). Presumably, this result is explained best by the strong Lewis acid-base interactions between the sulfonate groups of DOS1 and MAO which appear to surpass the interactions of the silica surface hydroxyl groups with MAO.

Thus, applying a similar catalyst loading leads to a much higher Al/Zr ratio in case of DOS1. As a result, the activity of the catalytic system Cp_2ZrCl_2/MAO in ethylene polymerization is higher when supported on DOS1 compared to the immobilization on silica gel. The polymer particles obtained from Cp_2ZrCl_2/MAO supported on DOS1 consist of relatively small sphere-like primary particles which form agglomerates in the size range of 20–100 μm (Fig. 4a). As DOS1 is readily dispersed in many organic solvents, the micrometer-sized support frag-

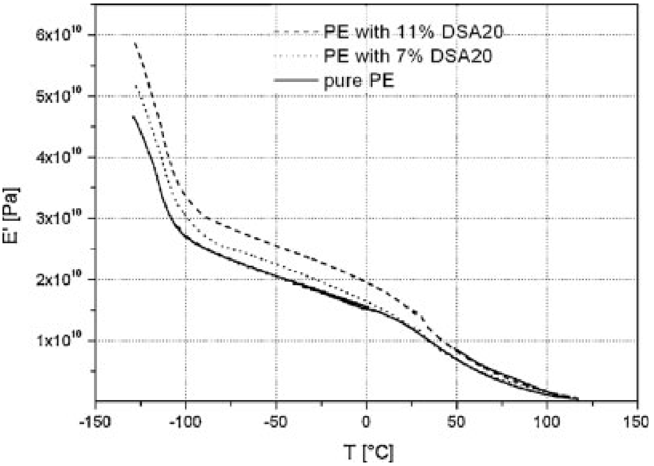

Figure 3.
DMA analysis of some nanocomposites.

Table 3.
MAO content, catalyst activity and polymer properties for DOS1 and silica gel.

	Al Alkyl eq. [mmol/g support]	Cp_2ZrCl_2 [μmol/l]	Al/Zr	activity [kg_{PE}/mol_{Zr}·h]	M_w [10^5 g/mol]	PDI
DOS1	12.1	17	700	990	400	2.9
Sylopol 948	5.7	16	360	740	295	4.8

Conditions: ethylene pressure = 3 bar; T = 40 °C; t = 120 min; V = 500 ml

ments into nano-scaled catalyst particles during catalyst preparation and polymerization. Presumably, these nano-catalysts form sphere-like primary polymer particles upon polymerization of ethylene which appear to agglomerate to larger clusters of irregular shape during the polymerization process. As a result of the good dispersibility of DOS1, the support material is finely dispersed within the formed polymer, showing agglomerate sizes of less than 100 nm (Fig. 4b).

Conclusion

Metallocene-catalyzed ethylene polymerization in presence of dispersed organophilic boehmites resulted in the formation of new PE-boehmite hybrid materials. The presence of unmodified boehmite and boehmites containing only 2 wt.% organic modifiers led to increased catalyst acitivity but inferior filler dispersion in the PE matrix. In contrast, in situ polymerization in presence of boehmites containing 20 wt.% organic modifiers resulted in the formation of nanocomposites with homogeneous nanoparticle distribution and reduced catalyst activity. Furthermore, sulfonate modified boehmite has been shown to be an effective support for MAO-activated metallocene catalysts, enabling the heterogeneous production of boehmite based nanocomposites.

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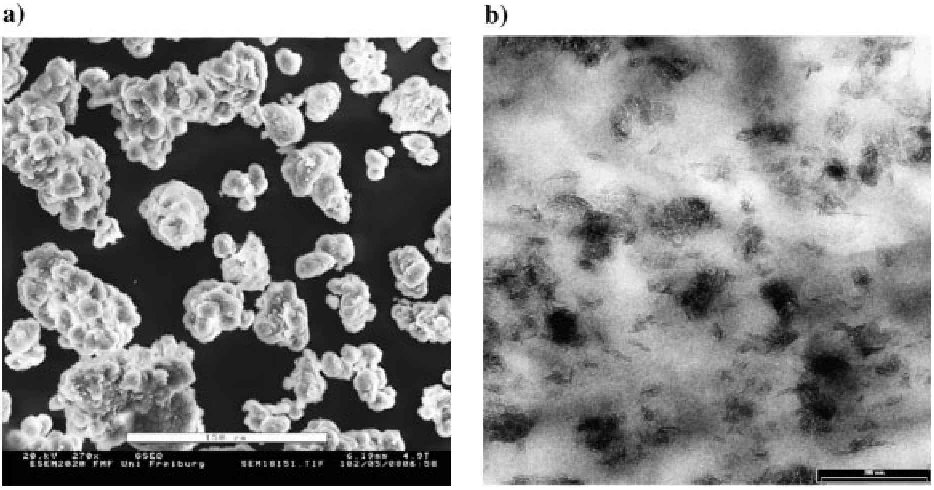

Figure 4.
(a) ESEM image of a representative sample of PE particles prepared with Cp_2ZrCl_2/MAO supported on DOS1; (b) TEM image of the melted PE-DOS1 nanocomposite (bar = 200 nm).

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