Exfoliated PP/Clay Nanocomposites Using Ammonium-Terminated PP as the Organic Modification for Montmorillonite

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Although the miscibility of silicates, including clay minerals, with organics and polymers has been known since the early 1950s, an industrial report of a nylon-6/montmorillonite (mmt) material from Toyota[1] has recently revitalized the field. Those materials were synthesized by polymerization of the monomer in the presence of the inorganic filler and showed remarkable enhancements of several thermal and mechanical properties with a moderate inorganic loading (2−5 wt %). Later, Giannelis et al.[2] discovered that it is possible to melt-mix polymers with clays bearing cationic organic surfactants, eliminating the need for organic solvents or in situ polymerization schemes. Such melt-blending approaches generally yield similar concurrent enhancements of many materials properties by the nanodispersion of inorganic silicate layers, which cannot be realized by conventional fillers; for example, simultaneously increasing tensile strength, flex modulus, and impact toughness, contributing a general flame-retardant character,[3] and affording a dramatic improvement in barrier properties.[4,5]

On the basis of theoretical models, Balazs[6a] suggested that an increase in the length of the organic molecules tethered on clays is a promising approach to further promote dispersion of clay sheets in a polymer matrix. Toward this end, recent reports[7] employing a variety of polymers (such as polystyrene,[7a] poly(methyl methacrylate),[7b] and poly(ϵ-caprolactone)[7c]) grafted on montmorillonite surfaces observe varied extents of clay dispersion. Furthermore, subsequent annealing of these polymer-bearing clays, or mixing them with the respective homopolymers, can lead to retention or collapse of the clay dispersion depending on the polymer.[7] The differences in these responses were attributed to the specific polymer−clay interactions[6b] in each case, indicating[7] that where there exist strong interactions the clay dispersions collapse, whereas in those cases with weak polymer−clay interactions the dispersions can be retained.

Many research efforts[8] have also focused on dispersing montmorillonite in polypropylene (PP), which is a fast growing thermoplastic that dominates the industrial applications due to its attractive combination of properties and low cost. As expected, because of the absence of any strong interactions, it has been a scientific challenge to disperse silicate clays in the highly apolar polyolefins.[6b] The general approach for improving the compatibility of PP with organically modified clays has been the addition of polar functional groups to the PP polymer, typically resulting in PP/clay

nanocomposites with a mixed nanomorphology, including both intercalated and exfoliated structures coexisting in the system.[8g] Unfortunately, the availability of functional PP is very limited due to synthetic chemical difficulties, and most of such approaches are employing a single, commercially available, maleic anhydride-grafted PP (PP-g-MAH) polymer, despite its shortcomings (e.g., PP-g-MAH is typically characterized by very complicated molecular structure due to many side reactions,[9] including severe chain degradation during the free radical grafting process as well as many impurities).

The hurdle of obtaining appropriately functionalized PP can be overcome by a general functionalization approach involving the combination of metallocene catalysts and reactive comonomers,[10] which can yield a broad range of side-chain functionalized polyolefins with relatively well-defined molecular structures. Recently, we also discovered a facile route using reactive chain transfer agents to prepare end-functionalized polyolefins[11−13] containing a terminal functional group (OH, NH_2, COOH, anhydride, etc.), while maintaining a well-controlled polymer molecular weight and narrow molecular weight and composition distributions.

The availability of a broad range of well-defined functionalized polyolefins provides us with a great advantage in evaluating their applications in polyolefin/clay nanocomposites. The most desirable ammonium group-terminated i-PP (PP-t-NH_3^+) polymers[14] (discussed in the Supporting Information) were prepared by the combination of rac-$Me_2Si[2$-Me-4-Ph(Ind)]$_2ZrCl_2$/MAO catalyst and p-NSi_2-St/H_2 (p-NSi_2-St: 4-{2-[N,N-bis(trimethylsilyl)amino]ethyl}styrene) chain transfer agent. Both pristine Na^+-montmorillonite clay (Na^+-mmt), with an ion-exchange capacity of ca. 0.95 mequiv/g, and a dioctadecylammonium-modified montmorillonite organophilic clay (2C18-mmt) were obtained from Southern Clay Products. Static melt intercalation[2] was employed to prepare all PP/clay nanocomposites.

Both PP-t-$NH_3^+Cl^-$/Na^+-mmt and PP-t-$NH_3^+Cl^-$/2C18-mmt nanocomposites were prepared and evaluated under the same conditions. Figure 1 compares the X-ray diffraction (XRD) patterns before and after static annealing of a physical mixture (90/10 weight ratio) of an ammonium-terminated i-PP (PP-t-$NH_3^+Cl^-$; M_n = 58 900 and M_w = 135 500 g/mol; T_m = 158.2 °C) and a pristine Na^+-mmt clay. Namely, simple mixing of dried PP-t-$NH_3^+Cl^-$ powder and Na^+-mmt, ground together by mortar and pestle at ambient temperature, creates the XRD pattern in Figure 1a, with a (001) peak at $2\theta \cong 7°$, corresponding to the characteristic Na^+-mmt d spacing of ca. 1.26 nm. The mixed powder was then heated—annealed under static conditions—at 190 °C for 2 h under vacuum. The resulting PP-t-NH_3^+/mmt hybrid shows a featureless XRD pattern in Figure 1b, indicating the formation of an exfoliated clay structure, which corresponds to the thermodynamically stable state, as the ammonium-terminated PP exchange the alkali (Na^+) cations at the mmt surfaces.

Similar results were also observed in the PP-t-NH_3^+-Cl^-/$2C_{18}H_{37}$-$2CH_3$-N^+-mmt nanocomposite case, suggesting that the dioctadecylammonium cations in organophilic clay may also be ion-exchanged by PP-t-NH_3^+ to form a similar PP-t-NH_3^+/mmt structure.[17] It is clear

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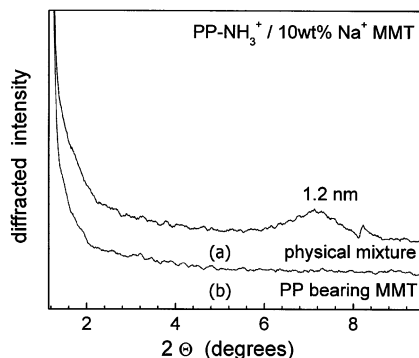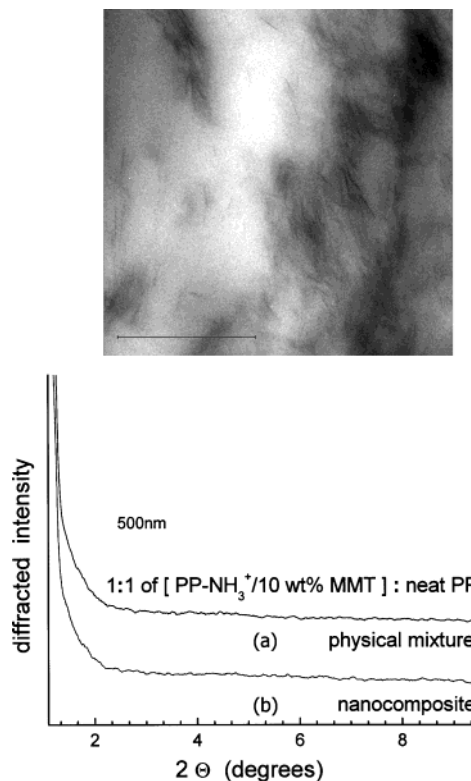
Figure 1. X-ray diffraction patterns of PP-t-NH$_3$+Cl$^-$/Na$^+$-mmt (90/10 weight ratio): (a) physical mixture by simple powder mixing at ambient temperature and (b) the same mixture after static melt-intercalation (PP-t-NH$_3$+/mmt hybrid).

that an organic surfactant is not needed to promote compatibility between PP-t-NH$_3$+Cl$^-$ and pristine Na$^+$-mmt clay; beyond any economic benefits, such an elimination of the mmt's organic surfactant also offers some significant materials advantages; for example, it eliminates two major concerns relating to the thermal stability of the surfactant during high-temperature melt processing and to the long-term stability of the small organic surfactant in the polymer/clay nanocomposite under various application conditions.

The binary PP-t-NH$_3$+/mmt hybrid was subsequently further mixed/blended (at a 50/50 weight ratio) with a neat−unfunctionalized−i-PP (M_n = 110 000 and M_w = 250 000 g/mol). Figure 2 shows the XRD patterns of (a) the physical mixture and (b) the melt blending of the exfoliated PP-t-NH$_3$+/mmt structures with neat i-PP. The exfoliated structure is maintained after further mixing with i-PP, which is compatible (cocrystallizable) with the backbone of the largely isotactic PP-t-NH$_3$+ polymer, as also directly observed in the TEM inset (Figure 2). Apparently, the i-PP polymer chains largely serve as diluents in the ternary PP-t-NH$_3$+/mmt/i-PP system, with the thermodynamically stable[15] PP-t-NH$_3$+/mmt exfoliated structure dispersed in the i-PP matrix.[16]

For comparison, several functionalized PP polymers, containing randomly distributed functional groups in the side chains or lumped together in a block copolymer microstructure, were also evaluated in PP/montmorillonite nanocomposites. Similar static melt-intercalation procedures were followed, except for employing alkyl-ammonium-modified montmorillonites (2C18-mmt for all random copolymers and C18-mmt for the block copolymer). Figure 3 shows the XRD patterns of four nanocomposites made with 6 wt % of 2C18-mmt clay and 94 wt % of three side-chain-functionalized PPs (M_n = 95 000 and M_w = 210 000 g/mol) containing (a) 1 mol % *p*-methylstyrene, (b) 0.5 mol % maleic anhydride, and (c) 0.5 mol % hydroxy side groups and the original 2C18-mmt clay All the functionalized PPs were derived from the same random PP copolymer synthesized by metallocene catalysis, which contained 1 mol % *p*-methylstyrene (p-MS) comonomer. Subsequently, the p-MS's were selectively functionalized toward hydroxy (OH) and maleic anhydride without changing the PP backbone. Moreover, we show (Figure 3) the XRD pattern of PP-*b*-PMMA block copolymer/6 wt % C18-mmt which contains a 5 mol % methyl methacrylate block. These XRD patterns clearly show that there is a definite


Figure 2. X-ray diffraction patterns of the 50/50 mixture by weight of exfoliated PP-t-NH$_3$+/mmt structure (90/10 weight ratio) and neat−unfunctionalized−i-PP. The XRD traces shown correspond to (a) the physical mixture of PP-t-NH$_3$+/mmt and i-PP and (b) the same mixture after static melt-intercalation. Bright-field TEM image of the melt-mixed ternary PP-t-NH$_3$+/mmt/PP system (b in the XRD) shows the typical exfoliated montmorillonite structure.
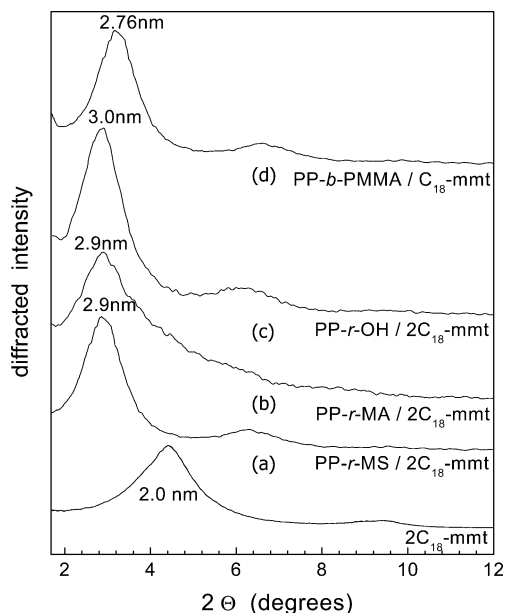
Figure 3. X-ray diffraction patterns of 2C18-mmt clay and four nanocomposites with 6 wt % of alkylammonium-mmt and 94 wt % of three side-chain-functionalized PPs containing (a) 1 mol % *p*-methylstyrene, PP-*r*-MS; (b) 0.5 mol % maleic anhydride, PP-*r*-MA; and (c) 0.5 mol % hydroxy, PP-*r*-OH. Also shown, a 6 wt % C18-mmt nanocomposite of a PP-*b*-PMMA block copolymer, with 5 mol % of methyl methacrylate.

intercalated structure for all the side-chain-functionalized PP cases, manifesting itself through an interlayer *d* spacing increase of about 1 nm compared to that of

(a)

(b)
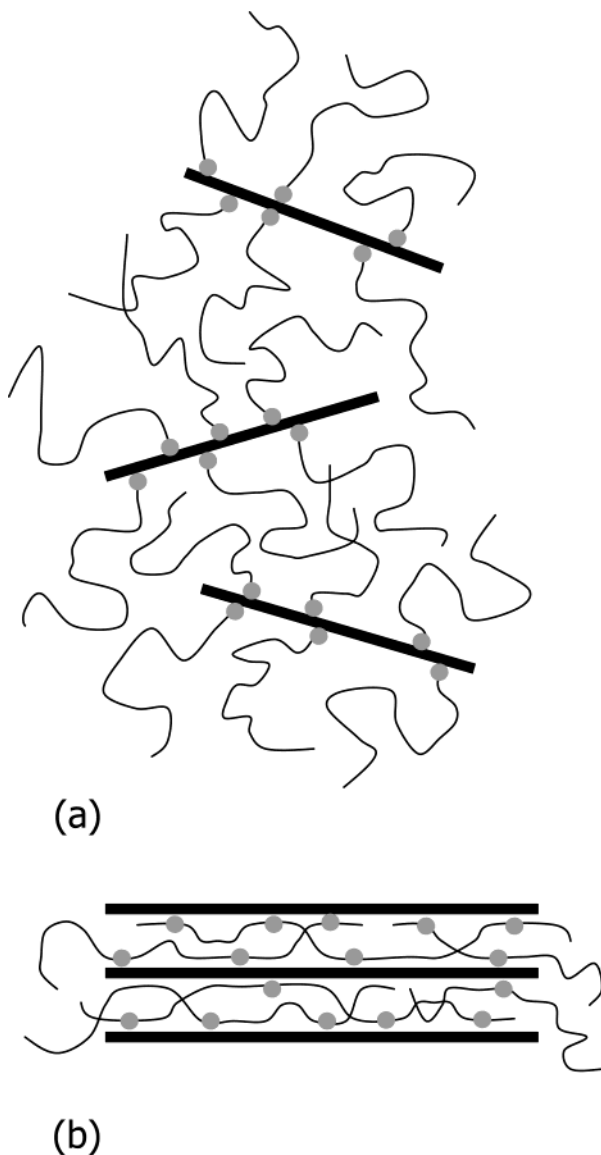
Figure 4. Illustration of the molecular structures of (a) chain-end-functionalized polyolefin and (b) side-chain-functionalized polyolefin located between clay interlayers.

the parent alkylammonium-mmt. TEM was also employed to examine the degree of exfoliated (disordered) structure, and the quantitative image analysis indicates only between 20 and 40% exfoliated layers in all four systems.[8g]

Summarizing, the herein experimental results demonstrate the advantage of chain-end-functionalized PP (PP-t-NH$_3^+$) that seems to adopt a unique molecular structure atop of the clay surfaces and results in an exfoliated montmorillonite structure[16] (Figure 4a). The terminal hydrophilic NH$_3^+$ functional group anchors the PP chains (via ion exchange) on the inorganic surfaces, and the hydrophobic high molecular weight and semi-crystalline PP "tail" effectively exfoliates the clay platelets, an exfoliated structure which is maintained even after further mixing with neat PP. In contrast, side-chain-functionalized or block copolymer PPs form multiple contacts with each of the clay surfaces, as illustrated in Figure 4b, which not only results in aligning the polymer chains parallel to the clay surfaces but also can bridge consecutive clay platelets promoting intercalated structures, especially for the higher lateral size montmorillonites.

Supporting Information Available: Experimental procedures, syntheses details, and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) The fact that all polymer/inorganic mixings were carried out under melt intercalation[2] (static annealing in absence of mechanical shear or solvent) underlines that the dispersions achieved are thermodynamically favored rather than kinetically trapped by the processing conditions. For more information the reader can refer to previous review articles.[6,7b]

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(17) There is no sufficient thermodynamic driving force for PP-t-NH$_3^+$ to exfoliate, or even intercalate, an alkylammonium-modified montmorillonite.[6b,8g] At the same time, the existence of a thermodynamic driving force for the replacement of the alkylammonium surfactant to be ion-exchanged by PP-t-NH$_3^+$ is also doubtful, albeit more probable. The ion-exchange mechanism for the development of an exfoliated structure in this case is speculative.