Polypropylene/Silicate Nanocomposites, Synthetic Routes and Materials Properties

E. Manias*, A. Touny, L. Wu, B. Lu,
K. Strawhecker, J.W. Gilman†, T.C. Chung
Materials Science & Engineering department
The Pennsylvania State University
University Park, PA 16802
† Materials Fire Research group
National Institute of Standards & Technology Gaithersburg, MD 20899

Introduction

Ultra-thin (~10Å) layers of allumino-phylllosilicate have been used as fillers in many polymer systems, resulting in hybrid organic/inorganic composites with impressive materials properties [1]. Due to their extremely high aspect-ratio, when such layered filler particles are finely dispersed in a polymer matrix, the polymer properties can be modified to a dramatic extent even for very moderate amounts of filler (less than 10 wt%). In some cases, many of the materials properties are concurrently enhanced, for example the heat distortion temperature is elevated, while at the same time there is no sacrifice of the impact strength or the toughness [1,4]. More commonly, where naturally occurring silicates –such as montmorillonite (mmt)– are used for hybrid nanocomposites, there exist both intercalated and exfoliated structures throughout the polymer matrix. In such cases, careful choice of the inorganic layered host can achieve a great enhancement of selected properties. Consequent silicates layers in their pristine form are separated by hydrated films of metal cations (Na⁺, Li⁺, Ca⁺), which can be easily exchanged by organic cationic surfactants (usually alkyl-ammoniums) to create organically modified forms. Where polymers are hydrophilic and coordinate effectively the cations (e.g. polyethyleneoxide, polyvinylalcohol) then nanocomposites can be formed with the pristine silicates, whereas polymers with sufficiently polar character (e.g. nylons, polystyrene, polysiloxanes, polyimides and so on) can disperse the organically modified silicates. None of these two methods can be applied to polypropylene (PP) for alkyl-ammonium modified silicates and clays, and as a result no high quality smectic reinforced PP has been reported, despite the considerable attention and interest that such nanocomposites attract [2].

Here, we report our first successful efforts of obtaining high quality PP/silicate nanocomposites, with alkyl-ammonium exchanged montmorillonites (o-mmt). For all the hybrid materials discussed in this preprint there coexist intercalated and exfoliated mmt layers throughout the polymer matrix.

Results and Discussion

Synthetic routes to nanocomposite formation. PP is not expected to produce miscible nanocomposites with alkyl-ammonium modified montmorillonite unassisted by solvents or extensive shear, as is anticipated from thermodynamics arguments [3; fig 5a]. However, along the same lines, if minute amounts of polar functional groups are attached to the polymer –in blocks or randomly grafted– polypropylene will be rendered miscible with alkyl-ammonium modified mmt, and nanocomposites can be formed either by direct melt intercalation, or co-extrusion of PP with the o-mmt.

Materials. Two o-mmt were synthesized in our lab by simple cation exchange of Na⁺ mmt (Southern Clay Products, TX) by dioctadecyl-dimethyl-ammonium and octadecyl-ammonium bromides (Aldrich), and subsequently mictually washed and filtered by ethanol to remove any excess surfactants [4]. The functionalized PP polymers chosen to form nanocomposites with 2c18mmt and c18mmt are tabulated in table 1.

Table 1. Characteristics of the PP Polymers Used

<table>
<thead>
<tr>
<th></th>
<th>x (wt %)</th>
<th>Mw</th>
<th>Tm (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>PP-r-(PMMA)</td>
<td>0.5</td>
<td>2 x 10⁶</td>
</tr>
<tr>
<td>B</td>
<td>PP-r-(PP-MA)</td>
<td>0.5</td>
<td>2 x 10⁶</td>
</tr>
<tr>
<td>C</td>
<td>PP-r-(PP-OH)</td>
<td>0.5</td>
<td>2 x 10⁶</td>
</tr>
<tr>
<td>D</td>
<td>PP-b(PMMA)</td>
<td>5.0</td>
<td>1.5 x 10⁴</td>
</tr>
</tbody>
</table>

* to whom correspondence should be addressed, at: manias@psu.edu

Random copolymers of PP with typically 0.5wt% of functionalized PP monomers were synthesized by Chung and coworkers as described in [5,6]. These functionalized PPes were derived from a random PP copolymer that contained 0.5wt% P-methylstyrreny (P-MS) monomers, and was synthesized by metallocene catalysis [5]. Subsequently, the P-MS were interconverted to functional groups containing OH and maleic anhydride (MA) by lithiation and free-radical reactions respectively; the details about the polymer synthesis and functionalization are given elsewhere [5]. The PP-b-PMMA diblock copolymers contained 5wt% polymethylmethacrylate and their synthesis involved PP preparation by metallocene catalysis, hydroboration of the olefinic chain-end and free radical polymerization of the PMMA block [6].

These new synthetic methods have recently attracted much interest as they can produce a wide variety of functionalized polyolefins, with controllable molecular structure and no detectable side reactions (chain scission, cross-linking). Furthermore, they can be easily scaled up from the lab scale bearing great potential for industrial application.

PP/mmt nanocomposite preparation. In order to determine the effect on the nanocomposite structure, PP/layered silicate nanocomposite samples were prepared using three different techniques:

(i) Melt Extrusion. Powdered PP and organically exchanged mmt were premixed and subsequently coextruded using a single-screw mini-extruder under N₂ at 180°C for up to 10min. (ii) Melt Blending. PP and o-mmt were mixed inside a blender (Brabender Plasti-Corder) heated at 170-180°C for up to 20min. (iii) Solvent Intercalation. A 10% trichlorobenzene solution of PP and o-mmt was ultrasonicated for up to 5 minutes until a good suspension was created. The solvent was then evaporated for several hours at ambient temperature, in a fumee hood, until a very viscous gel was created. The gel was then placed in a vacuum oven at 70°C for up to 5 hours until all the solvent was removed.

Characterization of the composite structure. Hybrids contained typically 2 to 10wt% of organically modified mmt, for all the PP variants, and their structure was characterized by wide angle X-Ray Diffraction (XRD) and Transmission Electron Microscopy (TEM). The nanocomposite structure and the layer dispersion in the polymer matrix are qualitatively the same for all the three preparation paths used, i.e. identical XRD patterns, and TEM that revealed a coexistence of intercalated tactoids and exfoliated layers. A systematic quantitative study of the effect of the preparation and polymer composition on the composite structure –and its connection to the hybrid materials properties– is currently underway. All the results reported herein are from the nanocomposites created in the Brabender blender (method ii).

Wide angle XRD is a very fast test of nanocomposite formation. Shift of the o-mmt diffraction peak to lower 2θ values denotes an intercalated polymer layer between consequent silicate layers. In figure 1 the XRD patterns of the organically modified mmt and of the PP nanocomposites are shown. The moderately functionalized PP random copolymers (containing 0.5wt% of P-PS, OH, and MA comonomers) are miscible with dimethyl-dioctadecyl-ammonium mmt (2C18mmt), increasing the gallery d-spacing of the o-mmt from 24Å to 30Å for the MA functionalized PP [7], and to 34Å for the OH and MS containing polymers. Moreover, the PP-b-PMMA diblock copolymers create a nanocomposite with the octadecyl-ammonium mmt (C18mmt) and increase the d-spacing from 22Å to 32Å. The peaks are quite wide in the PMMA block (due to variations of the d-spacing between different tactoids, and due to broadening from finite size of the disf contracting structures) there exist second order (002) reflections denoting that where intercalated structure exists,
The o-mmt disappears in all the hybrid nanocomposites, thus all the layered silicate is miscible with the polymer. Moreover, the diffraction peak that corresponds to the o-mmt disappears, denoting that the absence of any immiscible o-mmt layers.

Figure 1. Wide angle XRD for the organically modified mmt and the corresponding PP nanocomposites. For all hybrid structures the peak of the o-mmt disappears, denoting that the absence of any immiscible o-mmt layers.

Although XRD can give a fast answer on the miscibility of polymer/silicate systems, it does not give all the structural information for the nanocomposites. For example, in all the above systems (figure 1) XRD provides no information about any exfoliated or disordered mmt layers, since these possess no periodic structure and thus are XRD silent. However, TEM can directly observe the nano-structure and—for all the above systems—suggests that these properties originate from the hybrid structure and the nanometric dispersion of the inorganic layers in the polymer. For example, a common mechanism underlying the reduced flammability of several polymer/silicate nanocomposites (including PP-(PP-MA) hybrids) was found to be connected with the char formation caused by the finely dispersed (exfoliated & disordered layers) in the polymer matrix.

Furthermore, they are more resistant to solvents (solvent-uptake decreases markedly compared to PP) and preliminary work suggests also improved scratch resistance.

These common enhancements of the materials properties—general for all these nanocomposites—suggests that these properties originate from the hybrid structure and the nanometric dispersion of the inorganic layers in the polymer. For example, a common mechanism underlying the reduced flammability of several polymer/silicate nanocomposites (including PP-(PP-MA) hybrids) was found to be connected with the char formation caused by the finely dispersed (exfoliated & disordered layers) in the polymer matrix.

Materials properties. A systematic study of the mechanical and thermal properties of these PP nanocomposites is reported elsewhere [7,8]. Summarizing our findings to date, all these nanocomposites exhibit enhanced mechanical properties compared to the neat PP (higher moduli, and strength) [8] whereas at the same time are thermally more stable than the pure PP and exhibit impressively enhanced flammability characteristics (figure 3) and [7].

Figure 2. Bright field TEM of the PP-(PP-MA) nanocomposite. In the area shown here exist montmorrilonite layers that are intercalated (A) and give rise to the XRD reflection shown in figure 1, layers assembled in disordered clusters containing several layers without any parallel registry (B), and exfoliated layers (singles, or in stacks of 2 to 4) throughout the polymer.

Figure 3. Mass loss rates for PP-(PP-MA), and for two mmt nanocomposites from cone calorimeter combustion experiments; from reference [7].