Improved Thermal Stability of Imidazolium **Treatments for Polymer Layered-Silicate** Nanocomposites

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Nanocomposites result from the combination of materials with vastly different properties at the nanometer scale. Some examples of these include: polymers combined with layered-silicates $(LS)^1$, polymers combined with nano-silica^{2,3}, hybrid materials prepared by sol-gel methods⁴, and polyhedral oligometric silsequioxanes (POSS) nanocomposites⁵. All these materials exhibit many unique properties, such as improved thermal stability,⁶ reduced flammability,⁷ and improved mechanical properties.⁸ However, nanocomposites must maintain their unique chemical and physical properties during processing. We have observed degradation during processing of polystyrene (PS)/LS9 and polyamide (PA-6)/LS nanocomposites.¹⁰

In light of these results, which show both polymer molecular mass degradation and alkyl ammonium degradation during processing, we have focused our efforts on the development of organic treatments for montmorillonite clay (MMT) with improved thermalprocessing stability. We report here on results for imidazolium treated MMT, which show improved stability compared to traditional alkyl ammonium treatments. We decided to focus on imidazolium salts, since the delocalized cation has been shown to have better thermal stability than the alkyl ammonium cation.¹¹ To make the imidazolium treated clay the imidazolium tetrafluoroborate was used to treat NaMMT via ion exchange. We prepared a series of trialkyl imidazolium salts and ion exchanged them with Na-MMT. All of the trialkyl imidazolium-MMT prepared had improved thermal stability. The TGA for the imidazolium MMT with the longest alkyl chain: dimethyl hexadecyl imidazolium MMT (DMHDIM-MMT) shows that it has a 100°C higher onset of decomposition as compared to the standard alkyl ammonium-MMT. A typical T_{dec} reported for alkyl ammonium treated MMT is 200 °C.¹² DMHDIM-MMT was melt blended with PS in a mini twin-screw extruder. The TEM (Figure 1) of the resulting mixture reveals successful nano-dispersion and formation of a mixed intercalated and exfoliated nanocomposite.



Figure 1. TEM image of PS/ 5 % DMHDIM-MMT nanocomposite.

To rigorously test the thermal-processing performance of DMHDIM-MMT we used it to prepare a nanocomposite from poly ethylene terephthalate (PET), which processes at 285°C; to date no reports have appeared in the literature describing the successful melt blending preparation of

PET/MMT nanocomposites. However, melt compounding of DMHDIM-MMT with PET in the mini twin-screw extruder resulted in a well dispersed nanocomposite. The TEM (shown in Figure 2) reveals a mixed intercalated and exfoliated morphology; some single layers are observed along with stacks of 4-6 MMT layers together.



Figure 2. TEM image of PET/ 5 % DMHDIM-MMT nanocomposite.

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