

### A Direct-Blending Approach for Polypropylene/Clay Nanocomposites Enhances Properties

The commercial importance of polypropylene (PP) has driven the investigation of PP composites reinforced by particulates, fibers, and layered inorganic fillers. Specifically, with respect to layered inorganic fillers, the aluminosilicate minerals talc and mica have been of greatest interest. However, recent advances in polymer/clay and polymer/silicate nanocomposite materials have motivated efforts to disperse fillers in PP based on montmorillonite, a naturally occurring mineral in the 2:1 aluminosilicate family. Because of PP's nonpolar (aliphatic) nature, it has proved challenging to develop a clay-based filler that is directly miscible with neat (i.e., nonfunctionalized) PP.

To date, most of the efforts that have shown some success employ a two-step process. First, a polymer/clay "master batch" is compounded, usually by mixing a functionalized (e.g., maleic anhydride) PP with high loadings of alkyl-ammonium-modified montmorillonite. This "master batch" is subsequently blended with neat PP, usually assisted by strong mechanical shear in an extruder or mixer. In this manner, the PP polymer and the master batch are effectively at  $\theta$  conditions (i.e., the energy of the mixture is the same as the

energy of the separate components), and the extrusion is only promoting mixing of the clay in the neat-PP matrix due to the effect of the mechanical shear. As a result, the structure and the properties of the hybrid material produced depend strongly on the processing conditions and range from moderate dispersions and modest property improvements to good dispersions and better performing hybrids. It is still under investigation whether the clay dispersion in these structures is amenable to further processing or whether the fillers reaggregate.

The resulting PP/inorganic hybrids produced by this two-step process typically have enhanced modulus and barrier properties, but poor thermal and impact

behaviors. Even more important, reliability suffers in that hybrids with consistent properties are not formed even when the same materials and processing conditions are used. This is not surprising, since the filler dispersion in the PP matrix is achieved by a process that traps the separate inorganic layers.

At The Pennsylvania State University, researchers have developed an alternate route of nanocomposite formation that uses a carefully selected semi-fluorinated organic surfactant to modify the montmorillonite clays. They use favorable mixing thermodynamics to promote and stabilize the clay dispersion in neat PP. Some representative materials properties are given in Table I.

The mechanical response is compara-

**Table I: Typical Materials Properties for Polypropylene (PP)/Clay Nanocomposites Formed by Direct Blending of PP with Fluoro-Organic-Modified Montmorillonite (f-mmt)**

Properties	Neat PP	PP/f-mmt Nanocomposites	
		3-wt% f-mmt	6-wt% f-mmt
<b>Mechanical Properties</b>			
Young's (tensile) modulus (MPa)	665.8	906.9	959.3
Yield stress (MPa)	28.9	31.3	30.6
Strain at break (%)	744.6	646.9	716.5
<b>Other Properties</b>			
Heat-deflection temperature (°C)	109	144	152
Max. heat-release rate (kW m <sup>-2</sup> )	1508	452	390
Light transmittance (at $\lambda = 600$ nm)	0.58	0.57	0.49

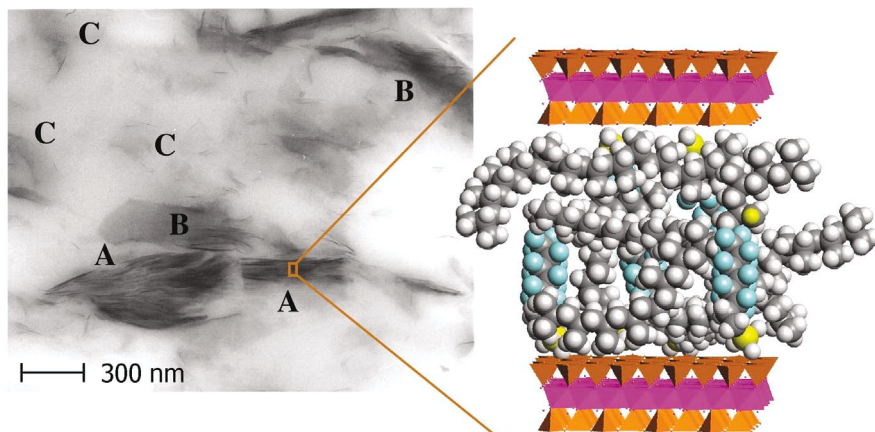


Figure 1. Bright-field transmission electron micrograph of the polypropylene (PP)/clay structure; black lines correspond to the clay layers and gray regions to the PP matrix. Note the coexistence of (A) intercalated (parallel-stacked and separated by 2–3 nm of PP) and (B) disordered (with comparable PP separations, but without parallel registry) tactoids—bunches of clay layers—with (C) exfoliated formations of 1–3 clay layers (separated by tens of nanometers of polymer). A, B, and C refer to the way that the dark lines (clay layers) are dispersed in the gray background (polymer).

ble with that of PP/clay hybrids formed by the “master batch” process; namely, an increased (by 150–200%) Young’s (tensile) modulus is the best that can be achieved without sacrificing the yield stress and the elongation at break. However, in the case of the fluoro-organic-modified montmorillonite-based (f-mmt) nanocomposites, there is also a notable elevation (by 35–43°C) of the *heat-deflection temperature* (i.e., the temperature at which a standard plastic test bar deflects a specified amount under an established load, per ASTM) and no marked loss of clarity in the visible wavelengths. Also, the barrier properties are improved, with water-vapor and oxygen permeabilities reduced by one-half at a 4-wt% f-mmt level. Clay dispersion also promotes flame-retardant properties, a characteristic common to almost all PP/clay hybrids independent of their preparation and structure. This last property enhancement arises from a surface char formation, which is thermally insulating and thus retards further combustion. The char layer is also highly impermeable to gases and fumes.

Beyond the improvement in properties, one of the most important features of the PP/f-mmt hybrids is that the clay dispersion (see Figure 1) is achieved independently of the conditions employed for the nanocomposite formation. This implies that the properties arising from the nanocomposite structure are maintained. For example, the improvement in heat-deflection temperature shown in Table I remains almost unchanged for direct PP/f-mmt blending by static melt intercalation, extrusion, solvent-assisted dispersion, and compression molding. Moreover, the

nanometer filler dispersion is maintained after subsequent processing, even at high temperatures and high shear rates; this has been verified under extrusion, mixing in an industrial mixer (Brabender), and cyclic compression-molding of the nanocomposite. This stability of the filler dispersion under further processing is expected, since the dispersion is determined by the thermodynamics of the system, in contrast with the trapping mechanism of the two-step process.

The researchers are currently exploring general design principles to concurrently enhance selected properties. They have developed a scheme (based on the extent of the surfactant fluorination) that allows for controlling the clay dispersion from mostly intercalated to almost fully exfoliated. This control becomes important when impact properties are considered, since exfoliation promotes Young’s modulus enhancement at the expense of impact strength, whereas intercalated structures promote impact strength. Thus, a mixed intercalated/exfoliated structure can be used to achieve a balance of high modulus and impact. Preliminary work suggests that the ability to control the clay dispersion would allow tailoring this balance at will.

#### Opportunities

Penn State is interested in establishing relationships with industrial partners to aid in the commercialization of this technology.

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