Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

for

Highly dispersed clay-polyolefin nanocomposites free of compatibilisers, via the *in situ* polymerization of α-olefins by clay-supported catalysts

Susannah L. Scott, Brian C. Peoples, Cathleen Yung, René S. Rojas, Vikram Khanna, Hironari Sano, Toru Suzuki, and Fumihiko Shimizu

1. Clay Treatments:

Natural montmorillonite from Mizusawa, Japan was washed with deionized water and sieved, to give an average particle size of 0.28 mm.

Acid-treated montmorillonite was prepared by stirring natural montmorillonite in a 17 wt% H_2SO_4/1 M Li_2SO_4 solution at 100 °C for 6 h, followed by washing with deionized water and drying at 200 °C for 2 h. Prior to reaction with the organometallic complexes, acid-treated montmorillonite was dried under vacuum over night (10^{-2} Torr) and stored under nitrogen.

Methylaluminoxane (MAO)-modified clay was prepared by the dropwise addition of 5.4 g MAO solution (10.3 wt% Al) to a suspension of 5 g acid-treated montmorillonite in 100 mL toluene. The slurry was stirred for 2 h, the solution decanted, and the solid washed twice with 25 mL fresh toluene. The modified clay was dried under vacuum (10^{-2} Torr) overnight and stored under nitrogen.

Triisobutylaluminum (TIBA)-modified clay was prepared by the addition of 1.0 g 1.0 M TIBA in hexanes to 1.0 g acid-treated montmorillonite in 10 g toluene. The suspension was stirred for 5 mins, the solution decanted, and the solid washed twice with 5 g fresh toluene. The solid was used as prepared.

Trimethylsilyl (TMS)-modified montmorillonite was prepared by the addition of 100 mL trimethylchlorosilane to a suspension of 50 g montmorillonite in 200 mL toluene, and stirred overnight. After the solution was decanted, the solid was washed twice with 100 mL fresh toluene and dried at 100 °C under vacuum (10^{-2} Torr) overnight.

2. Representative Polymerization Procedures:

Preparation of the supported catalysts and their transfer to the polymerization reactor were carried out in a N_2-filled glove box equipped with O_2 and H_2O sensors. Polymerizations were carried out in Parr autoclave reactors (100, 160 and 300 mL), using a glass insert with a diameter approx. 4 mm smaller than the interior of the reactor. A small amount of toluene was placed between the insert and the reactor wall to improve thermal contact. Toluene was degassed with argon and passed through drying columns (Glass Contour) before use. Ethylene (99.999%, Praxair) was further purified by passage through an Agilent OT3 combined O_2/H_2O trap.

2a. Polymerizations with clay-activated Cp_2ZrMe_2

10 mg Cp_2ZrMe_2 in 1.0 g toluene was added to a slurry of 300 mg acid-treated montmorillonite in 75 g toluene. The mixture was sealed in a 300 mL Parr reactor and brought the desired temperature with stirring. Reaction temperatures from 20 – 80 °C were tested. Ethylene was added on demand at 100 psi for 1 h, then the pressure was released and the polymer product precipitated with acetone. Yield: 0.2 g.

10 mg Cp_2ZrMe_2 in 1.0 g toluene was added to a slurry of 300 mg MAO-modified montmorillonite in 75 g toluene. The mixture was sealed in a 300 mL Parr reactor and brought to 60 °C with stirring. Ethylene was added on demand at 100 psi for 1 h, then the pressure was released. The polymer product was precipitated with acetone and dried under vacuum overnight. Yield: 4.2 g.

2b. Polymerizations with clay-supported $Zr(CH_2C_6H_5)_4$

70 mg $Zr(CH_2C_6H_5)_4$ in 10 g toluene was added to a slurry of 1.0 g acid-treated montmorillonite in 75 g toluene. The mixture was sealed in a 300 mL Parr reactor and brought to 60 ºC with stirring. Ethylene was added on demand at 100 psi for 1 h, then the pressure was released. Acetone was added to the solution in the reactor; no polymer was recovered.

140 mg $Zr(CH_2C_6H_5)_4$ in 5.0 g toluene was added to a slurry of 1.4 g TMS-montmorillonite in 75 g toluene. The mixture was sealed in a 300 mL Parr reactor and brought to 60 ºC with stirring. Ethylene was added on demand at 100 psi for 1 h, then the pressure was released. The polymer was precipitated with acetone and dried under vacuum overnight. Yield: 13.9 g.

140 mg $Zr(CH_2C_6H_5)_4$ in 5 g toluene was added to a slurry of 1.4 g TIBA-montmorillonite in 75 g toluene. The mixture was sealed in a 300 mL Parr reactor and brought to 60ºC with stirring. Ethylene was added on demand at 100 psi for 1 h, the pressure released and the polymer precipitated with acetone and then dried under vacuum overnight. Yield: 19.5 g.

50 mg $Zr(CH_2C_6H_5)_4$ in 5.0 g toluene was added to a slurry of 1.3 g TIBA-montmorillonite in 75 g toluene. The mixture was sealed in a 300 mL Parr reactor and brought to 40 ºC with stirring. Propylene was added on demand at 140 psi for 1 h, then the pressure was released. The polymer was precipitated with acetone and dried under vacuum overnight. Yield: 1.7 g.

2c. Polymerizations with clay-supported Ni complexes

4 mg **1** in 1.0 g toluene was added to a slurry of 100 mg acid-treated montmorillonite in 30 g toluene. The mixture was sealed in a 100 mL Parr reactor and brought to 40 ºC with stirring. Ethylene was added on demand at 100 psi for 30 mins, then the pressure was released. The polymer precipitated with acetone and then dried under vacuum overnight. Yield: 5.5 g.

2.5 mg **2** in 0.5 g toluene was added to a slurry of 250 mg acid-treated montmorillonite in 90 g toluene. The mixture was sealed in a 300 mL Parr reactor and brought to 40 ºC with stirring. Ethylene was added on demand at 100 psi for 30 mins, then the pressure was released. The polymer was precipitated with acetone, then dried under vacuum overnight. Yield: 3.1 g.

2d. Polymerization with clay-activated Ti complex

9 mg bis[2,4-di-*tert*-butyl-6-[phenyl(pentafluorophenylimino)methyl]-phenolato]di-chlorotitanium in 1.0 g toluene was added to a slurry of 700 mg MAO-modified montmorillonite in 75 g toluene. The mixture was sealed in a 300 mL Parr reactor and brought to 20 °C with stirring. Ethylene was added on demand at 100 psi for 15 min, then the pressure was released. The polymer product was precipitated with acetone and dried under vacuum overnight. Yield: 11.85 g.

2e. Polymerization with clay-activated Fe complex

5 mg 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridineiron(II) chloride in 1.0 g toluene was added to a slurry of 450 mg MAO-modified montmorillonite in 75 g toluene. The mixture was sealed in a 300 mL Parr reactor and brought to 30 °C with stirring. Ethylene was added on demand at 100 psi for 15 min, then the pressure was released. The polymer product was precipitated with acetone and dried under vacuum overnight. Yield: 10.7 g.

3. Analytical procedures

3a. IR spectroscopy

Branching frequency was evaluated by infrared spectroscopy. Polymer samples were first dried at room temperature under vacuum (10^{-4} Torr) overnight. Approx. 500 mg of dry material was pressed at 10,000 psi and 175 °C for 3 mins into a thin film of 3 cm diameter, using a Carver heated press. The films were mounted on a standard IR sample holder. Spectra were acquired on a Shimadzu IRPrestige FT-IR spectrometer equipped with a purge gas generator, using a range of 4000 – 400 cm^{-1} and a resolution of 0.5 cm^{-1}. Spectra were normalized to the intensity of the $\delta(CH_2)$ mode at 1368 cm^{-1}.

3b. X-Ray diffraction

Powder X-ray diffraction patterns were acquired using a Scintag X2 θ-θ diffractometer equipped with a sealed 2kW Cu tube and a solid-state point detector. Clay samples were placed on a polycarbonate sample plate and leveled with a razor blade. Scans were taken from 2 – 30° 2θ, in steps of 0.02° with a dwell time of 5 s. The X-ray tube was powered at -40 kV and 10 A.

3c. Differential scanning calorimetry

Melting points were measured by differential scanning calorimetry (TA Instruments DSC 2920), while heating at a rate of 10 °C/min for three cycles over a temperature range from 0 to 200 °C. No changes were observed after the second cycle. The reported melting points are those measured in the second cycle.

3d. Dynamic mechanical analysis

Dynamic mechanical analysis was performed using a TA instruments DMA 2980. Approx. 3 g of material was pressed at 10,000 psi and 175 °C for 3 mins into a bar measuring 3 x 5 x 60 mm, using a Carver heated press. The bar was mounted in the dual cantilever clamp. The sample was thermally soaked at 35 ºC for 5 mins. The stress applied to the sample was increased to 18 N at a rate of 3 N/s. The flexural modulus was obtained as the slope of the tangent to the stress-strain curve at zero strain.

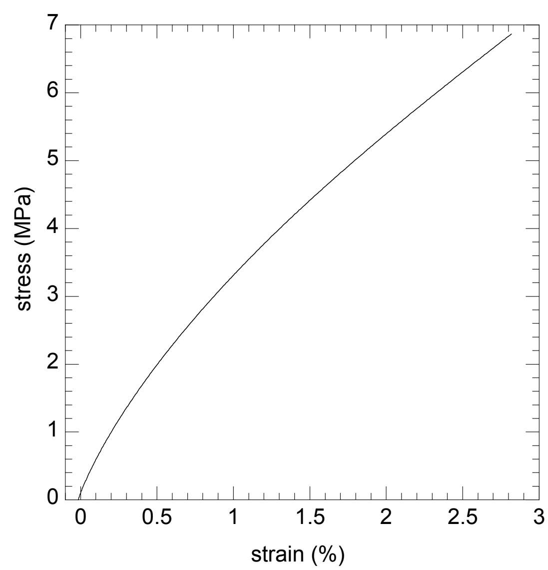

Figure S1. DMA of a clay-polyethylene nanocomposite (5 wt%) produced by *in situ* polymerization with complex **1** supported on acid-treated montmorillonite.

4. Transmission electron microscopy

Transmission electron microscopy studies were performed on pressed polymer films. Bulk polymer samples were pressed at 160 °C using a Carver heated press, followed by a rapid quench (<1 min) in liquid nitrogen. The sample surface was cut at -190 °C. Sections of the polymers 80 nm thick were then cut using a Leica Ultracut UCT ultramicrotome with a diamond knife at room temperature. The TEM images were obtained using an FEI Tecnai G2 Sphera TEM, operating at 200 kV.

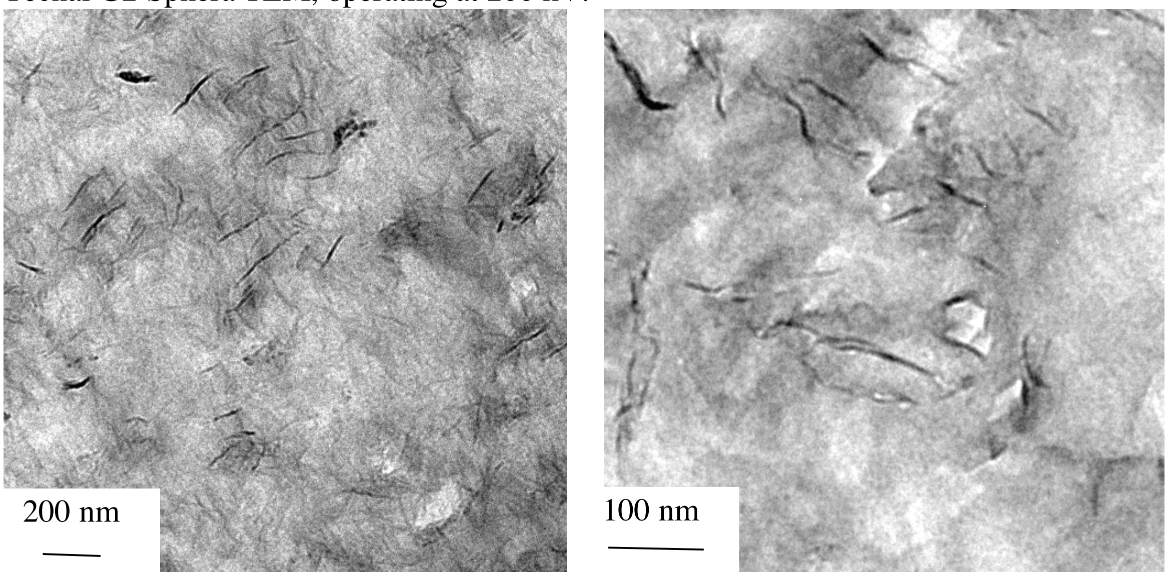

Figure S2. TEM images of nanocomposites (4.5 wt% clay), generated by *in situ* polymerization using clay-supported complex **2**.

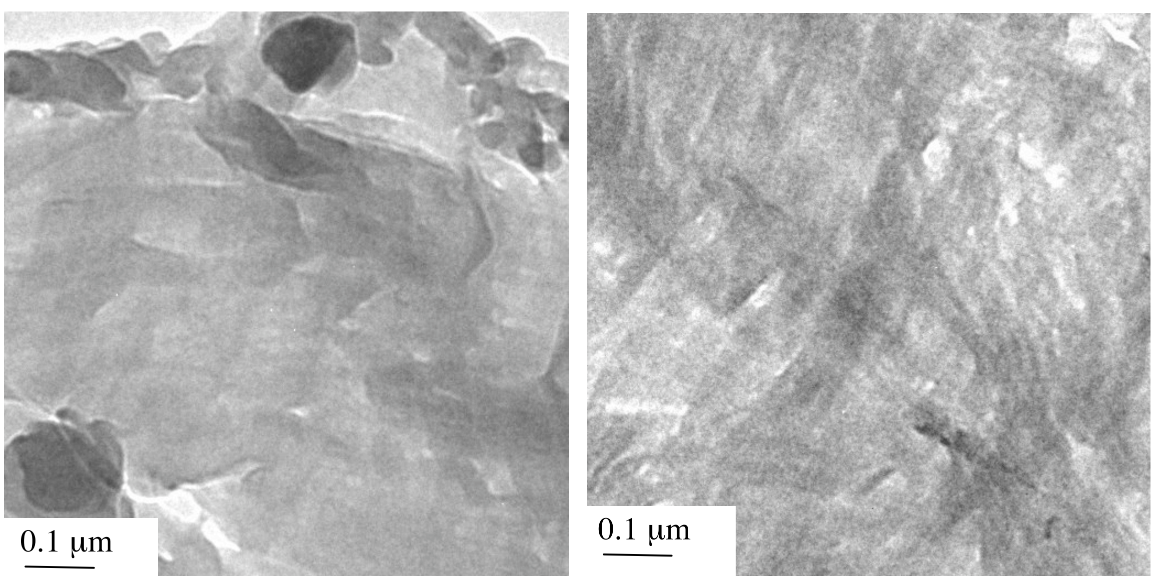

Figure S3. TEM image of polyethylene generated by *in situ* polymerization, using bis[2,4-di-tert-butyl-6-[phenyl(pentafluorophenylimino)methyl]phenolato]dichloro-titanium activated by MAO-treated clay.