

Supporting information

Exfoliated PP/Clay Nanocomposites Using Ammonium-Terminated PP As the Interfacial Agent

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Experimental

All manipulations were carried out under inert atmosphere or by using standard Schlenk technique. ^1H NMR was measured on a Bruker AM-300 or WM-360 spectrometer with DISNMR software. The measurements were usually taken at 120°C using d_2 -1,1,2,2-tetrachloroethane as solvent. The molecular weight and molecular weight distribution of the polymers were determined by Gel Permeation Chromatography (GPC) using a Waters 150 C with a refractive index (RI) detector. The measurements were taken at 140°C using 1,2,4-trichlorobenzene (TCB) as solvent and a mobile phase of 0.7 ml/min flow rate. Broad molecular weight PE samples were used as standards for calibration. Differential scanning calorimetry (DSC) was measured on a Perkin Elmer DSC-7 instrument controller. The DSC curves were recorded during the second heating cycle from 30° to 180°C with a heating rate of $20^\circ\text{C}/\text{min}$. XRD data were collected on a diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 0.1506\text{ nm}$). Bragg's law ($\lambda = 2d \sin\theta$) was used to calculate the spacing. Direct observation of the PP/clay nanocomposite structure was realized by bright field TEM of nanocomposite films under strain in a JEOL -1200EX operating at 120kV. Ultrathin sections of the PP/clay with a thickness of approximately 50 nm were prepared at room temperature using an ultramicrotome equipped with a diamond knife. The sections were transferred dry to carbon-coated Cu grids of 200 mesh.

$\text{Me}_2\text{Si}(2\text{-methyl-4-phenyl-indenyl})_2\text{ZrCl}_2$ (Boulder Scientific Co.), TiCl_4 , AlEt_2Cl , AlEt_3 , TiCl_4 , anhydrous MgCl_2 , 2-ethylhexanol, phthalic anhydride, dibutyl phthalate, dicumyl peroxide, and dimethoxymethylphenylsilane (Aldrich) were used as received. MAO (Albemarle) in 30 wt % of solution in toluene was isolated by vacuum removal of toluene and re-compounded to 2.5 M toluene solution prior to use. CP grade propylene gas (MG Industries), para-Methylstyrene (p-MS) (Aldrich) was distilled over CaH_2 prior to use. CP grade toluene, hexane, and THF were deoxygenated by argon purge before refluxing for 48 hours and then distilled over sodium benzophenone right before use.

The MgCl_2 supported titanium Ziegler-Natta catalyst (MTC) was prepared in the following manner. A mixture of 120 mmol of anhydrous MgCl_2 ($\text{H}_2\text{O} < 5\%$) and 360 mmol of 2-ethylhexanol were suspended in 80 ml of decane in a 250 ml air-free flask with a magnetic stir bar and a condenser under nitrogen atmosphere. After 1 hour at 150°C , 18 mmol of phthalic anhydride was added and the reaction was continued for another hour to produce a clear, colorless solution. In another 500 ml flask, 300 ml of TiCl_4 was added and cooled to -25°C . The above solution was added dropwise while stirring at low speed. After the addition of the solution, the reaction was warmed to room temperature and heated slowly to 115°C , at which time 6 ml of dibutyl phthalate was added. After a 2 hour reaction at 115°C , the reactant was filtered to produce a deep brown solid powder. The powder was further treated by 200 ml of TiCl_4 at 115°C for 2 hours before being filtered and washed repeatedly with dry hexane and dried. A black catalyst powder was obtained containing 1.67 wt % of titanium determined by element analysis.

Synthesis of 4-{2-[*N,N*-Bis(trimethylsilyl)amino]ethyl}styrene (p-NSi₂-St)

A silane protected chain transfer agent p-NSi₂-St was prepared in two steps. In a 500 ml flask equipped with a magnetic stirring bar, 100 g of lithium bis(trimethylsilyl)amide dissolved in 200 ml of THF was slowly added into a mixture of 50 ml (0.658 mol) of chloromethyl methyl ether and 50 ml of THF at 0°C under a nitrogen atmosphere. After completing the addition, the solution was allowed to warm up to room temperature for 2 hours before evaporating the excess chloromethyl methyl ether and THF solvent. *N,N*-Bis(trimethylsilyl)methoxymethylamine (80% yield) was isolated by distillation. In the second step, p-NSi₂-St was prepared by treating 4-vinylbenzylmagnesium chloride with *N,N*-bis(trimethylsilyl)methoxymethylamine. In a 500 ml flask equipped with a magnetic stirring bar and a condenser, 15.2 g of magnesium was suspended in 50 ml dry ether, and 80 ml of 4-vinylbenzyl chloride diluted with 50 ml dry ether was then introduced dropwise through the condenser. The solution was refluxed for 4 hours before the addition of 117 g of *N,N*-bis(trimethylsilyl)methoxymethylamine over a period of 2 hours. The reaction was allowed to proceed at room temperature for another 2 hours before adding 100 ml of aqueous NaOH solution (30%). The organic layer was separated and dried, and the residual was then distilled over CaH₂ to obtain p-NSi₂-St with 70% yield.

Synthesis of NH₂ Group Terminated PP (PP-t-NH₂)

The p-NSi₂-St terminated PP polymers (PP-t-St-NSi₂) were prepared by the combination of *rac*-Me₂Si[2-Me-4-Ph(Ind)]₂ZrCl₂/MAO catalyst and p-NSi₂-St and H₂ as the chain transfer agents. A systematic study was conducted to evaluate the effects of p-NSi₂-St and H₂ concentrations on the catalyst activity and polymer molecular weight. The PP-t-NH₂ polymers were then prepared from PP-t-St-NSi₂ polymers by treating them with hydrogen chloride, which can be accomplished during the sample work-up step. Alternatively, the isolated PP-t-St-NSi₂ (2 g) was suspended in 50 ml of THF at 50°C before adding dropwise 2 N methanolic hydrogen chloride solution. The mixture was stirred for 4 hours at 50°C, and then poured into 1 N methanolic NaOH solution. The PP-t-NH₂ polymer was collected by filtration and washed with 1 M aqueous ammonia and water under a nitrogen atmosphere. The polymer was dried overnight at 50°C under vacuum. The PP-t-NH₂ polymer yield was quantitative. Table 1 summarizes the experimental results.

Table 1. A summary of PP-t-NH₂ polymers^a prepared by the combination of *rac*-Me₂Si[2-Me-4-Ph(Ind)]₂ZrCl₂/MAO catalyst and p-NSi₂-St/H₂ chain transfer agents

Ex.	St-NSi ₂ (mol/l)	H ₂ (psi)	Cat. activity ^b	NH ₂ in PP (mol%)	M _n (×10 ⁻³)	PDI (M _w /M _n)	T _m (°C)
Control 1	0.125	0	~ 0	-	-	-	-
1	0.125	6	1,327	0.07	56.3	2.1	159.1
2	0.125	12	8,480	0.06	55.4	2.5	158.4
3	0.125	20	31,655	0.08	58.9	2.3	158.2
Control 2	0.250	0	~ 0	-	-	-	-
4	0.250	12	2,622	0.18	25.3	2.2	156.3
5	0.250	20	10,066	0.19	24.2	2.3	155.9

a. Reaction conditions: 50 ml toluene, [Zr] = 1.25 × 10⁻⁶ moles, [MAO]/[Zr] = 3000, temperature = 30°C, time = 15 min.

b. Catalyst activity = kg of PP/ mol of catalyst.h.

Overall, the PP-t-NH₂ molecular weight is governed by the chain transfer agent - the higher the concentration of the p-NSi₂-St, the lower the molecular weight of the resulting polymer. It is clear that the chain transfer reaction to p-NSi₂-St (with rate constant k_{tr}) is the dominant termination process, and that it competes with the propagating reaction (with rate constant k_p). The degree of polymerization (X_n) follows a simple comparative equation $X_n = k_p[\text{olefin}]/k_{tr}[\text{St-NSi}_2]$ with a chain transfer constant of $k_{tr}/k_p = 1/34$. ¹H NMR spectra of PP-t-St-NSi₂ polymer and the corresponding PP-t-St-NH₂ show clean deprotection reaction with the complete disappearance of the silane protecting group at 0.24 ppm.

Synthesis of Poly(propylene-co-p-methylstyrene)

The MgCl₂ supported Ti catalyst (MTC/external donor (ED) /AlEt₃) was used for the copolymerization reaction of propylene and p-MS. In a typical example using the MTC/ED/AlEt₃ catalyst system, 100 ml of toluene, 8.1 g of p-MS, 1.57 mmol of AlEt₃ and 0.11 mmol of dimethoxymethylphenylsilane (DMMPS) were added to a 450 ml of Parr autoclave with a mechanical stirrer under argon. The reactor was purged with propylene gas and saturated with 29 psi of propylene. At 50° C, 50 mg of the catalyst slurry in toluene was injected into the reactor to initiate the polymerization. Additional propylene was continuously fed into the reactor to maintain a constant pressure of 29 psi during the whole course of the polymerization. After 1 hour, the polymerization was terminated by the addition of HCl acidified methanol. The resulting polymer was isolated by filtration, washed with methanol and hot toluene, and dried under vacuum.

Synthesis of Poly(propylene-co-p-hydroxypropylstyrene)

In a typical reaction, 8 g of poly(propylene-co-p-MS), containing 1 mol % of p-MS was suspended in 95 ml of anhydrous cyclohexane in a 250 ml of air free flask with a magnetic stir bar. 5.6 ml of 1.3 M sec-BuLi in cyclohexane and 2.2 ml of TMEDA were added to the flask under argon atmosphere. The reaction was then heated to 70° C under nitrogen. After 4.5 hour the polymer was isolated by filtration and washed repeatedly in the dry box with hexane (6 times) until complete decoloration of the filtrate and dried under vacuum. The lithiated poly(propylene-co-p-MS) was suspended in 20 ml of dry THF, 0.5 g of ethylene oxide was added and stirred at room temperature for 2 hours before pouring into HCl aqueous solution. The resulting polymer was purified by filtering and washing with water and methanol and drying under vacuum.

Synthesis of Poly(propylene-co-maleic anhydride methylene styrene)

In a typical reaction, 5 g of poly(propylene-co-p-MS), containing 1 mol % of p-MS was suspended in 50 ml of biphenyl in a 250 ml flask, equipped with a magnetic stir bar, at 125° C under nitrogen, then 2 g maleic anhydride and dicumyl peroxide (DCP) were added. The reaction solution was stirred at 125° C for 3 hours before precipitating the reaction mixture into 200 ml acetone. The polymer was isolated by filtration, washed with acetone 4 times, and dried under vacuum at 50° C for 24 hours.

Preparation of PP-t-NH₃⁺Cl⁻/ Na⁺-Montmorillonite Clay Nanocomposite

Na⁺-montmorillonite clay (Na⁺-mmt) with an ion-exchange capacity of ca. 95 mequiv/100g (WM) was obtained from Southern Clay Product. PP-t-NH₃⁺Cl⁻ (T_m=158.2° C; M_n= 58,900 and M_w=135,500 g/mole) was prepared using excess HCl reagent. Static melt intercalation was employed to prepare PP-t-NH₃⁺Cl⁻/ Na⁺-montmorillonite nanocomposite. PP-t-NH₃⁺Cl⁻ dried powder and Na⁺-mmt with 90/10 weight ratio were first mixed and ground together in a mortar and pestle at ambient temperature. The XRD pattern of this simple mixture shows a (001) peak at 2θ ~7, corresponding to Na⁺-mmt interlayer structure with a d-spacing of 1.45 nm. The mixed powder was then heated at 190° C for 2 hours under nitrogen condition. The resulting PP-t-NH₃⁺Cl⁻/ Na⁺-mmt nanocomposite shows a featureless XRD pattern, indicating the formation of an exfoliated clay structure.

Preparation of PP/PP-t-NH₃⁺Cl⁻/ Na⁺-Montmorillonite Clay Nanocomposite

The binary PP-t-NH₃⁺Cl⁻/Na-mmt exfoliated nanocomposite was further melt mixed (50/50 weight ratio) with commercial neat i-PP (M_n= 110,000 and M_w= 250,000 g/mol). First, the PP-t-NH₃⁺Cl⁻/Na-mmt exfoliated nanocomposite and neat i-PP with 50/50 weight ratio were ground together in a mortar and pestle at ambient temperature. This simple mixture shows a featureless XRD pattern. The mixed powder was then heated at 190° C for 2 hours under nitrogen condition. The resulting ternary PP/PP-t-NH₃⁺Cl⁻/ Na⁺-mmt nanocomposite also shows a featureless XRD pattern, indicating that the stable exfoliated structure in the binary PP-t-NH₃⁺Cl⁻/Na-mmt exfoliated nanocomposite is clearly maintained after further mixing with PP that is compatible with the backbone of PP-t-NH₃⁺Cl⁻.

Organically Modified Montmorillonites

The organically modified montmorillonites used for the nanocomposites of Figure 3 were prepared from Na⁺ montmorillonite (Na-Cloisite, Southern Clay Products, with a CEC of ca. 0.95 mequiv/g) and dimethyl-dioctadecyl-amine or octadecyl-ammonium-bromide (Aldrich). The cation exchange was carried out in a 1% solution in 50:50 water:ethanol, at 60°C, following standard procedures described in literature [Vaia *et.al.*, *Macromolecules* **1995**, 28, 8080]. The dimethyl-dioctadecyl-ammonium modified mmt is comparable with the commercially available dimethyl-ditallow-ammonium montmorillonites (e.g., Southern Clay Products: Cloisite 20A.; Nanocor: Nanomer-I42E). Melt-intercalation of our functionalized PP with these commercial organo-clay materials gave the same structures as those in Figure 3. Moreover, there also exist commercially available organo-mmt's bearing octadecyl-ammonium surfactants (such as the Nanocor: Nanomer-I30E).