JZUS

PE/CaCO₃-nanocomposites synthesized by in-situ polymerization

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Abstract: Polyethylene-nanocomposites with $CaCO_3$-weight fractions from 0 to 15 wt.% were prepared by in-situ polymerization with $Me_2Si(Ind)_2ZrCl_2$/MAO metallocene catalysts. A high activity especially in the presence of TIBA was observed. The morphology was investigated by using raster electron microscopy (REM) showing that the $CaCO_3$-nanoparticles are uniformly distributed. The melting temperatures and the crystallization temperatures are not much influenced by increasing filler content.

Key words: Nanocomposites, $CaCO_3$, Polyethylene, Metallocene catalysts
doi:10.1631/jzus.2007.A0987   **Document code:** A   **CLC number:** TM215

INTRODUCTION

A lot of research has focused on nanocomposites during the past years. The nanocomposites are interesting because they can exhibit novel properties. Exceptionally strong materials could be synthesized by the combination of a soft polymer matrix with nanosized, rigid filler particles (Mülhaupt *et al*., 2001). Nanoparticles dispersed in a polymer matrix cause an increase of some physical properties of polymers, such as a dramatically improved stiffness, high gas barrier properties, significant flame retardancy and better gloss (Zilg *et al*., 1998; Beyer, 2001; Bharadwaj, 2001; Gorrasi *et al*., 2003; Andrews *et al*., 2002; Kharchenko *et al*., 2004).

The nanocomposites can be produced by solution blending (Andrews *et al*., 2002), the in-situ synthesis of the nanofillers in the presence of the polymer (Wei *et al*., 2004), melt-compounding and in-situ polymerization.

The in-situ polymerisation approach should lead to a better dispersion of nanoparticles in the polymer matrix, because the active centers for the polymerization are linked directly to the surface of the particles. Metallocene catalysts are predestinated for this procedure (Kaminsky, 1996; 2004; Scheirs and Kaminsky, 2000). They are soluble in hydrocarbons and can be adsorbed from a solution on the surface of the nanoparticles. First the methylaluminoxane is adsorbed and reacts partially with the OH-groups on the surface. By the addition of the metallocene the active center is formed. If ethene or propene is added the particles are covered by films of polyolefins of different thickness, depending on the polymerization time and other polymerization conditions. In the past we have synthesised some polypropylene nanocomposites by in-situ polymerisation (Kaminsky and Wiemann, 2003; 2006; Wiemann *et al*., 2005; Kaminsky *et al*., 2006).

EXPERIMENTAL DETAILS

A suspension of the dried calcium carbonate nanoparticles Socal P3 from Solvay chemicals GmbH with an average diameter of 200 nm were sonicated in an ultrasonic bath for 15 min by room temperature. Methylaluminoxane (MAO) was added to the mixture and the suspension was stirred at room temperature for 24 h. Then the complete suspension was transferred under argon into the reactor.

All polymerizations were carried out in a büchi glass reactor. The pressure of ethene was 3.5 bar. The system was kept at a temperature of 60 °C, the normal

volume was 200 ml of toluene, as a solvent. For the reactions with triisobutylaluminium (TIBA), a TIBA-solution was added first to the solvent, followed by the nanoparticle/MAO-suspension in toluene. The solution was satured with ethene at 3.5 bar. The polymerization was started by adding a toluene solution of 5×10^{-8} mol $Me_2Si(Ind)_2ZrCl_2$-catalyst. Polymerizations with and without TIBA were typically quenched with ethanol. The polymers produced in the presence of TIBA were stirred with a solution with ethanol and sodium hydroxide overnight, the polymers produced without TIBA were stirred with a solution with ethanol over night. All polymers were filtered, washed and dried under vacuum at 60 °C for 12 h.

ANALYTICAL TECHNIQUES

The melting temperatures and the crystallization temperatures were measured by a differential scanning calorimetry (DSC) with a DSC 821e from Mettler-Toledo. The DSC was calibrated with cyclopentane ($T_m=-93.9$ °C), mercury ($T_m=-38.8$ °C), gallium ($T_m=29.8$ °C), indium ($T_m=156.6$ °C) and zinc ($T_m=419.5$ °C). Samples of 4~8 mg were used for DSC analysis. Melting temperatures were determined from the second heating cycle at a heating rate of 20 °C/min. Crystallization temperatures were determined by DSC from the cooling curve after complete melting at 200 °C for 5 min. The cooling rate was 10 °C/min.

The electron microscopy and the EDX-measurements were coupled and performed on an LEO 1525. The samples were coated with a several-nanometer layer of gold from a sputtering machine.

ACTIVITY

Fig.1 shows the activity of the in-situ polymerization with $CaCO_3$-nanoparticles as fillers. The polymerization activity decreases with increasing wt% of the filler from 0 till 5 wt%. The activities stand constant for runs with 5~15 wt% of calcium carbonate filler by 200000 kg polymer/(mol cat.·h·mol$_{mon}$/L) without TIBA. The polymers produced with TIBA have higher activity than those without TIBA. 600000 kg PE/(mol Zr·h·mol$_{mon}$/L)

can be reached, which is more than the half of the ethene polymerization without nanocomposites with $[Me_2Si(Ind)_2]ZrCl_2$/MAO. The TIBA eliminates contaminations and also builds a complex with the oxygen of the calcium carbonate. So the calcium carbonate cannot deactivate the catalyst so fast.
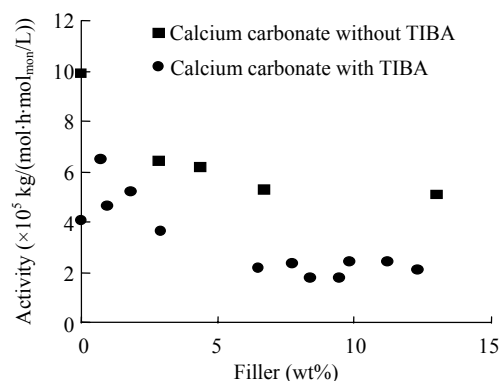

Fig.1 Activity of PE/CaCO₃-polymers with and without TIBA

MORPHOLOGY

Figs.2 and 3 show that the nanoparticles were encased of polyethylene. The nanoparticles are uniformly distributed. The nanoparticles were connected of the PE-filaments. No agglomeration of the $CaCO_3$-nanoparticles can be seen.
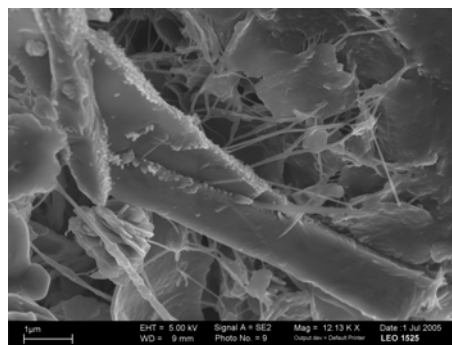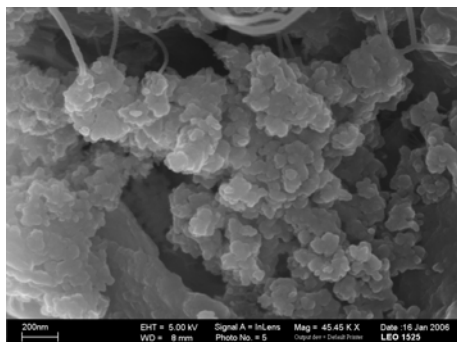

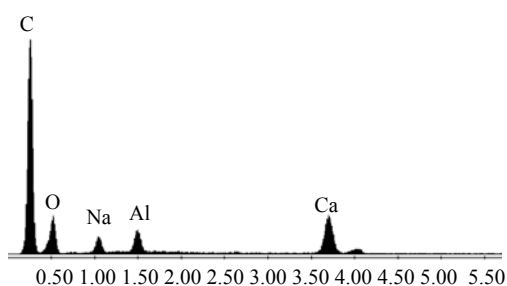**Fig.2 Nanocomposite with 8.60 wt% calcium carbonate prepared with TIBA as a scavenger**

EDX

With EDX it was possible to investigate the presence of $CaCO_3$ in the polymer. EDX was used to confirm the presence of all elements in the nanocomposites.

Fig.3 Nanocomposite with 9.85 wt% CaCO₃ prepared without TIBA

Figs.4 and 5 show EDX-spectra. The first EDX-spectrum shows a nanocomposite produced in the presence of TIBA and the second one in the absence of TIBA.

The EDX-spectrum in Fig.4 shows carbon, oxygen, aluminium, sodium and calcium. The nanocomposites, produced with TIBA, and which were stirred with sodium hydroxide and ethanol, after the quenching with ethanol to eliminate the aluminium of the TIBA, have sodium and aluminium in the polymer. The polymer, produced without TIBA, and stirred only in ethanol has after the quenching only small amounts of aluminium from the MAO in the polymer (Fig.5).


Fig.4 Nanocomposite with 8.60 wt% calcium carbonate and TIBA
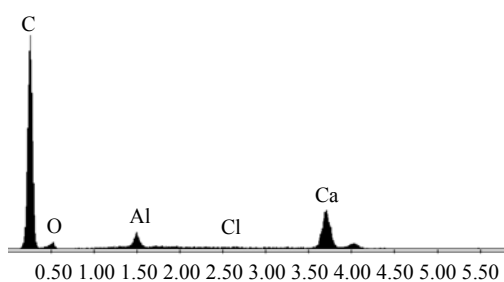
**Fig.5 Nanocomposite with 9.85 wt% calcium carbonate and without TIBA**

MELTING POINTS

For the characterization of the polymers the DSC was used to investigate the crystallization behaviour of the polymers. Fig.6 shows the melting points of the nanocomposites. The melting points of the nanocomposites vary between 133 °C and 142 °C. The variation of the melting points depends on heterogenous distribution of the calcium carbonate and on the variation of the molecular weight of the polyethylene. By higher filler contents (over 3%) the melting points for runs without TIBA are lower than the homo polyethene.
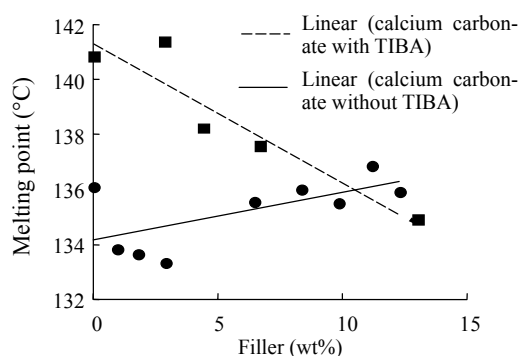
Fig.6 Melting points of PE/CaCO₃-polymers with and without TIBA

CRYSTALLINITY

The crystallinity is calculated consider to 100% crystal material (PE: 290 J/mol). Fig.7 shows that the crystallinity of the nanocomposites is between 30% and 60%. The higher amount of the calcium carbonate in polymer causes lower crystallinity of the polymer. Perhaps the chains are shorter with more filler.
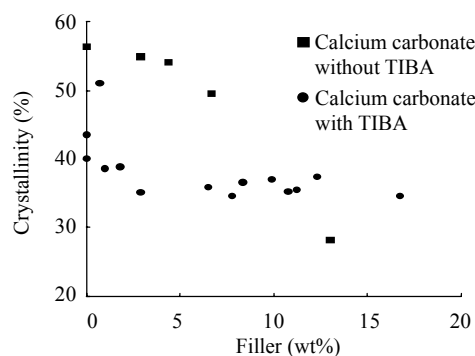
Fig.7 Crystallinity of PE/CaCO₃-polymers with and without TIBA

The polymers prepared with TIBA have a higher crystallinity than those without TIBA, because of the use of TIBA as a scavenger. The values decrease slightly from 57% to 30% with increasing amounts of $CaCO_3$. The homopolymer shows a value for the crystallinity of 60%. In contrast to this the crystallinity is nearly constant for composite materials prepared without TIBA.

CONCLUSION

Nanocomposites of polyethene and $CaCO_3$-nanoparticle were prepared by in-situ polymerization with metallocene/MAO catalysts. The nanocomposites can be produced in the presence and absence of TIBA. The activity decreases first with increasing wt% of the filler to be constant by higher filler content. The activities of the polymers with 5~15 wt% of calcium carbonate are similar. The polymers produced with TIBA have higher activity than those without TIBA.

The REM investigation shows that the nanoparticles were wrapped up with polyethene. All particles were surrounded by the polymer. No agglomeration can be seen. This is the advantage and difference to the preparation by melt compounding. The melting points of the nanocomposites are between 133 °C and 142 °C. The crystallinity is between 30% and 60% and for small amounts of filler similar to polyethylene without nanoparticles.

References

Andrews, R., Jaques, D., Quian, D., Rantell, T., 2002. Multi-wall carbon nanotubes: synthesis and application. *Acc. Chem. Res.*, **35**(12):1008-1017. [doi:10.1021/ar010151m]

Beyer, G., 2001. Nanocomposites. Part 2. A novel flame protection system for polymers. *Gummi, Fasern, Kunststoffe*, **54**(5):321-325.

Bharadwaj, R.K., 2001. Modeling the barrier properties of polymer-layered silicate nanocomposites. *Macromolecules*, **34**(26):9189-9192. [doi:10.1021/ma010780b]

Gorrasi, G., Tortora, M., Vittoria, V., Kaempfer, D., Mülhaupt, R., 2003. Transport properties of organic vapors in nanocomposites of organophilic layered silicate and syndiotactic polypropylene. *Polymer*, **44**(13):3679-3685. [doi:10.1016/S0032-3861(03)00284-2]

Kaminsky, W., 1996. New polymers by metallocene catalysis. *Macromol. Chem. Phys.*, **197**(12):3907-3945. [doi:10.1002/macp.1996.021971201]

Kaminsky, W., 2004. The discovery of metallocene catalysts and their present state of the art. *J. Poly. Sci.*, **42**(16):3911-3921. [doi:10.1002/pola.20292]

Kaminsky, W., Wiemann, K., 2003. Polypropene/silica-nanocomposites synthesized by in-situ polymerization. *Expected Materials for the Future*, **3**(11):6-12.

Kaminsky, W., Wiemann, K., 2006. Polypropene nanocomposites by methallocene/MAO catalysts. *Composite Interfaces*, **13**(4):365-375. [doi:10.1163/156855406777408557]

Kaminsky, W., Funck, A., Wiemann, K., 2006. Nanocomposites by *in situ* polymerisation of olefins with metallocene catalysts. *Macromol. Symp.*, **239**(1):1-6. [doi:10.1002/masy.200690084]

Kharchenko, S.B., Douglas, J.F., Obrzut, J., Grulke, E.A., Migler, K.B., 2004. Flow-induced properties of nanotube-filled polymer materials. *Nat. Mater.*, **3**(8):564-568. [doi:10.1038/nmat1183]

Mülhaupt, R., Engelhardt, T., Schall, N., 2001. Nanocomposites - auf dem Weg zur Anwendung. *KU Kunststoffe*, **91**(10):178-190.

Scheirs, J., Kaminsky, W. (Eds.), 2000. Metallocene-Based Polyolefins, Volume 2. Wiley Series, Chichester.

Wei, L., Tang, T., Huang, B., 2004. Synthesis and characterization of polyethylene/clay-silica nanocomposites: A montmorillonite/silica-hybrid-supported catalyst and *in situ* polymerization. *Journal of Polymer Science Part A: Polymer Chemistry*, **42**(4):941-949. [doi:10.1002/pola.11053]

Wiemann, K., Kaminsky, W., Gojny, F., Schulte, K., 2005. Synthesis and properties of syndiotactic poly(propylene)/carbon nanofiber and nanotube composites prepared by in situ polymerization with metallocene/MAO catalysts. *Macromol. Chem. Phys.*, **206**(15):1472-1478. [doi:10.1002/macp.200500066]

Zilg, C., Reichert, P., Dietsche, F., Engelhardt, T., Mülhaupt, R., 1998. Plastics and rubher nanocomposites based upon layered silicates. *Kunststoffe*, **88**(10):1812-1820.