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Synthesis of nanocomposites by *in situ* metallocene-catalyzed polymerization of propene

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ABSTRACT

Organo-modified aluminophosphate with kanemite-like structure was used for the *in situ* synthesis of polypropylene (PP) nanocomposites performed by metallocene-catalyzed polymerization. The filler exhibits a layered structure with different organic pending groups arranged in the interlayer space. Melt-compounded composites with the same filler were prepared for comparison.

X-ray diffraction (XRD) and transmission electron microscopy (TEM) proved exfoliation of the filler in the PP matrix and formation of nanocomposite after *in situ* synthesis. In contrast, in the melt-composites the filler is agglomerated and only microcomposites are obtained.

1. Introduction

Nanocomposites of inorganic or organic nanoobjects dispersed in polymer matrices on nano-scale have been object of intensive research in the last decades due to the expectation of a significantly improved property profile caused by the large area of interphases between matrix and nanofiller. The most desired target improvements when using inorganic nanoparticles concern mechanical properties as stiffness, strength, and toughness, wear and abrasion properties by reinforcement of the matrix polymers as well as enhanced fire resistance and burning behavior [1–8].

Moreover, the formation of nanocomposites can improve other interesting properties. Depending on the nanoparticles chosen, polymer nanocomposites can display enhanced barrier properties for beverage bottles and auto fuel systems. They may also show enough electrical conductivity to improve electrostatic dissipation. Certain organophilic modifications were observed to enhance antimicrobial characteristics. Membranes made from nanocomposites with nanoscale thicknesses are suitable candidates for a new generation of membrane-based sensor arrays [8–10].

The effects behind these improved properties are caused by the nanoscale dispersion of the inorganic filler together with a strong interaction between the filler surface and the polymer matrix. The desired properties are not only the results of the smart combination of polymer matrix and nanofiller but also result of the special microstructure of the polymer, which can also be influenced by the chosen preparation process [11]. Well-known methods to prepare nanocomposites include the melt compounding, solution blending and *in situ* polymerization [12–15].

Inorganic nanoparticles most studied are layered silicates and clays [16], metal oxides, self-assembled nanoboehmites [4], and layered double hydroxides [17]. Recent

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studies focused on nanocomposites with carbon nanotubes, carbon nanofibers, expanded and exfoliated graphite as well as nanocrystalline metals [11,18]. Comprehensive overviews are given by Paul and Robeson [19] and Leuteritz et al. [13–15].

In particular, polyolefin nanocomposites are highly interesting as materials with novel and improved properties since polyolefins are known to have the highest turnover of all polymeric materials in use. The preparation of polyolefin composites by melt compounding with different types of fillers has been reported over the past 15 years by numerous authors [8,9,20–22]. However, a fine dispersion of the filler in the polymer and good adhesion to the PP matrix is seldom obtained even if highly advanced preparation methods and method combinations are employed. Conventional melt compounding techniques of PP with montmorillonite, for instance, yield normally only partially exfoliated PP nanocomposites [13–15]. To obtain composites with a very fine dispersion of the inorganic materials at the nanoscale, the *in situ* polymerization is more favorable. Using this method, it is generally possible to graft monomers on the surface of the nanoobjects or to intercalate the formed chains between inorganic layer-like structures [5,22–33].

In situ polymerization of olefins in the presence of nanoobjects can be performed by two different ways. One way is the reaction of the nanofiller with the cocatalyst, mostly methylalumoxane (MAO) to anchor the cocatalyst on the nanoobject surface. After solvent and monomer are charged, the injection of the metallocene catalyst starts the polymerization. A second way is the immobilization of the catalyst on the surface of the nanofiller as a supported entity. The addition of olefin starts the polymerization [31,34–39].

Some of us reported recently [40] that organo-modified aluminophosphates are versatile base materials for a series of molecular sieves. It was also shown that it can be prepared in a very fast synthesis process with high yields. The material is a typical lamellar-built solid whose layers are crystallized and constituted of 6-membered rings, completely connected one to the other. There is perfect alternating of $[AlO_4]$ and $[PO_4]$ tetrahedra in the structure; Al–OH and $P–O^{-}–R^{+}$ are found in the interlayer space. The control of the identity of R^{+} groups can be made directly during the synthesis. The solid can be prepared with only one type of alkyl ammonium groups or with a mixture of controlled composition of different alkyl ammonium cations.

In the present work, AlPO-kanemite with n-dodecylammonium and n-butylammonium as organic counterions to the $P–O^{-}$ groups were prepared and used as novel inorganic nanoparticles for the preparation of polypropylene nanocomposites. To the best of our knowledge, this particular inorganic material was not used as nanofiller in polymers and particularly in PP before. The advantages of this layered material in comparison to other fillers are a defined structure with adjustable distance of the interlayer space and the lack of impurities, which would negatively affect the polymerization process. The objective of the study was to prepare polypropylene nanocomposites with superior degree of exfoliation directly in the synthesis of the polyolefin by metallocene-catalyzed polymerization by using a metallocene-supported MAO modified organo-aluminophosphate.

2. Experimental section

2.1. Materials

The amines used for the preparation of the nanoparticles, n-butylamine (99.5%) and n-dodecylamine (98 %), were acquired from Acros and used without purification. Pseudo-bohemite (Catapal B) was a donation from Sasol; orthophosphoric acid (85%) was received from Sigma Aldrich. Toluene (Fluka, p.a.) was sodium/potassium dried and distilled prior to use. The metallocene, *rac*-ethylene bis-indenyl zirconium dichloride (*rac*-$Et[Ind]_2ZrCl_2$), methylalumoxane (MAO) solution (10 wt% solution in toluene) and triisobutyl aluminum (TIBA) (all from Chemtura, Germany) were used as received. Propene (2.8 grade) was purchased from Riessner-Gase and purified by passing through 3 Å molecular sieve followed by R3–11 copper oxide catalysts (BASF). As commercial polypropylene for the compounding, Novolen 1106 H (BASF, Germany) with $\overline{M}_n$ = 193,200 g mol^{-1} was used.

2.2. Preparation of the inorganic filler and the composites

2.2.1. Preparation of the alkylammonium–AlPO–kanemite

The alkylammonium–AlPO–kanemite was prepared according to the literature [41] with the use of n-butylamine and n-dodecylamine as the organic reactants. The general chemical formula of this material is $[AlPO_3(OH)_2(CH_3(CH_2)_xNH_2]$, where x changes according with the type of amines used in the syntheses. The material used in this work was prepared using two different kinds of organic chains, n-butylamine (25 mol%/mols of organics) and n-dodecylamine (75 mol%/mol of organics) in the synthesis.

In a typical procedure, into a 250 mL beaker containing 22 mL of water, pseudobohemite (72% Al_2O_3, 28% H_2O) was slowly added under mechanical stirring and kept under stirring for 15 min. Then, 15.5 mL of concentrated orthophosphoric acid (H_3PO_4, 85 wt%) was slowly dripped into the reaction mixture and 40 mL of distilled water was directly added to the synthesis gel followed by 15 min of vigorous mechanical stirring. The n-butylamine (5.7 mL) was slowly added followed by the slow addition of 32.02 g of n-dodecylamine. After that, the synthesis gel was homogenized for 15 min and then transferred to Teflon-lined stainless-steel autoclaves where it was treated at 190 °C for 48 h in a conventional oven. The solid obtained was then filtered and extensively washed with distilled water until the pH of the washings was neutral. The final solid of the alkylammonium–AlPO–kanemite, which is composed of n-butylammonium (38 mol%/total mol of organics) and n-dodecylammonium (62 mol%/total mol of organics) was named 38but,62dod–AlPO-kan.

2.2.2. Preparation of the in situ nanocomposites

An amount of 1 g of 38but,62dod–AlPO-kan, previously dried at 100 °C overnight, was dispersed in 100 mL of