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Nanocomposites by *In Situ* Polymerization of Olefins with Metallocene Catalysts

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Summary: Nanoparticles such as silica balls (monopheres), calcium carbonate, carbon nanotubes (CNT) or fibers (CF) are uniformly coated with a film of polyolefins of variable thickness using metallocene/methyl-aluminoxane (MAO) catalysts. The catalyst is adsorbed on the filler surface, leading to a polymer growth directly on its surface. Highly filled and stiff nano composites, basing on polyethene (PE) and syndiotactic or isotactic polypropene (sPP/iPP) with a content up to 85 wt% of silica or 7 wt% of multi-walled carbon nanotubes (MWCNT) are obtained. MWCNT treated with MAO in the same way form a heterogenous cocatalyst for the preparation of iso- and syndiotactic PP/MWCNT composites, too. The uniformity of the dispersion depends primarily on the pretreatment of the filler.

Keywords: metallocene catalysts; polyolefine; reinforced nano composites

Introduction

New materials with exellent properties could be synthesized by filled polyolefins with nanosized, rigid particles or fibers [1]. The first step of preparation is the absorbence of solved MAO onto the filler surface [2, 3]. This process is supported by interactions between MAO and functional groups, such as hydroxyl, containing heteroatoms, which are located on the filler particals. These groups can react with MAO by the formation of covalent oxygen aluminum bond, without deactivating effects for the catalysts. The anchored MAO is still able to form a catalytically active complex with the metallocene. Thus a heterogeneous cocatalyst is formed (Figure 1). The polymer is growing directly on the filler surface and can cover the particles perfectly [4]. The thickness of the polyolefin film can be controlled in between nm and μm range by the polymerisation time. The in-situ polymerization gives a better filler dispersion especially at higher filler contents than simple melt compounding [5, 6]. Especially, fillers with high aspect ratio like carbon nanotubes tend to stay aggregated during this process because of a high surface energy and numerous π-π interactions between the tubes. The in-situ polymerization of monomers in the presence of nanofillers is a promising approach for a more homogeneous distribution due to of the close contact of polymer and filler during synthesis. As known from the literature metallocene/MAO catalysts are also excellent tools in the synthesis of tailored microstructures and tacticities of polypropylenes [4, 7]. PP with an isotactic, syndiotactic or atactic configuration are obtained by using C_2-, C_{2V}- or C_S-symmetric zirconocenes [8, 9]. Polyolefin nanocomposites are expected to have a high potential as strong materials with novel properties, especially in the automotive industries, e.g. as anti-static devices [10]. Intrinsic properties of the nanofillers like electrical conductivity or barrier properties are some additional advantages. Some

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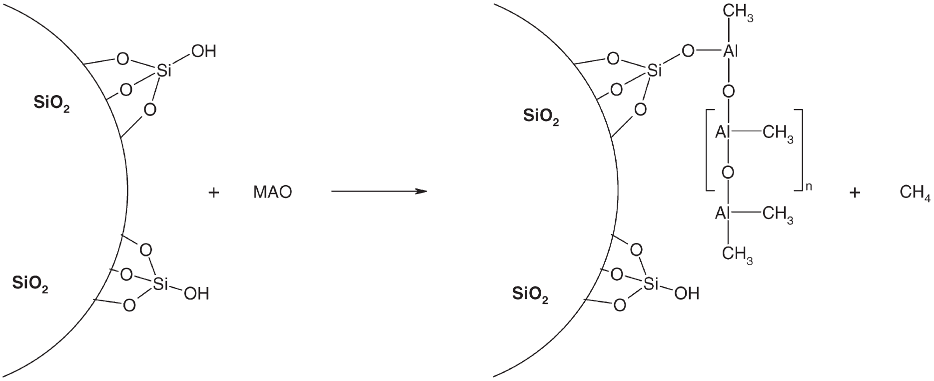

Figure 1.
Reaction between MAO and the silica surface. The MAO is covalently anchored due to the formation of an aluminum ester.

disadvantages of some neat polymers e.g. a low durability or spinnability can be improved by using nanofillers.

Materials and Methods

In our experiments monophere (ball of silica, diameter 200–250 nm), carbon fibers (CF, diameter 200 nm, length 0.5–3 mm), carbon nanotubes (MWCNT, diameter 15–25 nm, length 50 μm) and oxidized MWCNT (Preparation [11, 12]: H_2SO_4/HNO_3, 3:1, 90 °C, 3 h) were used as fillers. Before polymerization, the fillers were separated and then treated by MAO. The MAO reacts partially with the OH-groups of the filler surface (Figure 1).

Catalytically active centers are formed after adding the zirconocenes or other transition metal complexes. The thickness of the polyolefins can be controlled by the pressure of ethene or propene and by the polymerization time [13].

The carbon nanofibers and multiwalled carbon nanotubes (MWCNT) were sonicated in a toluene suspension using a Bandelin Sonopuls homogenizer HD 2200 equipped with a KE 76 sonotrode. The amplitude (10–50%) and the sonication time (5–120 min) were varied to achieve an optimum distribution of fillers in the polymer. The sonicated fillers were then either introduced directly into the toluene-charged reactor (without pre-reaction) or stirred with 2 ml of MAO-solution (c = 100 g/l) for 24 h (with pre-reaction).

All polymerizations were carried out in a 1l glass reactor that had been heated to 90 °C for 1 h and then flushed with argon. The reactor was charged with 200 ml of toluene and heated to the desired polymerization temperature. In case of the polymerizations without pre-reaction, MAO and the fillers were introduced into the reactor and the dispersion was then saturated with ethane or propene at the desired pressure using a mass-flow controller (Brooks instruments, 5850 series).

The reaction was started by injection of the metallocene. In case of the polymerizations with pre-reaction, 2 ml of TIBA solution (1 mmol/ml toluene) were added to the toluene before saturation with propene. The pre-activated catalyst (filler/MAO/metallocene) was introduced into the reactor when saturation was completed using a pressure lock. Polymerizations were typically quenched after 45 min by addition of 5 ml of ethanol. All polymers were stirred with a quench-solution (water, ethanol, hydrochloric acid) over night, filtered, washed and dried under vacuum at 60 °C.

Melting temperatures, T_m, were determined by differential scanning calorimetry (DSC) with a DSC 821e (Mettler-Toledo) from the second heating cycle at a heating rate of 20 $K \cdot min^{-1}$. Crystallization temperatures, T_c, were determined by DSC from the cooling curve (cooling rate

10 K · min^{-1}) after complete melting at 200 °C for 5 min. The half-time of crystallization were analyzed of isothermal DSC experiments. The samples were quenched to the desired isothermal crystallization temperature (cooling rate 40 K · min^{-1}) after they were entirly molten at 200 °C for 5 min. Electron microscopy was performed on a Leo 1530 FE-SEM. For studies on morphology composite powder and cryo-fractures were used. Tensile testing was performed on a Zwick Z101 equipped with a long distance extensiometer according to DIN EN ISO 527.2 with a crosshead speed of 10 mm · min^{-1}. The yield strength was calculated from the data after normalization to the sample dimensions. Sample bars were prepared by hot pressing of the nanocomposite powder at 200 °C.

Results and Discussion

By this method highly filled nanocomposites from polyethene and polypropene can be obtained with a monopheres (silica) content of up to 85 wt %.The metallocene used for sPP based nanocomposites was [(p-MePh)$_2$C(Cp)(2,7-bis^{t}BuFlu)]ZrCl$_2$ and for composites with iPP matrix *rac*-[Me$_2$Si-(2-Me-Ind)$_2$]ZrCl$_2$ was used as catalyst. The experiments with monopheres as filler were carried out at polymerization temperatures between 0 and 60 °C. The activity was, as expected, the highest at 60 °C with 3000 kg$_{PP}$/mol$_{Zr}$ · h · mol$_P$/l. The molecular weight was 230 000 g/mol at 60 °C and 790 000 g/mol at 0 °C. Such combined materials are stiff and hard. Most particles are surrounded by a thin film of polyolefin with a thickness of 30 to 100 nm as seen in Figure 2.

Carbon fibers and carbon nanotubes can be covered also within isotactic or syndiotactic polypropene. Because of the hydrophobic character of the carbon surface, the polymer is drawing on the fiber [4]. This leads to a reinforced combined polymer with special properties.

The electron micrographs indicates a good adhesion of the polymer to the nanofibers (Figure 3) or MWCNT.

The melting and crystallization temperatures were especially influenced by the presence of carbon nanotubes in the nanocomposites. The crystallization temperature (T$_c$) rises with rising filler content. This effect is especially pronounced for the samples prepared with pre-reacted nanotubes. The crystallization temperature lies between 10 and 20 K above that of the neat syndiotactic polypropylene (91 °C). In case of an iPP/MWCNT nanocomposite there is

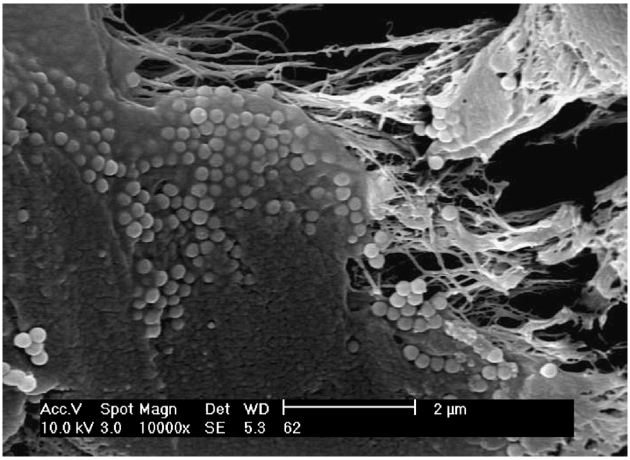

Figure 2.
Monophere particles covered with syndiotactic polypropene.

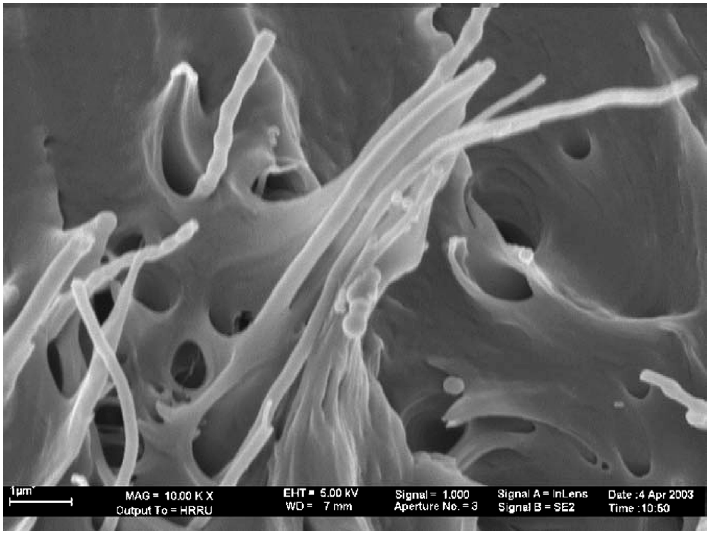

Figure 3.
Carbon fibers wetted with sPP. The fibers were separated from each other. It can be seen that the fillers are wetted well. It is also obvious that polymer is present in between the CF.

a comparable effect. Pure iPP had a T_c of about 111 °C while the addition of 0.1 wt.% MWCNT led to an increased T_c by 4 to 5 K. At higher filler contents the enhancement of the crystallization temperature raised rapidly to a certain extent of 9 K above pure iPP which was reached at a MWCNT content of 1.5 to 2 wt.% (Figure 4). Higher CNT contents did not led to a further increase of the crystallization temperature. A comparable but less distinct effect was found for the melting temperatures of sPP/MWCNT composites.

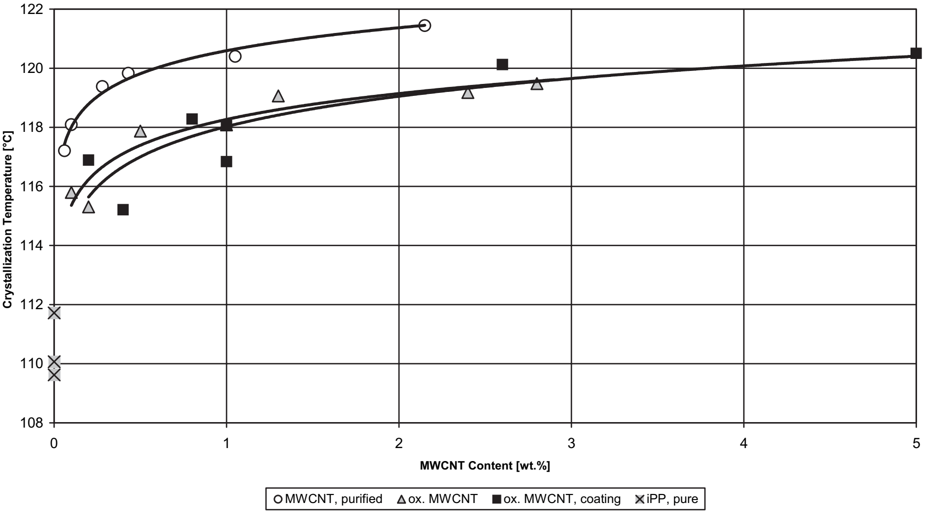

Figure 4.
Crystallization temperatures of the pure iPP and the different nanocomposites in dependence on the MWCNT content. Purified and oxidized MWCNT and also a coating process [14] with heterogenous MAO were compared.

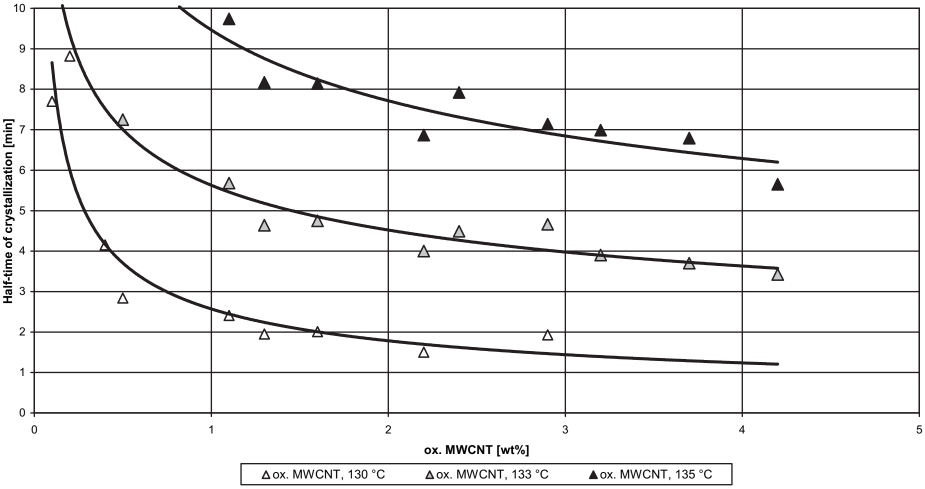

Figure 5.
Half-time of crystallization of iPP/ox. MWCNT nanocomposites at different crystallization temperatures.

The carbon nanofibers had a lesser impact on the crystallization behavior of the examined PP. In these composites, the crystallization temperature was increased by a maximum of 10 °C compared to neat PP. The increase in crystallization temperature by addition of nanofibers and nanotubes to the polypropylene is in accordance with the results presented in references [6] and [13] and is an expression of the nucleating effect of the fillers.

Another expression of the nucleating effect was found in the half-time of crystallization ($t_{0.5}$), which plays an important role during the industrial processing og these materials. By reduction of the cooling time required for part solidification, cycle times could be shortened. Figure 5 shows the dependence of $t_{0.5}$ on the ox. MWCNT content at different isothermal crystallization temperatures. At the temperatures shown neat iPP did not crystallize or it took too long to provide reliable results, while the crystallization of the obtained nanocomposites was too fast in the range of temperature where iPP gave adequate

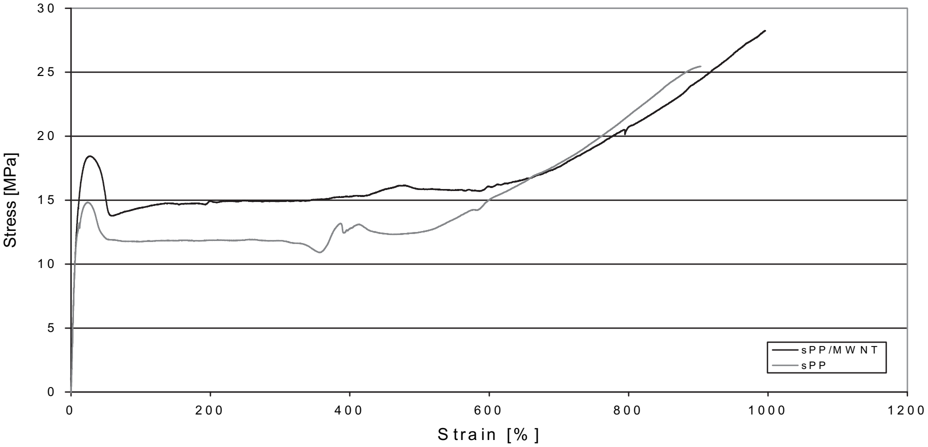

Figure 6.
Tensile properties of neat sPP and sPP/MWCNT composites.

results. However in Figure 5 it can be seen that the half-time of crystallization was reduced significantly with low amounts of oxidized nanotubes at all temperatures. At 130 °C, for instance, $t_{0.5}$ was 8 min for a iPP/ox. MWCNT composite with 0.1 wt.% filler content. When 2.5 wt.% were incorporated, $t_{0.5}$ was reduced to only 1.5 min. When the percentage of MWCNT was raised to more than 3 wt.% no appreciable reduction of $t_{0.5}$ was obtained anymore. That seems to be the lower limit. The half-time of crystallization of CNT nanocomposites was found to decrease in all cited references with regard to the pure polymers [5, 15, 16, 17].

Mechanical Properties

The present investigations point to improvements of the tensile properties of the composite upon addition of MWCNTs to the polymer matrix. First evidence can be seen in the determined stress/strain-behavior in Figure 6. The yield strength of the sPP/MWNT-nanocomposite containing 0.6 wt.% MWCNT is considerably higher than in neat PP. The strain to failure is also increased notably.

Conclusion

Metallocene/MAO catalyzed via in-situ polymerization was an excellent way to prepare sPP/silica and PP/MWCNT-nanocomposites. It could be shown that the uniformity of the dispersion was dependent on the pretreatment of the filler and the polymerization procedure. The incorporation of MWCNTs as well as CF and monopheres into PP led to an increase of the crystallization temperature. First mechanical tests point to a significant improvement of the tensile properties of the PP/MWCNT composites compared to neat polypropene.

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