

Synthesis and characterization of polyolefin–silicate nanocomposites: a catalyst intercalation and *in situ* polymerization approach†

Jeffrey S. Bergman,^a Hua Chen,^b Emmanuel P. Giannelis,^b Malcolm G. Thomas^c and Geoffrey W. Coates*^a

^a Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, NY 14853, USA.
E-mail: gc39@cornell.edu

^b Department of Materials Science and Engineering, Cornell University, Ithaca, NY 14853, USA

^c Cornell Center for Materials Research, Clark Hall, Cornell University, Ithaca, NY 14853, USA

Received (in Columbia, MO, USA) 7th July 1999, Accepted 27th September 1999

An organically modified fluorohectorite intercalated by a well-defined cationic palladium complex forms an exfoliated polyolefin–silicate nanocomposite material when exposed to olefinic monomer.

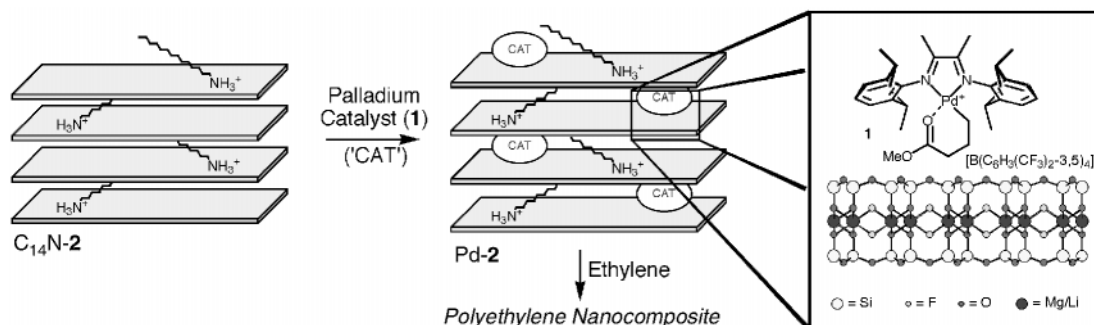
Polymer nanocomposites are a class of hybrid materials composed of an organic polymer matrix that is imbedded with inorganic particles which have at least one dimension in the nanometer size range.¹ At this scale, they can strongly impact the macroscopic properties of the polymer even though the materials typically contain only a few weight percent of the inorganic modifier. Dramatically improved properties such as higher heat distortion temperatures, enhanced flame resistance, increased modulus, better barrier properties, decreased thermal expansion coefficient, and altered electronic and optical properties have been discovered.^{1–3} Due to the synergistic effects that result from adding a small amount of an inexpensive silicate, the synthesis and characterization of polymer nanocomposites has been intensely investigated in the last decade.⁴ The majority of these studies have employed layered, anionic phyllosilicates as the inorganic component due to their high aspect ratio and ease of ionic modification. However, a simple physical mixture of the polymer and an intact, multilayered silicate does not typically yield improved properties. It is imperative that the polymer separates the individual silicate sheets, either in an intercalated morphology (silicate registry is retained) or preferably in a delaminated (or exfoliated) structure that is microscopically isotropic.

Despite the prime importance of polyethylene and polypropylene in a diverse array of applications, the synthesis of polyolefin–silicate nanocomposites remains a scientific challenge. Polymer nanocomposites can be synthesized by three primary strategies. The first is the melt intercalation of a polymer into an organically modified silicate.⁵ Although this strategy works well with polar polymers such as polysiloxanes, polyethers and polystyrene,¹ polypropylene nanocomposites have only been formed using maleic anhydride modified polypropylene oligomers,⁶ and ammonium-modified silicates

are only partially intercalated by polyethylene.⁷ The second strategy is the *in situ* formation of a layered silicate in an aqueous polymer solution.⁸ Even though the development of this promising technique is just in its infancy, it will likely be limited to polymers that are soluble in water. A third strategy that is receiving increasing attention involves a silicate that is intercalated by an initiator or catalyst,⁹ and, upon introduction of a monomer an intercalated or exfoliated polymer nanocomposite is formed (Scheme 1). This approach can eliminate both entropic and enthalpic barriers associated with intercalating polar silicates with nonpolar polymers, and has been used to synthesize a range of polymer nanocomposites. Concerning polyolefins, O'Hare and coworkers have reported the intercalation of synthetic layered silicates with a cationic Ziegler–Natta catalyst after protecting the internal surfaces with methylaluminoxane.^{10,11} Addition of propylene produced polypropylene oligomers, however the post-polymerization structure of the silicate–polymer mixture was not reported.¹⁰ It must be noted that the silicate galleries often contain protic impurities and polar functional groups; therefore only a select group of initiators and catalysts can be employed in unprotected silicate galleries. Although the vast majority of olefin polymerization catalysts are highly sensitive to Lewis bases and water, Brookhart and coworkers have reported a remarkable class of late-transition metal olefin polymerization catalysts that are particularly stable under these conditions.^{12,13} In this paper we report the synthesis of polyolefin nanocomposites by employing these robust catalysts using an *in situ*, ‘ship-in-the-bottle’ polymerization approach.

We chose to investigate Brookhart's single component palladium-based complex **1**; $[(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3\text{N}=\text{C}(\text{Me})\text{C}(\text{Me})=\text{NC}_6\text{H}_3\text{Pr}^i_2\text{-}2,6)]\text{Pd}(\text{CH}_2)_3\text{CO}_2\text{Me}][\text{B}(\text{C}_6\text{H}_3(\text{CF}_3)_2\text{-}3,5)_4]^{13}$ and the well-studied synthetic silicate fluorohectorite (**2**)¹⁴ as the polymerization catalyst and inorganic component of our composite, respectively. Lithium cations occupy the galleries of synthetic fluorohectorite; initial attempts to intercalate **2** with **1** failed, as evidenced by an immutable powder X-ray diffraction (XRD) pattern. Therefore we turned to an organically modified fluorohectorite ($\text{C}_{14}\text{N-2}$) that had 1-tetradecylammonium cations in the place of the interlayer lithium cations.¹⁴ Suspension of $\text{C}_{14}\text{N-2}$ in a toluene solution of **1**† yielded an orange–brown powder (Pd-2) that was visually

† Electronic supplementary information (ESI) available: Scanning transmission microscope (STEM) bright-field image of Pd-2. See <http://www.rsc.org/suppdata/cc/1999/2179/>



Scheme 1

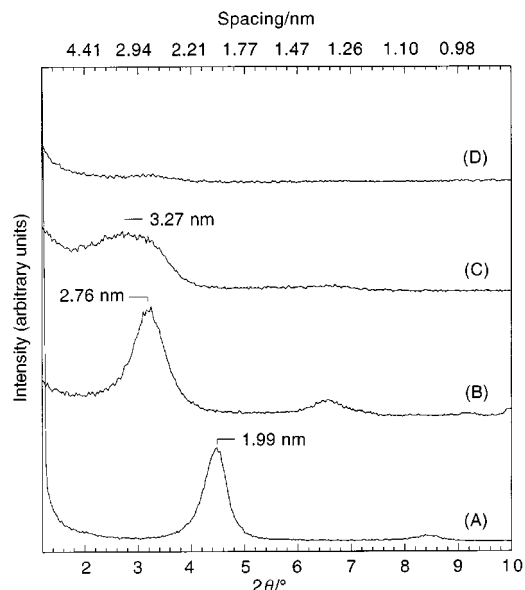


Fig. 1 Plot of powder X-ray diffraction intensity *versus* scattering angle: (A) 1-tetradecylammonium modified fluorohectorite ($C_{14}N-2$); (B) $C_{14}N-2$ after intercalation by **1** (Pd-2); (C) Pd-2 after exposure to ethylene for 135 min; (D) Pd-2 after exposure to ethylene for 24 h.

different from the white, pristine $C_{14}N-2$. This reaction is irreversible, as **1** cannot be extracted from Pd-2 with excess toluene. Powder XRD of Pd-2 revealed a structural change of the silicate, as an increase in the basal spacing of $C_{14}N-2$ from 1.99 to 2.76 nm was measured. Molecular modeling shows that an interlayer spacing of at least 2.1 nm is necessary for **1** to exist in the interlayer galleries; therefore the new spacing of 2.76 nm can easily accommodate the palladium complex. However, on the basis on these results, it was not clear whether this reaction was a cation exchange process, in which ammonium ions were exchanged for the cation of **1**, or whether the entire ionic palladium complex entered the silicate without ammonium discharge. Analysis of the material remaining in solution after intercalation using 1H NMR spectroscopy revealed the absence of shifts due to the aliphatic ammonium cation, and the ratio of signal intensities assigned to the cation and anion of unintercalated **1** remained unchanged. These results clearly demonstrate that both the cation and anion of **1** enter the ammonium-modified silicate, and the ammonium cation remains in the silicate as well. The driving force for this reaction is not currently known.

To investigate the polymerization activity of Pd-2, the dry solid was exposed to ethylene gas.[‡] Over a two hour period, we observed monomer consumption and a dramatic increase in the size of the silicate-catalyst composite. After 12 h, the Pd-2 material was unrecognizable; in the place of a small amount of orange, Pd-2 powder was a large mass of colorless, rubbery polymer. Based on the elemental analysis of Pd-2 and the assumption that all intercalated palladium species produced polyethylene, the turnover frequency [TOF = mol ethylene/(mol Pd h)] of the catalyst in Pd-2 is 162 h^{-1} . Consistent with the results of Brookhart, the polymer produced is highly branched. Analysis of the toluene-extracted polyethylene by gel-permeation chromatography revealed high molecular weight polymer ($M_n = 159\,000$; $M_w = 262\,000$ *versus* polystyrene standards).¹³ To establish the arrangement of the silicate sheets in the polymer matrix, the polyethylene composite formed after 24 h was examined by powder XRD. The complete absence of diffraction peaks strongly suggests the formation of an exfoliated polymer nanocomposite. Under the same conditions addition of propylene gas to Pd-2 also produces a polypropylene-silicate nanocomposite, however at a much slower rate (TOF = 5.6 h^{-1}).

To further confirm that silicate delamination occurs during ethylene polymerization, we monitored the progress of the reaction using XRD. Shown in Fig. 1 are the XRD data as a

function of reaction time. At $t = 0$, the mean repeat distance of the silicate sheets is 2.76 nm. After exposure of Pd-2 for 135 minutes the interlayer spacing increases to 3.27 nm. The significant increase in peak width is due to the loss of crystallinity of the silicate. Finally, at 24 h the XRD revealed the absence of significant diffraction, consistent with dispersion. Since XRD only provides informative data at spacings less than 5 nm, we employed scanning transmission electron microscopy (STEM) to provide structural information at larger layer spacings (longer reaction times). By terminating the reaction at 12 h, we were able to identify layer spacings in the 5–8 nm range, well outside the range that we could achieve by XRD. A bright-field STEM image of the nanocomposite is available as supplementary data (<http://www.rsc.org/suppdata/cc/1999/2179>). It shows overlaid stacks of the silicate layers (dark area), where the polymer-intercalated layers remain predominantly coplanar at this stage of the reaction.

In conclusion, we report the first synthesis and characterization of polyolefin nanocomposite materials using an *in situ* polymerization approach. In the initial stages of the reaction polymer-intercalated silicates are formed; at later stages of the reaction the XRD data are consistent with silicate exfoliation. Efforts to extend this strategy for the synthesis of nanocomposite materials using isotactic polypropylene and linear polyethylene as the continuous phase are currently underway.

We gratefully acknowledge the Cornell Center for Materials Research (an NSF-funded MRSEC, DMR-9632275) and its facilities for support of this research. We thank Professor M. Brookhart for helpful discussions. G.W.C. gratefully acknowledges a Camille and Henry Dreyfus New Faculty Award, an Alfred P. Sloan Research Fellowship, an NSF Career Award, as well as Dupont and 3M for support of this research.

Notes and references

† Fluorohectorite (**2**) employed in these experiments had a cation exchange capacity of $1.5\text{ mmol Li}^+ \text{ g}^{-1}$ ($Li_{1.12}[Mg_{4.88}Li_{1.12}]Si_8O_{20}F_4$). The initial interlayer spacing is 1.20 nm. The catalyst-intercalated fluorohectorite was synthesized by adding 50 ml of dry toluene to 95 mg of $C_{14}N-2$ and 155 mg of **1**, and stirring for 12 h at 22 °C. The suspension was filtered off, washed with toluene, and dried *in vacuo* to give 174 mg of Pd-2. Based on the increase in weight of $C_{14}N-2$, the composition of Pd-2 is calculated to be $(1)_{0.55}\{H(CH_2)_{14}NH_3\}_{1.12}[Mg_{4.88}Li_{1.12}]Si_8O_{20}F_4$. Based on the interplanar spacing of Pd-2 (27.6 Å) and an estimated volume of **1** (1750 Å^3), the composition of Pd-2 is calculated (neglecting the contribution of surface-bound **1**) to be $(1)_{0.4}\{H(CH_2)_{14}NH_3\}_{1.12}[Mg_{4.88}Li_{1.12}]Si_8O_{20}F_4$. Elemental analysis of Pd-2 corresponds to $(1)_{0.7}\{H(CH_2)_{14}NH_3\}_{1.12}[Mg_{4.88}Li_{1.12}]Si_8O_{20}F_4$; calc. (found): C, 36.38 (36.47); H, 3.92 (4.15); N, 1.75 (1.58%). Therefore, the composition of Pd-2 can only be estimated at the current time.

‡ Ethylene gas (80 psi) was reacted with solid Pd-2 (129 mg) at 22 °C for 12 h, yielding 3.50 g of a rubbery, white solid.

- 1 E. P. Giannelis, *Adv. Mater.*, 1996, **8**, 29.
- 2 Z. Wang and T. J. Pinnavaia, *Chem. Mater.*, 1998, **10**, 3769.
- 3 Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi and O. Kamigaito, *J. Mater. Res.*, 1993, **8**, 1185.
- 4 R. Dagani, *Chem. Eng. News*, 1999, **77**(23), 25.
- 5 R. A. Vaia, K. D. Jandt, E. J. Kramer and E. P. Giannelis, *Chem. Mater.*, 1996, **8**, 2628.
- 6 M. Kawasumi, N. Hasegawa, M. Kato, A. Usuki and A. Okada, *Macromolecules*, 1997, **30**, 6333.
- 7 H. G. Jeon, H. T. Jung, S. W. Lee and S. D. Hudson, *Polym. Bull.*, 1998, **41**, 107.
- 8 K. A. Carrado and L. Xu, *Chem. Mater.*, 1998, **10**, 1440.
- 9 M. W. Weimer, H. Chen, E. P. Giannelis and D. Y. Sogah, *J. Am. Chem. Soc.*, 1999, **121**, 1615.
- 10 J. Tudor, L. Willington, D. O'Hare and B. Royan, *Chem. Commun.*, 1996, 2031.
- 11 J. Tudor and D. O'Hare, *Chem. Commun.*, 1997, 603.
- 12 L. K. Johnson, C. M. Killian and M. Brookhart, *J. Am. Chem. Soc.*, 1995, **117**, 6414.
- 13 L. K. Johnson, S. M. Mecking and M. Brookhart, *J. Am. Chem. Soc.*, 1996, **118**, 267.
- 14 R. A. Vaia, R. K. Teukolsky and E. P. Giannelis, *Chem. Mater.*, 1994, **6**, 1017.