Polypropylene/Montmorillonite Nanocomposites. Review of the Synthetic Routes and Materials Properties

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The synthetic routes and materials properties of polypropylene/montmorillonite nanocomposites are reviewed. The nanocomposite formation is achieved in two ways: either by using functionalized polypropylenes and common organo-montmorillonites, or by using neat/unmodified polypropylene and a semi-fluorinated organic modification for the silicates. All the hybrids can be formed by solventless melt-intercalation or extrusion, and the resulting polymer/inorganic structures are characterized by a coexistence of intercalated and exfoliated montmorillonite layers. Small additions—typically less than 6 wt %—of these nanoscale inorganic fillers promote concurrently several of the polypropylene materials properties, including improved tensile characteristics, higher heat deflection temperature, retained optical clarity, high barrier properties, better scratch resistance, and increased flame retardancy.

Introduction

The very large commercial importance of polypropylene (PP) has also been driving an intense investigation of PP composites reinforced by particulates, fibers, and layered inorganic fillers. In particular, in the case of layered inorganic fillers, talc and mica had been traditionally attracting the most interest. However, recent advances in polymer/clay and polymer/silicate nanocomposite materials have inspired efforts to disperse montmorillonite-based fillers in PP. Although it has been long known that polymers can be mixed with appropriately modified clay minerals and synthetic clays, the field of polymer/silicate nanocomposites has gained large momentum recently. Two were the major findings that pioneered the revival of these materials: First, the report of a nylon-6/montmorillonite material from Toyota research, where very remarkable enhancements of thermal and mechanical properties. Second, Giannelis et al. found that it is possible to melt-mix polymers with clays without the use of organic solvents. Since then, the high promise for industrial applications has motivated rigorous research, which revealed concurrent dramatic enhancements of many materials properties by the nanodispersion of inorganic silicate layers. Where the property enhancements originate from the nanocomposite structure, these improvements are generally applicable across a wide range of polymers. At the same time, there were also discovered property improvements in these nanoscale materials that could not be realized by conventional fillers, as for example a general flame retardant characteristic and a dramatic improvement in barrier properties.

Montmorillonite (mmt) is a naturally occurring 2:1 phyllosilicate, which has the same layered and crystal-line structure as talc and mica but a different layer charge. The mmt crystal lattice consists of 1-nm-thin layers, with a central octahedral sheet of alumina fused between two external silica tetrahedral sheets (in such a way that the oxygens from the octahedral sheet also belong to the silica tetrahedra). Isomorphic substitution within the layers (for example, Al3+ replaced by Mg2+ or Fe2+) generates a negative charge—defined through the charge exchange capacity (CEC)—and for mmt is typically 0.9–1.2 mequiv/g depending on the mineral origin. These layers organize themselves in a parallel fashion to form stacks with a regular van der Waals gap between them, called interlayer or gallery. In their pristine form their excess negative charge is balanced by cations (Na+, Li+, Ca2+) which exist hydrated in the interlayer. Obviously, in this pristine state mmt is only miscible with hydrophilic polymers, such as poly(ethylene oxide) and poly(vinyl alcohol). To render mmt miscible with other polymers, one must exchange the alkali counterions with cationic-organic surfactants, such as alkylammoniums.

Synthetic Routes and Nanocomposite Structures

The Thermodynamic Challenge. In general, an interplay of entropic and enthalpic factors determines the outcome of whether an organically modified mmt (o-mmt) will be dispersed—intercalated or exfoliated—in a polymer. Dispersion of mmt in a polymer requires sufficiently favorable enthalpic contributions to overcome any entropic penalties. Favorable enthalpy of mixing for the polymer/o-mmt interactions is achieved when the polymer/mmt interactions are more favorable compared to the surfactant/mmt interactions. For most polar or polarizable polymers, an alkylammonium surfactant (the most commonly used organic modifica-
mmt materials. In the first studies aiming to develop PP/mmt miscibility, organically modify the mmt, they will promote PP/alkylammonium modification. This can be achieved by PP “functionalization”, that is, introducing polar or polarizable groups in the polymer.

There are two ways to overcome this challenge:

1. Improve the interactions between the polymer and the mmt so as to become more favorable than the alkyl-surfactant/mmt interactions. This can be achieved by PP “functionalization”, introducing polar or polarizable groups in the polymer.

2. Decrease the enthalpic interactions between the surfactant and the mmt, which effectively will render the PP/mmt contacts favorable. This second route is more challenging, as the alkyl-surfactant/mmt interactions are already very poor (that is exactly the reason these surfactants work so well in dispersing most nonaliphatic polymers). However, semi-fluorinated surfactants do have more unfavorable interactions than the hydrogenated polyolefins, and if used appropriately to organically modify the mmt, they will promote PP/o-mmt miscibility.

**Initial Efforts.** Surprisingly, none of these two routes was employed in the first studies aiming to develop PP/o-mmt materials. Instead, polypropylene oligomers modified with either maleic anhydride (MA) or hydroxyl groups (OH) were first mixed with octadeca(methylammonium)-exchanged montmorillonite, creating a master batch, which was subsequently blended with neat PP, usually assisted by strong mechanical shear in an extruder or mixer. In this way, the PP polymer and the MA-polypropylene pretreated o-mmt are effectively at theta conditions, and the extrusion is only promoting mixing due to the effect of the mechanical shear. As a result, the structure and the properties of the resulting hybrid materials depended strongly on the processing conditions and ranged from very moderate dispersions and property improvements to good dispersions and better performing hybrids.

Obviously, a MA-polypropylene pretreatment with very low maleic anhydride content did not promote the nanocomposite formation, and very high maleic anhydride content made the master batch so robust that mmt did not mix further with neat PP.

**Nanocomposite Formation through PP Functionalization.** The incorporation in the PP polymer of any functional group, which is attracted by the mmt surfaces to a greater degree than the methylene and methine, will promote PP miscibility with alkylammonium-modified mmt. To test this approach, random copolymers of PP with typically 1 mol % of functionalized monomers were synthesized. The polymer characteristics are given in Table 1. All the functionalized PPs were derived from the same random PP copolymer synthesized by metallocene catalysis, which contained 1 mol % p-methylstyrene (p-MS) comonomers. Subsequently, the p-MS’s were interconverted to functional groups (OH) were first mixed with octadecylammonium-modified mmt, creating a master batch, which was subsequently blended with neat PP, usually assisted by strong mechanical shear in an extruder or mixer. In this way, the PP polymer and the MA-polypropylene pretreated o-mmt are effectively at theta conditions, and the extrusion is only promoting mixing due to the effect of the mechanical shear. As a result, the structure and the properties of the resulting hybrid materials depended strongly on the processing conditions and ranged from very moderate dispersions and property improvements to good dispersions and better performing hybrids.

<table>
<thead>
<tr>
<th>Functionalized PP: random copolymers</th>
<th>x (mol %)</th>
<th>( M_n )</th>
<th>( T_m ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-(PP-MS)k</td>
<td>1.0</td>
<td>200 000</td>
<td>154</td>
</tr>
<tr>
<td>PP-(PP-MA)k</td>
<td>0.5</td>
<td>200 000</td>
<td>155</td>
</tr>
<tr>
<td>PP-(PP-OH)k</td>
<td>0.5</td>
<td>200 000</td>
<td>155</td>
</tr>
<tr>
<td>PP-(PP-OH)</td>
<td>1.0</td>
<td>200 000</td>
<td>155</td>
</tr>
</tbody>
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<table>
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<tr>
<th>Functionalized PP: diblock copolymer</th>
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<tr>
<td>PP-(PMMA)k</td>
</tr>
<tr>
<td>PP-(PMMA)k</td>
</tr>
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</table>

* These metallocone-synthesized PPs are mostly isotactic, with a broad molecular weight distribution (typically \( M_w/M_n = 4-6 \)); details of the polymerizations are published elsewhere (refs 28–32). The neat/unmodified PP used is a commercial material with \( M_w = 580000 \) and \( M_w/M_n = 3.49 \).

The X-ray diffraction scans for the low 2θ values, where the basal reflection of the interlayer d spacing appears, are shown in Figure 1 for functionalized-PP/2C18-mmt samples formed under static melt-intercalation conditions (i.e., the nanocomposites were formed by annealing the polymer/o-mmt physical mixture in a vacuum oven at 180 °C, unassisted by shear or solvent). There is a definite intercalated structure, for all the different functional groups that we tried, manifesting itself through an interlayer d-spacing increase of about 1 nm compared to that of the 2C18-mmt. Since these hybrids were formed in the absence of mechanical shear, this is direct evidence of sufficiently favorable thermodynamics for the nanocomposite formation. However, the XRD can only detect the periodically stacked mmt layers; for all these nanocomposites there also exists a large number of exfoliated layers as well, which can be directly observed by transmission electron microscopy (TEM). In Figure 2 we show a bright-field TEM of the maleic anhydride functionalized polypropylene (PP-MA) nanocomposite, containing 6 wt % of 2C18-mmt. From the TEM it becomes clear that there are intercalated tactoids (A) and disordered/exfoliated stacks of layers (B) coexisting in the nanocomposite structure. The intercalated structures are characterized by a parallel registry that gives rise to the XRD reflection of Figure 1, whereas the disordered mmt formations have no
periodic stacking and thus remain XRD silent. This behavior is common for most polymer/mmt nanocomposites, and in accord with this general behavior, in our PP/mmt hybrids the larger—i.e., lateral size—mmt layers create intercalated tactoids, whereas the smaller layers tend to exfoliate.

Quantitative analysis of TEM images can be used to evaluate the percentage of silicate exfoliation. Namely, for each nanocomposite material, we capture 20–40 independent TEM images at 50 K magnification (a view of approximately 4 × 5 μm). Subsequently, we use image analysis software to enumerate (a) the total number of layers seen edge-on, (b) the layers in stacks of more than 10 layers separated by <3 nm (intercalated tactoids); and (c) bunches of up to 3 layers that are separated by more than 50 nm (exfoliated layers) or nonparallel layers separated by <20 nm (disordered layers). The percentage of the last group is an estimation of the exfoliated and disordered structures in the system (this number is recorded in Figure 1 and onward). Admittedly, these definitions are ad hoc and 20–40 images cover a very small total area to carry high statistical significance; however, for the present study they were sufficient to contrast the different PP/mmt nanocomposite structures.

The functional groups added to the PP polymer do not have to be introduced in a random-copolymer fashion; alternatively, functional groups can be incorporated as a block, forming a PP diblock copolymer. To test this approach, we synthesized diblocks with poly(methyl methacrylate) (PP-b-PMMA) containing 1 and 5 mol % PMMA. Their synthesis involved PP preparation by metallocene catalysis, hydroboranation of the olefinic chain end, and free radical polymerization of the PMMA block. Obviously, in this case it is necessary to use an organic modification for the mmt that will promote miscibility with PMMA, namely, a primary ammonium with an octadecyl tail (C18-mmt). The resulting composites contained approximately 20% of the layers in an exfoliated/disordered manner and the rest in an intercalated manner as shown in Figure 3.

Nanocomposite Formation through Fluoro-Organic Modified mmt. Our aim, when designing the functionalized PP above, was to render the polymer/mmt interactions more thermodynamically favorable than the surfactant/mmt interactions. Exactly the same effect can be achieved by introducing an organic modification in the mmt which is thermodynamically less favorable than the olefinic polypropylene; such a modification can be a semi-fluorinated surfactant. Expectedly, an o-mmt that is completely modified by fluorinated organic surfactants would be very difficult to obtain (since the
ultralow surface tension surfactants will not exchange the alkali counterions under normal exchange conditions. Instead, a mixture of hydrogenated- and fluorinated-alkyl surfactants can be employed. Specifically, we first exchanged all the native mmt cations by octadecylammoniums, and subsequently we introduced a second semi-fluorinated alkyltrichlorosilane surfactant (CF3- (CF2)5- (CH2)2- Si- Cl3). This second surfactant is tethered to the mmt surface through a reaction of the trichlorosilane groups with hydroxyls in the cleavage plane of the mmt.12 The resulting o-mmt contains octadecylammoniums at full CEC and ≈60% additional semi-fluorinated surfactants (as quantified by TGA analysis). The XRD of the initial C18-mmt and the subsequent fluoro-organic mmt (f-mmt) are shown in Figure 4. In the same figure, we also show the XRD of unfunctionalized-PP/f-mmt nanocomposites, which were formed by melt-intercalation and by extrusion. The hybrid formed by melt-intercalation (i.e., by just annealing a physical mixture of polymer and f-mmt) reveals that there exist favorable thermodynamics for the nanocomposite formation [Figure 4 (melt)]. Moreover, the usage of mechanical shear [Figure 4 (extruded)] promotes further dispersion and exfoliation of the f-mmt layers.

At this point, we should note that this approach is qualitatively different than the “swelling agent” approach, as for example by Wolf et al.9 In such approaches an alkylammonium-modified montmorillonite is intercalated by an organic “swelling agent”, such as ethylene glycol, naphtha, or heptane (all with boiling points below the processing/extrusion temperature).9 Subsequently, the swollen organo-modified clay is compounded with PP in a twin-screw extruder at 250 °C. At this processing temperature, the swelling agent evaporates, leading to the formation of a “nano”composite which is XRD silent. In principle, this is the same as the solution intercalation process, where a solvent is employed to mix the o-mmt with the polymer, and an exfoliated structure is trapped when evaporating the solvent.29 Such trapped structures are not thermodynamically stable and are not amiable to processing. Similar nanocomposites9 can also be obtained by coprecipitation of PP and alkylammonium-mmt from a trichlorobenzene solution (as discussed in the following section).

**Synopsis of the Synthetic Routes and the Nanocomposite Structures.** Guided by simple thermodynamic arguments, we proposed two general synthetic routes to PP/organo-mmt nanocomposite formation and demonstrated their feasibility: (i) the first one implements “ordinary” organic modifications for the mmt33 and functionalized polypropylene polymers; (ii) alternatively, neat/unfunctionalized polypropylene can disperse mmt modified by a mixture of hydrogenated and semi-fluorinated surfactants. In both cases, polymer/o-mmt nanocomposites can be formed by melt-intercalation (i.e., unassisted by mechanical shear or organic solvents) Moreover, in both cases the resulting hybrid structures contain intercalated mmt tactoids in coexistence with exfoliated/disordered mmt layers. Where extrusion is used to form the PP/o-mmt nanocomposites, instead of melt-intercalation, further dispersion and exfoliation of the mmt layers is promoted.

We should mention that the second approach (employing f-mmt) is generally applicable for nonpolar polymers, such as polycarbonates, polyolefins, and polydienes. Some representative material properties of these PP/o-mmt hybrid materials are discussed in the following section.

**Materials Properties**

**Stability of the Nanocomposite Structure.** One of the first questions that should be addressed is whether the mmt dispersion (nanocomposite structure) is retained after high-temperature processing of the hybrid. To qualitatively assess the stability of the nanocomposite structure, we carried out the following experiment: We precipitated hybrids from a co-suspension of polypropylene and o-mmt mixed in a common organic solvent (1,3,5-trichlorobenzene). As the solvent evaporates, the o-mmt layers become trapped in an almost exfoliated manner throughout the polymer matrix.19 Subsequently, we process these “hybrids” at 180 °C (i) by compression molding and (ii) by a commercial twin-head mixer (Brabender plasti-corder). Both these methods allow the polymer to melt and the trapped hybrid structure to relax. If the o-mmt dispersion is not thermodynamically stable, the layers will collapse in low d-spacing parallel stacks during the high-temperature processing, leading to a conventionally filled “macro” composite. However, if there exists a favorable free energy of the o-mmt/polymer mixing, the nanocomposite structure of Figures 1–4 will be largely recovered.

In Figures 5 and 6 we show the structure evolution under annealing—as revealed by XRD—for two kinds of systems: A neat-PP/dimethylidioctadecylammonium mmt (Figure 5), where PP and the alkyl-modified mmt are at theta conditions, and neat-PP/f-mmt (Figure 6a) PP-MA/dimethylidioctadecylammonium mmt (Figure 6b), where there exist favorable thermodynamics for the o-mmt dispersion in the polymer.

All systems were precipitated—at time 0 min—from a polymer/o-mmt co-suspension, and as cast they show an almost silent XRD pattern, which denotes that after the solvent was removed the mmt layers were trapped in an exfoliated or disordered dispersion. In the first
case, neat-PP/2C18-mmt was annealed in a compression molder at 180 °C and 15 tons of load (Figure 5). For the neat-PP/2C18-mmt the dispersed layers collapse toward immiscible/intercalated structures within 10–15 min of annealing (as denoted by \(d\)-spacings of 2.4–3.1 nm, Figure 5). For the PP-r-MA however, even after 30 min of annealing at 180 °C in the compression molder, there appears to be no intercalated peak (like that of Figure 1A); the trapped structure is maintained, even after prolonged annealing. This suggests that the MA groups have sufficiently strong interactions with the mmt to prevent the polymer from sliding away from the inorganic layers. Although this has been observed before for polymers with strong specific interactions with mmt (e.g., polymers that hydrogen bond to the silicates, such as poly(vinyl alcohol)\(^{19}\) and nylon-6), it is striking that only 0.5 mol % of MA can have the same effect.

The precipitated neat-PP/f-mmt hybrid was annealed in a Brabender mixer at 180 °C (Figure 6A). As expected, the mechanical shear markedly reduces the time necessary for the structure recovery, and the structure of Figure 4 is recovered after 8 min of mixing. In sharp contrast, precipitated systems of neat-PP and 2C18-mmt, also characterized by a silent XRD as cast, but even very moderate mixing in the Brabender (2–5 min at 180 °C) resulted in an immiscible/intercalated structure with a wide XRD reflection extending from 1.8 to 2.7 nm in \(d\)-spacing.

**Mechanical Properties.** Most of the PP/mmt nanocomposites studies report tensile properties as a function of mmt content (\(\phi_{\text{mmt}}\)), characterized by Instron.\(^5\)–\(^{12}\)

As a typical example of these tensile properties, we show in Figure 7 an Instron study of a neat-PP/f-mmt composite compared to a PP/2C18-mmt “conventional” composite (for these latter systems, the 2C18-mmt remains in tactoids, which are not intercalated or exfoliated by a polymer). The characteristic behavior for polymer/layered-inorganic nanocomposite materials\(^3\) is observed. Namely, there is a sharp increase of Young’s modulus for very small inorganic loadings (\(\phi_{\text{mmt}} < 3\) wt %) followed by a much slower increase beyond \(\phi_{\text{mmt}} \approx 4\) wt %. With increasing \(\phi_{\text{mmt}}\), the yield stress does not change markedly compared to the neat-polymer value, and there is only a small decrease in the maximum strain at break. PP systems conventionally filled by similar fillers (e.g., 2C18-mmt) do not exhibit as large increases in their tensile modulus (Figure 7). Similar improvements in mechanical properties can also be achieved by other layered particulate fillers; however, much higher filler loadings are required. For example, to obtain comparable tensile increases like the ones achieved by mmt dispersion (Figure 7), 30–60 wt % of talc or mica is needed.\(^2\) Obviously, as the polymer/inorganic adhesion is improv-
we report the HDT of PP and of its nanocomposites
a higher heat deflection temperature (HDT). In Table
is not limited only to the tensile modulus increase. The
reinforcement of PP due to the nanocomposite formation
(Figure 8b). In the work by Mühlaupt et al.,10 a
properties can be altered by the processing conditions
potentially significant and thus a higher increase in
Young's modulus is expected (Figure 8). For this reason,
compared to neat-PP/mmt hybrids (Figure 8a), the PM-
MAM/mmt's are characterized by larger modulus in-
creases for the same o-mmt loading (Figure 8b).

The tensile results obtained from this work are not
affected by the nanocomposite processing since the
nanocomposite structure does not change markedly with
the processing conditions (i.e., whether the hybrid is
formed by melt-intercalation or by extrusion). However,
in the absence of favorable thermodynamics for the PP/
ommt miscibility, the hybrid structure and the tensile
properties can be altered by the processing conditions
(Figure 8b). In the work by Mühlaupt et al.,10 a
systematic study of the dependencies on compatibilizer
functionality and mmt organic modification revealed
that considerable tensile enhancements can be achieved
only where appropriate PP-MA “compatibilizers” are
used to pretreat the o-mmt in conjunction with specific
organic modification of the mmt. Similar materials under different processing conditions showed much
smaller improvements in the mechanical properties.

Heat Deflection Temperature. The mechanical
reinforcement of PP due to the nanocomposite formation is not limited only to the tensile modulus increase.
The nano-dispersion of mmt in the PP matrix also promotes a higher heat deflection temperature (HDT). In Table
we report the HDT of PP and of its nanocomposites
based on f-mmt and alkylammonium mmt. In the case of
neat-PP/f-mmt there is a marked increase of the HDT, from 109 °C for the neat polymer to 152 °C for a 6 wt %
nanocomposite; beyond 6 wt % of f-mmt the HDT of the hybrid levels off. When the same neat-PP polymer is
filled with alkylammonium-modified mmt, the HDT is
also increased but to a smaller extent, reflecting the lower exfoliation level of the inorganic fillers. Moreover,
in the latter case, there is a strong dependence of the
HDT on the processing conditions during the composite
formation, for the same type of filler and the same
loading. The increase of HDT due to mmt dispersion is a very important improvement for PP, not only from
the application/industrial viewpoint but also because it is
difficult to achieve similar HDT enhancements by chemical modification or reinforcement by other fillers.4

The improvement of the HDT originates from the
better mechanical stability of the nanocomposite, com-
pared to the neat-PP, rather than any increase of the
polymer melting point. In all the PP/mmt hybrids studied, the melting temperature does not change
markedly from that of the respective neat polymer. This is qualitatively different from the behavior of other
polymers (e.g., nylon-6) where the mmt layers stabilize
a different crystalline phase than that found in the neat
polymer, with a higher melting point and also higher
HDT.15,16

Other Properties. Beyond the mechanical and HDT improvements, the nanocomposite formation results in concurrent enhancements of other materials properties.3 Because tensile properties can also be improved by other means,1,2 the highest promise for any potential uses of
PP/mmt nanocomposites do actually relate to these
“other property” enhancements. In brief, we will discuss some examples that qualitatively set apart the PP/mmt
nanocomposites from other conventional PP composites.

Albeit their micrometer lateral size, mmt’s are just
1-nm thin. Thus, when single layers are dispersed in a
polymer matrix, the resulting nanocomposite is optically
dark in the visible region. In Figure 9 we present the
UV/vis transmittance as a function of wavelength, both
for neat-PP/f-mmt and thick films of PP-r-MA/2C18-
mmt. There is no marked decrease in the clarity due to
the fillers (for o-mmt loadings up to ϕ = 9 wt %). One
has to load approximately 20 wt % of 2C18-mmt in
3-mm-thick films of PP-r-MA before there develops haze
observable by the naked eye. The loss of intensity in the
UV region (for λ < 250 nm) is mostly due to
scattering by the mmt particles. When a neat-PP/6 wt
% f-mmt nanocomposite is compared to a conventionally
filled neat-PP/3 wt % C18-mmt, it is observed that these
two materials have almost the same loss of intensity in
the visible region (Figure 9). Despite the double inor-
ganic loading in the PP/f-mmt system, due to the
exfoliation of the mmt layers, these two materials have a comparable concentration of tactoids. This suggests
that the intensity loss in the visible region is due to the
intercalated/miscible tactoids, whereas the exfoliated
layers do not seem to contribute. Hence, achieving a
fully exfoliated structure should lead to nanocomposites
as optically clear as the initial polymers.19

Generally, polymer/silicate nanocomposites are char-
acterized by a range of materials improvements, com-

Table 2. Heat Deflection Temperatures (HDT (ref 34)) of
PP/mmt Nanocomposites and the respective Unfilled
(First) PP

<table>
<thead>
<tr>
<th>filler loading</th>
<th>HDT (°C)</th>
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<tr>
<td>neat-PP/f-mmt</td>
<td>neat-PP/alkyl-mmt</td>
</tr>
<tr>
<td>0 (neat PP)</td>
<td>109 ± 3</td>
</tr>
<tr>
<td>3</td>
<td>144 ± 5</td>
</tr>
<tr>
<td>6</td>
<td>152 ± 5</td>
</tr>
<tr>
<td>9</td>
<td>153 ± 5</td>
</tr>
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</table>

a C18-mmt filler, extruder processed. b 2C18-mmt filler, twin-
head mixer.
mon to most polymers, which originate from the nature of the inorganic filler and its nanometer-thin layered structure.3,4 PP/mmt nanocomposites also exhibit most of these “general” property enhancements. Namely, the permeability to liquids and gases is reduced to half when 4 wt % of mmt is dispersed in the PP or the functionalized PPs, and at the same time, the solvent uptake decreases accordingly.12 Another property that is strongly affected by these inorganic fillers is a sharp increase of the scratch resistance for very moderate loadings (1–5 wt % of o-mmt). Montmorillonite-based fillers also promote the flame retardancy of PP. In Figure 10 we show the mass loss rate during combustion, measured by cone calorimetry. For a PP-r-MA nanocomposite with 4 wt % 2C18-mmt, there is a 75% reduction in flammability compared to the unfilled polymer.18 This flame-retardant character is traced to the response of a carbonaceous-char layer, which develops on the outer surface during combustion:18 This surface char has a high concentration of mmt layers and becomes an excellent insulator and a mass transport barrier (slowing the oxygen supply as well as the escape of the combustion products generated during decomposition).18

Finally, from a practical viewpoint, because only a few percent of inorganic fillers are needed in the PP/mmt nanocomposites, the resulting hybrids are lightweight. Moreover, where there exist favorable thermodynamics for PP/o-mmt miscibility, the organo-mmt can be incorporated in the final stages of polymer processing (e.g., extrusion, injection/compression molding) to obtain nanocomposite hybrids. Thus, PP/mmt nanocomposites are amenable to most of the common processing techniques in today’s industrial practices, which lowers the barriers toward commercialization for these nanocomposite hybrids. Additionally, o-mmt fillers can be used in conjunction with other PP reinforcements, such as fibers, thus combining the PP/mmt improvements and those from the fiber reinforcement in one composite material.

### Conclusions

Synthesis of PP/o-mmt nanocomposites, with a coexisting intercalated and exfoliated structure, was realized in two ways: (i) by introducing functional groups in PP and using common alkylammonium montmorillonites and (ii) by using neat/unmodified PP and a semi-fluorinated surfactant modification for the mmt. In the first case, the necessary level of PP functionalization is very low (random copolymers with 0.5 mol % of functionalized comonomers, or diblock copolymers with 1 mol % of non-PP blocks, sufficed). Functional groups that promoted nanocomposite formation with 2C18-mmt included p-methylstyrene, maleic anhydride, styrene, and hydroxyl-containing styrene; polypropylene-b-methyl-methacrylate diblocks also formed nanocomposites with C18-mmt. In the second case, a semi-fluorinated alkyltrichlorosilane was used to modify C18-mmt, rendering it miscible with neat/unfunctionalized PP and a semi-fluorinated surfactant modification for the mmt.

In all cases, nanocomposite formation was achieved by melt-intercalation (unassisted by mechanical shear or solvents), revealing sufficiently favorable thermodynamics of polymer/o-mmt mixing. As is typical in most polymer/silicate nanocomposites, PP/mmt hybrids exhibit concurrent improvements in several materials properties, for very moderate inorganic loadings (typically less than 6 wt % of mmt). Enhanced properties include improved tensile characteristics, higher heat deflection temperature, high barrier properties, better scratch resistance, and increased flame retardancy. Because these PP/mmt nanocomposite matrixes are amenable to common processing tech-
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References