# Polymer Layered-Silicate Nanocomposites from Thermally Stable Trialkyl-Imidazolium Treated Montmorillonite

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## Abstract

The limited thermal stability of alkyl ammonium cations and the processing instability of some polymers (polyamide-6 (PA-6) and polystyrene (PS)) in the presence of nanodispersed montmorillonite (MMT) has motivated the development of improved organophillic treatments for layered silicates. Success in this regard should enable preparation of polymer layered silicate nanocomposites from thermoplastic engineering polymers with high melt-processing temperatures, and from thermoset resins with high cure temperatures. Our efforts to address some of these issues focus on the use of new thermally stable imidazolium treated layered silicates for preparation of nanocomposites. Several trialkyl- imidazolium salt derivatives were prepared with propyl, butyl, decyl and hexadecyl alkyl chains attached to the imidazolium through one of the nitrogens. These imidazolium salts were used to prepare the corresponding treated layered-silicates. We report here that the use of 1-alkyl-2,3-dimethylimidazolium salts to replace the sodium in natural MMT gives

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organophillic-MMT with a *100 °C improvement* in thermal stability (in $N_2$) as compared to the alkylammonium treated MMT. The use of 1-alkyl-2,3-dimethylimidazolium salt in fluorinated synthetic mica (FSM) gives a *200 °C improvement* in thermal stability. The use of 1,2-dimethyl-3-hexadecylimidazolium treated MMT gives an exfoliated PA-6 nanocomposite and, depending on processing conditions, either, a partially exfoliated or, an intercalated polystyrene nanocomposite.

## INTRODUCTION

A new approach to address the ever increasing demand for higher performance polymeric products focuses on the use of mica-type layered silicates, such as montmorillonite (MMT), nano-dispersed (exfoliated) in polymers.[1] These "nanocomposites" exhibit the unusual combination of improved physical properties[2,3] and reduced flammability.[4,5,6,7,8] However, using the standard alkylammonium treated MMT to prepare nanocomposites from a variety of polymers (PS, EVA, PP, PA-6, epoxy, and cyanate ester) we have observed *less than* the expected improvement in properties (physical and flammability); in some instances, a loss in properties was observed relative to the unmodified polymer[9,10,11,12]. Several other groups have also found that these treatments have insufficient thermal stability to survive high temperature melt-processing or curing conditions.[13,14] Some solutions to this issue include the use of un-treated layered-silicate. In these approaches either the monomer[15] or the curing agent[16] is made cationic *in situ,* and this renders the layered-silicate organophillic. Other cations, such as phosphonium, pyridinium and imminium have also been used to treat the layered-silicate due to their greater thermal stability.[17] Thus, the need for organophillic treated layered silicates that offer improved stability under processing conditions is well documented.[18] New thermally stable systems should enable preparation of polymer layered-silicate nanocomposites from thermoplastic engineering polymers with high melt-processing temperatures (polycarbonate, polyethyleneterephthalate, syndiotactic polystyrene, polyetherimide), and from thermoset resins with

high cure temperatures (cyanate esters, aromatic epoxies), without loss of properties due to the presence of degradation products, loss of molecular mass[19] or network structural defects. Our efforts to address some of these issues focus on the use of new thermally stable trialkyl-imidazolium treated layered silicates for preparation of nanocomposites.[20]

# EXPERIMENTAL[?]

**Preparation of trialkyl-imidazolium salts:** Imidazolium bromide salts were typically prepared as follows; The alkyl bromide or chloride (1 mole), 1,2-dimethylimidazole (distilled, 0.95 mole) and acetonitrile (50 mL) were combined in a round bottom flask equipped with a reflux condenser. The mixture was refluxed for 7 d to10 d  under nitrogen. After the reaction was complete, a large excess of ethyl acetate was added to precipitate the imidazolium salt.  This solid was filtered and washed several times with ethyl acetate to remove the 1,2-dimethylimidazole. Residual solvent was removed under vacuum, at 80 $^{o}$C, for 12 h, from the resulting 1-alkyl-2,3-dimethylimidazolium salt. The solid was re-dissolved in a minimum of acetonitrile and precipitated with ethyl acetate.  The white solid was filtered and washed with ethyl acetate, and solvent removed under vacuum at 80 $^{o}$C. In some cases, the salts were converted to the tetrafluoroborate salt to improve purity. The products were characterized via mass spectroscopy (MS), $^{1}$H and $^{13}$C NMR, and thermal gravimetric analysis (TGA); The characterization data are consistent with data published on similar dialkyl imidazolium structures.[21] Complete details of the synthesis and characterization of all of the imidazolium salts presented here, and of other imidazolium salts, will be published in a separate manuscript.[22] The $^{1}$H and $^{13}$C NMR data for two of the trialkylimidazolium compounds are presented  in Table 1.

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[?]  The identification of any commercial product or trade name does not imply endorsement or recommendation by the National Institute of Standards and Technology or the Air Force Office of Scientific Research

Table 1. ^{1}H NMR data for 1-decyl-2,3-dimethylimidazolium chloride (DDMIM$^+$ Cl$^-$) and 1,2-dimethyl-3-hexadecylimidazolium tetrafluoroborate (DMHDIM$^+$ BF$_4^-$).[‡]

| [1]H | DMHDIM$^+$ BF$_4^-$ Chemical Shift (ppm) | DDMIM$^+$ Cl$^-$ Chemical Shift (ppm) |
|---|---|---|
| N-CH$_3$ | 3.65 | 3.75 |
| C2-CH$_3$ | 2.48 | 2.50 |
| H(4,5) | 7.22 | 7.40, 7.45 |
| N-C1 (CH$_2$) | 4.00 | 4.05 |
| N-C2 (CH$_2$) | 2.10 | 1.75 |
| N-C3 to C14 (CH$_2$)$_{12}$ | 1.25 | ---- |
| N-C3 to C9 (CH$_2$)$_7$ | ---- | 1.25 |
| N-C10 CH$_3$ | ---- | 0.85 |
| N-C15 (CH$_2$)$_1$ | 1.70 | --- |
| N-C16 CH$_3$ | 0.85 | --- |

Table 2. ^{13}C NMR data for 1,2-dimethyl-3-hexadecylimidazolium tetrafluoroborate (DMHDIM$^+$BF$_4^-$) and 1-decyl-2,3-dimethylimidazolium chloride (DDMIM$^+$ Cl$^-$).

| [13]C | DMHDIM$^+$ BF$_4^-$ Chemical Shift (ppm) | DDMIM$^+$ Cl$^-$ Chemical Shift (ppm) |
|---|---|---|
| N-CH$_3$ | 31.5 | 31.5 |
| C2 | 144.5 | 144.5 |
| C2-CH$_3$ | 9.0 | 9.0 |
| C4 | 121.0 | 121.0 |
| C5 | 122.0 | 122.0 |
| N-C1(CH$_2$) | 48.0 | 48.0 |
| N-C2(CH$_2$) | 35.0 | 35.0 |
| N-C3 (CH$_2$) | 26.0 | 26.0 |
| N-C4 to C8 (CH$_2$)$_5$ | ---- | 29.0 |
| N-C4 to C14 (CH$_2$)$_{11}$ | 29.0 | ---- |
| N-C9 | ---- | 22.2 |
| N-C10 | ---- | 13.0 |
| N-C15 | 23.0 | ---- |
| N-C16 | 13.0 | ---- |

**Preparation and Characterization of Ion exchanged layered-silicates:** Standard ion exchange procedures were employed for preparing the organic treated layered-silicates.[23] The

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[‡] The policy of the National Institute of Standards and Technology (NIST) is to use metric units of measurement in all its publications, and to provide statements of uncertainty for all original measurements. In this document however, data from organizations outside NIST are shown, which may include measurements in non-metric units or measurements without uncertainty statements.

following trialkylimidazolium layered-silicate complexes were prepared from the corresponding imidazolium chloride, bromide, or $BF_4$ salt: 1-butyl-2,3-dimethylimidazolium montmorillonite (BDMIM-MMT), 1-decyl-2,3-dimethylimidazolium montmorillonite (DDMIM-MMT) and 1,2-dimethyl-3-hexadecylimidazolium montmorillonite (DMHDIM-MMT), 1,2-dimethyl-3-hexadecylimidazolium fluorinated synthetic mica (DMHDIM-FSM). For comparison purposes dimethyldioctadecylammonium montmorillonite (DMDOA-MMT) was prepared from the corresponding bromide (Aldrich), also using the standard ion exchange methods; and dimethyl-di(hydrogenated tallow)ammonium montmorillonite (DMDHT-MMT) was obtained from Southern Clay Products.

The imidazolium treated layered-silicates samples were characterized using X-ray diffraction (XRD) and TGA. In the case of DDMIM-MMT and DMHDIM-MMT, thermal desorption mass spectroscopy (TDMS) and residual chloride analysis were also done.

Thermal desorption mass spectrometry (TDMS) was performed on a Finnigan TSQ-70 triple quadrupole mass spectrometer. Samples were prepared as a slurry in water and applied to the tip of a direct exposure probe, which consists of a small tungsten filament. The probe was then positioned in the ion source of the mass spectrometer. Samples were desorbed from the probe by passing a current through the wire and increasing the temperature of the probe tip. The desorption profile was generated by holding the current constant at 50 mA for 6 seconds, increasing the current (linearly) from 50 mA to 1000mA over 45 seconds, and holding the current constant at 1000 mA for 6 seconds. Molecules desorbed from the probe were ionized with 70 eV electrons. Mass spectra were obtained at 0.5 sec per scan.

Trace Analysis of Chloride. A cyclic Voltammogram (cathodic end only) was carried out on pure propylene carbonate, DDMIM-MMT and DMHDIM-MMT. All work was done under $N_2$ . The MMT samples were prepared by suspending the MMT (1 gm) in propylene carbonate (30 ml), and

stirring the samples vigorously for 1 h.  The suspension was filtered through a 0.45?m polypropylene frit, and placed in the cell. The cell was a 40 ml glass vial fitted with a teflon cap, containing a 6.35 mm graphite rod counter electrode, a 2 mm diameter Pt working electrode, and a 4.6 mm diameter Pt wire served as a psuedo-reference.

**Preparation and Characterization of Nanocomposites.** PS and PA-6 nanocomposites were prepared in a mini-twin screw extruder (intermeshing, conical, Daca Corp.). Polymer and organic-treated layered-silicate were charged into the mini-extruder and typically mixed at (200 to 300) rpm for (3 to 5) min above the melting point of the polymer. The nanocomposite were characterized using XRD, TEM and solid state nuclear magnetic resonance (NMR) (PA-6 nanocomposites only).[26]

XRD data were collected on a Phillips diffractometer using CuK? radiation, (?=0.1505945 nm). The d-spacing uncertainty is ± 0.03 nm (2 sigma).

Transmission Electron Microscopy:  All samples were ultra microtomed with a diamond knife on a Leica Ultracut UCT microtome at either room temperature (PS) or -110 °C (PA-6) to give sections with a nominal thickness of 70 nm.   The sections were transferred from water (room temperature) or dry (-110 °C) to carbon-coated Cu grids of 200 mesh.  Bright-field TEM images of nanocomposites (except for PA-6) were obtained at 120 kV, under low dose conditions, with a Philips 400T electron microscope, using Kodak SO-161 film.  Low magnification images were taken at 2800? and 10000?.  High magnification images were taken at 28000? and 60000?.  Bright-field TEM images of PA-6 nanocomposites were obtained at 120 kV, under low dose conditions, with a Philips CM-12 electron microscope, and were digitally imaged with a CCD camera.  High magnification images (60000?) could not be obtained with the CCD as the resolution of CCD digital cameras at this magnification is rather limited.  The materials were sampled by taking several images of various magnifications over 2 to 3 sections per grid to ensure that analysis was based upon a representative region of the sample.

Solid-state NMR spectroscopy. PA-6 nanocomposites prepared with DMHDIM-MMT were characterized using a solid state NMR proton longitudinal relaxation rates ($T_1^H$) method recently developed by VanderHart.[26] Solid-state $T_1^H$ were measured using a non-commercial NMR spectrometer operating at 2.35 T. $T_1^H$ values were measured by the inversion recovery method[24] using variable delays of 1 ms, 75 ms, 235 ms, 500 ms, 1.0 s, and 3.0 s. Proton polarization levels at each of these delays were monitored indirectly via $^{13}C$ cross-polarization, magic angle spinning (CPMAS) NMR at 25.19 MHz. CPMAS spectra were obtained using a 4.0 kHz magic angle spinning frequency, a 3.0 s recycle delay, a 1 ms CP period and rf levels corresponding to nutation frequencies of 60 kHz and 64 kHz for protons and $^{13}C$ nuclei, respectively. Total experiment time was 2 h per sample; 320 scans for each of the 6 delay values.

Water content and thermal history, in addition to the quality of MMT dispersion, can significantly alter the $T_1^H$ of PA-6/MMT nanocomposites.[10] Therefore, samples were carefully prepared in order to normalize the effect of water and thermal history on $T_1^H$, and to allow quantitative determination of the extent of nano-dispersion of the MMT in the PA-6.

Thermal gravimetric analysis: TGA was carried out using a TA Instruments SDT 2960 Simultaneous DSC-TGA at 10 $^o$C/min in nitrogen (samples 5 mg to 10 mg) . Typically, 3 replicates were analysed for each sample and the mean reported. Both the onset (5 % mass fraction loss) and peak mass loss rate have an uncertainty of 1.2 $^o$C (2 sigma).

## Results and Discussion

**Organo-modified Montmorillonite:** The processing stability of both the polymer and the organic treated layered-silicate has a significant influence on the flammability performance of the nanocomposite. In a previous TGA-FTIR study, of the pyrolysis of PS/MMT nanocomposites,

aliphatic decomposition products were observed before the onset of PS degradation. This data suggests the organic treatment in the MMT was degrading at a lower temperature than the PS.[6] This may contribute to the shorter ignition times observed in PS/MMT nanocomposites during combustion experiments. Gel permeation chromatography (GPC) analysis of the extruded PS nanocomposite samples also reveals some evidence of polymer degradation, in the form of lower $M_w$.[7] Finally, the molecular weight degradation only occurs if quaternaryalkylammonium MMT is present, and does not occur, either if pure polymer is extruded, or if the PS is extruded with sodium montmorillonite (NaMMT). It appears that the presence of the quaternaryalkylammonium, in the MMT, somehow contributes to the degradation of the PS as well. This degradation is of particular concern since we have found that the flame retardant effect is completely negated, when extensive degradation occurs.[7] In addition, this could also limit the improvements in other physical properties observed for PS/MMT nanocomposites.

High melt-temperature engineering polymers, such as PA-6, PET and polycarbonate, raise additional concerns when considering preparation of nanocomposites by melt extrusion, or when processing (injection molding) the nanocomposites into final molded products. The concern is that most alkylammonium treatments for MMT have an onset of thermal decomposition at about 200 °C or below.[18] To facilitate rapid manufacturing of filled PA-6 typical industrial melt-processing temperatures are in excess of 300 °C.[25] The issue is whether or not the alkylammonium treated layered-silicates can survive short residence times (<200 s) in high-shear processing environments (extruder or other molding equipment) at 300 °C or higher.

We have found that both the alkylammonium and the PA-6 may degrade during processing in the presence of nano-dispersed MMT.[26] Using NMR, we have observed degradation of dimethyl dihydrogenated tallow ammonium montmorillonite (DMDHT-MMT) during melt extrusion with PA-6.

The NMR analysis showed significant concentrations of tertiaryamine after extrusion. The concentration of tertiaryamine was directly proportional to the residence time in the extruder, and appears to be nearly independent of the thermal history in the absence of shear. It was found that as much as 80 % (± 10 %) of the quaternaryalkylammonium had degraded in the samples with extrusion residence times long enough to give delaminated nanocomposites.[10] A comparison of another delaminated PA-6/MMT nanocomposite from the same study, prepared using dihydroxyethyl dihydrogenated tallow ammonium/MMT, showed an order-of-magnitude less degradation of the organic treatment. This sample, with no observable degradation products and similar extent of nano-dispersion of the MMT, had superior mechanical properties compared to the PA-6/MMT nanocomposite with degradation products.[18] We also found large $M_n$ losses (50 %) and significantly higher concentrations of caprolactam monomer in PA-6/MMT nanocomposites that were injection molded at 300 °C.[27] In light of these results, we have focused our efforts on the development of organic treatments for MMT and other nano-additives with improved thermal-processing stability.

**Imidazolium treated layered-silicates.** It has been reported that the delocalized imidazolium cation has better thermal stability than the alkylammonium and pyridinium cations.[28,29] The imidazolium salts shown in Figure 1 were used to treat NaMMT, via standard literature ion exchange methods[3], to give a series of imidazolium-MMT (IM-MMT). The NMR characterization data for the DDMIM$^+$Cl$^-$ and DMHDIM$^+$ BF$_4^-$ salts are summarized in Table 1 and Table 2. The IM-MMT were analyzed by XRD to determine if the spacing between the layers (d-spacing) had changed. The XRD data showed that as the R-group increased in length the d-spacing increased (see Figure 2), with the exception of the butyl and propyl derivatives, which have nearly the same steric size and, hence, the same d-spacing. Using the same ion exchange procedure we also prepared and characterized 1,2-dimethyl-3-hexadecylimidazolium fluorinated synthetic mica (DMHDIM-FSM). The XRD data for these materials is shown in Table 3.
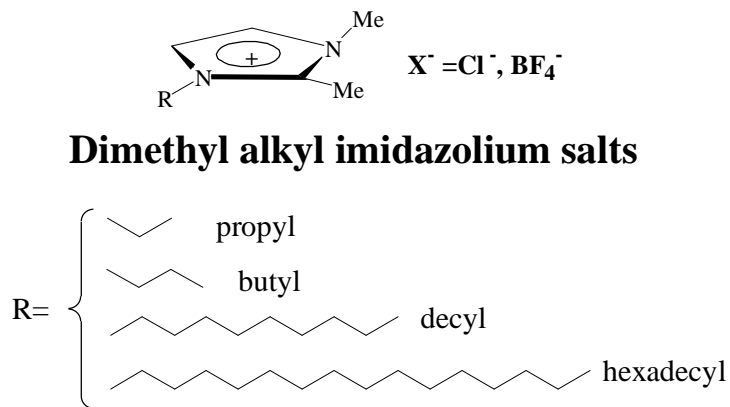
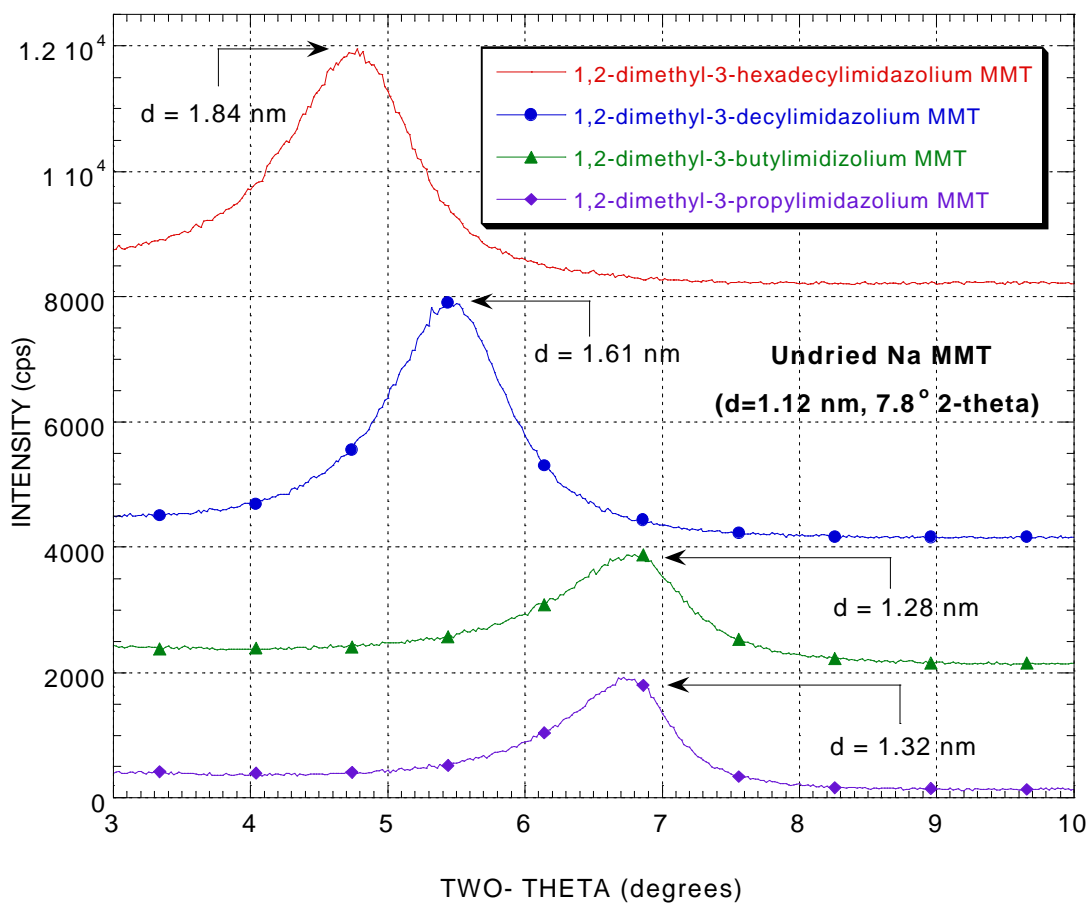Figure 1. Structures of various imidazolium salts used to treat sodium montmorillonite.



Figure 2. XRD data for several IM-MMT salts showing the d-spacing between MMT layers. The standard uncertainty in the d-spacing is ± 0.03 nm (2 sigma).

The thermal stability of the organic treatment of the layered-silicate is of prime importance, therefore TGA was carried out on these materials. For comparison, two quaternary alkylammonium treated MMT, were evaluated as well: dimethyl dioctadecyl ammonium montmorillonite (DMDOA-MMT) and dimethyl-di(hydrogenated tallow) ammonium montmorillonite (DMDHT-MMT). The TGA data, taken in a nitrogen atmosphere, summarized in Table 3 for the trialkylimidazolium and the tetraalkylammonium treated MMT samples, clearly show the improvements in thermal stability for all of the IM-MMT compared to both the DMDOA-MMT and DMDHT-MMT. Substitution of methyl at the methyne-position of the imidazolium was found to be critical, and provides $50^{o}$C higher thermal stability for the trisubstituted imidazolium compared to the disubsituted imdazolium (data not shown).[22]
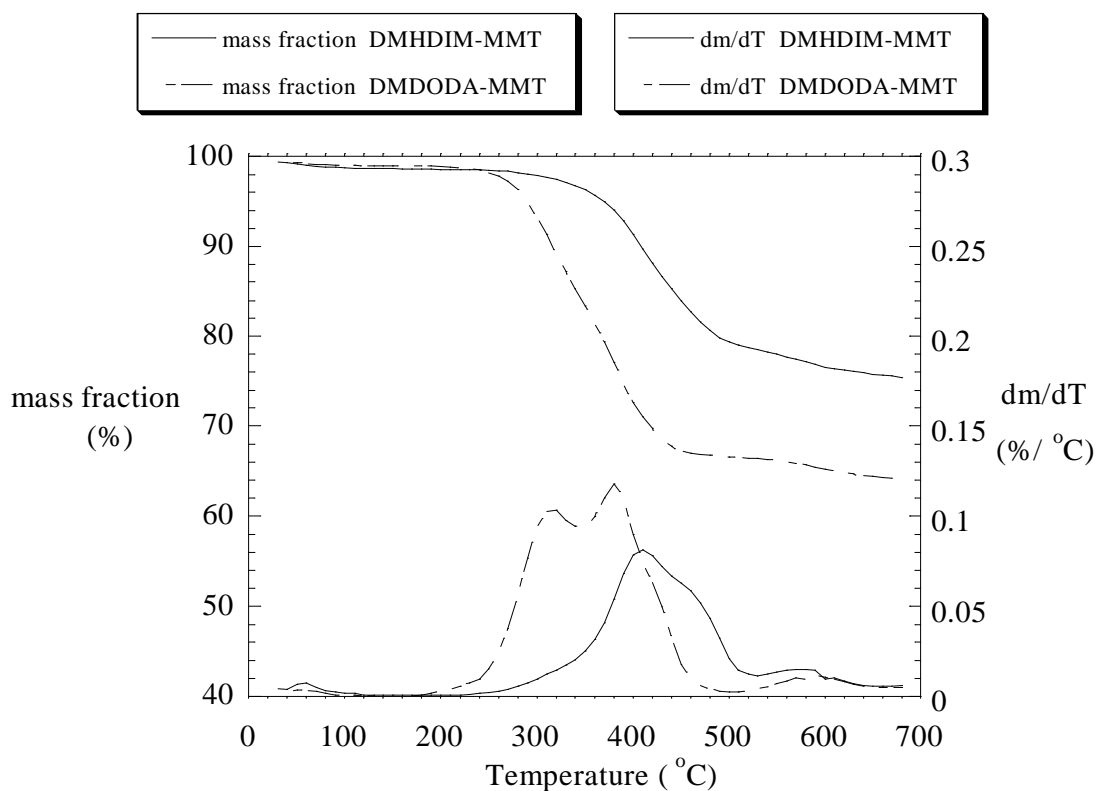


Figure 3. TGA data for 1,2-dimethyl-3-hexadecyl imidazolium–MMT and dimethy-dioctadecyl ammonium–MMT, which shows the ~100 $^{o}$C higher thermal stability of the imidazolium treated MMT.

Table 3. Thermal stability data for imidazolium and quaternaryalkylammonium treated MMT.

| Sample | Organic Fraction (+/- 0.5) | Onset decomposition temperature °C | Peak decomposition temperature °C | Change in d-spacing vs. NaMMT nm |
|---|---|---|---|---|
| 1,2-dimethyl-3-hexadecylimidazolium / MMT | 0.25 | 343 | 406 | 0.72 |
| 1-decyl-2,3-dimethylimidazolium / MMT | 0.17 | 320 | 432 | 0.49 |
| 1-butyl-2,3-dimethylimidazolium / MMT | 0.13 | 340 | 448 | 0.16 |
| 1,2-dimethyl-3-propyl imidazolium / MMT | 0.13 | 340 | 445 | 0.20 |
| 1,2-dimethyl-3-hexadecyl imidazolium / FSM | 0.16 | 420 | 450 | 0.27 |
| dimethyldioctadecylammonium bromide | -- | 221 | 233 | -- |
| dimethydioctadecylammonium bromide / MMT | 0.36 | 280 | 308 | 1.49 |
| dimethyldi(hydrogenated tallow)ammonium / MMT | 0.35 | 200 | 310 | 2.00 |

MMT : montmorillonite, FSM: fluorinated synthetic mica,
Uncertainty for onset and peak $T_{dec}$ measurements are $\pm$ 1.2 $^{o}$C (2 sigma)

The enhancement in thermal stability, which occurs when the imidazolium is intercalated into the MMT, was probed by thermal-desorption mass spectroscopy (TDMS). The greater thermal stability of the DMHDIM-MMT over the DMHDIM-Cl salt is evident by comparison of Figure 4 to Figure 5. Figure 4 shows the DMHDIM-MMT produces primarily one desorption peak at 0.57 min, which is that for thermal desorption of the DMHDIM cation (321.7 amu). The TDMS data for the DMHDIM-Cl salt (Figure 5) reveals a major peak at 0.49 min and a minor peak at 0.56 min. The peak at 0.56 min appears to be the same as the 0.57 min peak in Figure 4, i.e., due to the desorption of the parent ion (321.7 amu). The first peak in the TDMS of the DMHDIM-Cl salt at 0.49 min contains no parent ion, and several main decomposition products. The first of these products results from loss of one methyl

group (presumably off the imidazolium moiety) from the parent cation (321.7 amu) to give the 306.7 amu peak; the second major decomposition product results from loss of 2 methyls to give a 291.7 amu product. This difference in stability of the imidazolium cation is presumably due to the anion effect observed by others.[18] Here, the chloride ion appears to be much more reactive with the imidazolium than the silicate anion present in the MMT. This data raises the issue of the importance of purification after the ion exchange process used to prepare the DMHDIM-MMT. If residual DMHDIM-Cl ion is present after this reaction then the thermal stability of the DMHDIM-MMT will be lower. The imidazolium chloride must be completely washed out of the MMT product. This is similar to the effects Vaia observed in alkyl ammonium treated MMT.[18] This chloride ion effect motivated our electrochemical analysis of the IM-MMT after the ion exchange process to ensure complete ion exchange of the chloride by MMT, and hence provide maximum thermal stability. We succeeded in complete removal of residual chloride by ion exchange to the BF4 salt, or by 2 to 3 recrystalization from acetonitrile.
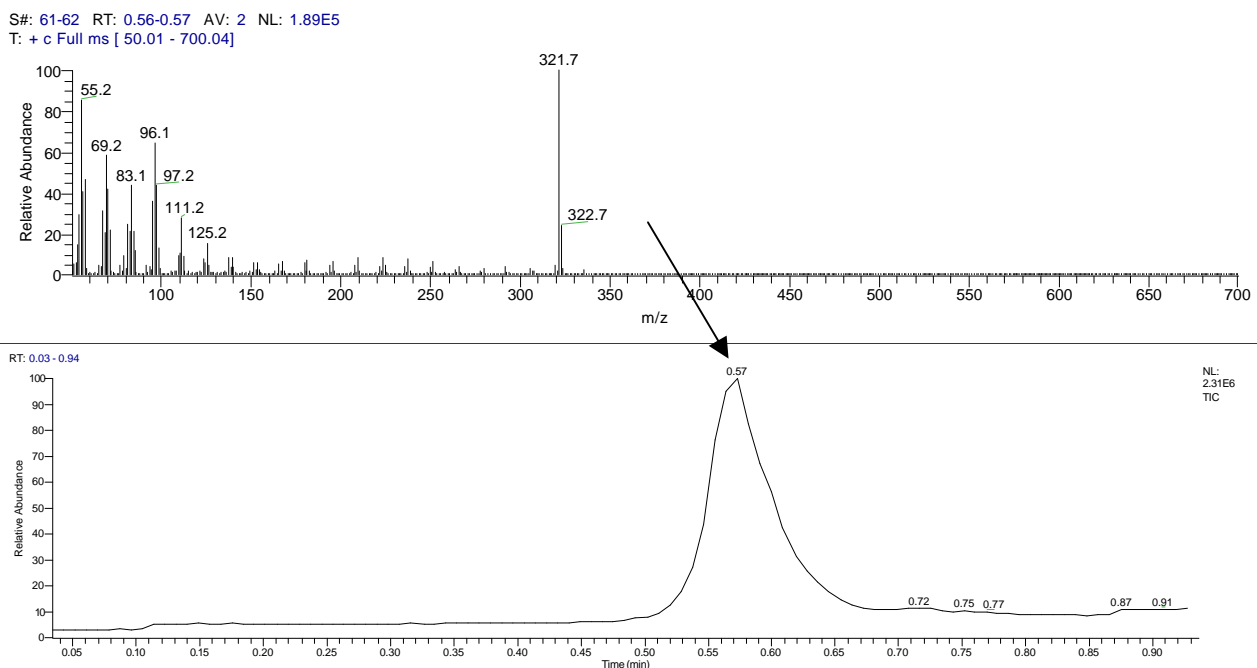


Figure 4. Thermal desorption electron ionization mass spectrum of DMHDIM-MMT and total ion plot of peak at 0.55 min.
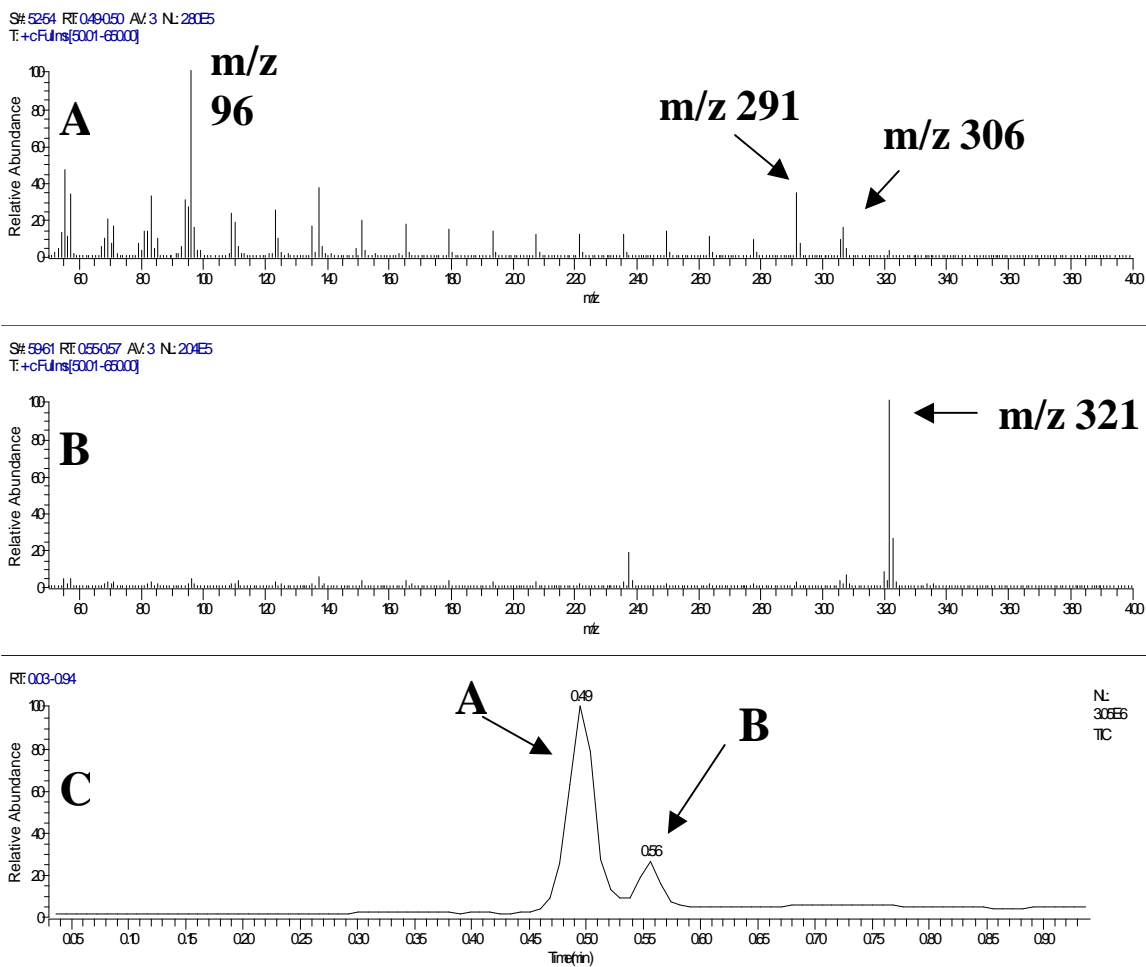
Figure 5. Thermal desorption electron ionization mass spectrum of DMHDIM$^+$ Cl$^-$ (C) and total ion plot of the peaks at 0.49 min (A) and 0.55 min (B).

While the improved thermal stability is of key importance to making polymer-clay nanocomposites, the organically treated MMT must also be compatible with the polymeric matrix, monomer, or solvent used to prepare the nanocomposite; otherwise the material will not disperse in the polymer during processing to form a nanocomposite.

The decyl and hexadecyl functionalized imidazolium MMTs (DDMIM-MMT and DMHDIM-MMT) were each blended with PS in a micro twin-screw extruder (5 min residence time, 200 $^{o}$C). XRD of PS / DDMIM-MMT (95:5) is shown in Figure 6, and reveals only a slight shift in the peak at 5.5$^{o}$ to 5.8$^{o}$ in the low angle region of the XRD, possibly due to loss of absorbed water during extrusion. This indicates poor miscibility of the DDMIM-MMT with PS. TEM (Figure 7) confirms the MMT is dispersed in the resin at the meso scale, but not delaminated. Many multi-layer tactoids, with small d-spacing, remain with very few single delaminated layers observed. The miscibility of the hexadecyl functionalized imidazolium MMT (DMHDIM-MMT) with PS, however, appears to be better than the decyl functionalized imidazolium MMT. The XRD (Figure 6) of the PS / DMHDIM-MMT (95:5) processed under the same conditions, produced new peaks at 2.8 $^{o}$ and 5.6$^{o}$ in the low angle region. This indicates intercalation of PS into the DMHDIM-MMT. TEM (Figure 8) reveals good dispersion of the MMT in the PS at the meso scale. A few individual layers appear in the TEM as well as many smaller (3-7 layers) tactiods with expanded layer spacings. The same sample, DMHDIM-MMT / PS, was also prepared using solution blending in toluene with shear supplied via sonication. After solvent evaporation, characterization by XRD showed loss of the low angle peak for the DMHDIM-MMT at 4.75$^{o}$. The TEM shown in Figure 9, reveals considerable exfoliation of the MMT, with some double and multi-layer tactiods still remaining. Previously, Manias has shown that using quaternaryalkylammonium treated MMT to prepare a PS/MMT nanocomposites, one obtains the same degree of exfoliation whether the mixing is done in an extruder or in toluene solution.[7] This result leads to the conclusion that the extrusion conditions were not optimum for preparing the DMHDIM-MMT / PS nanocomposites.
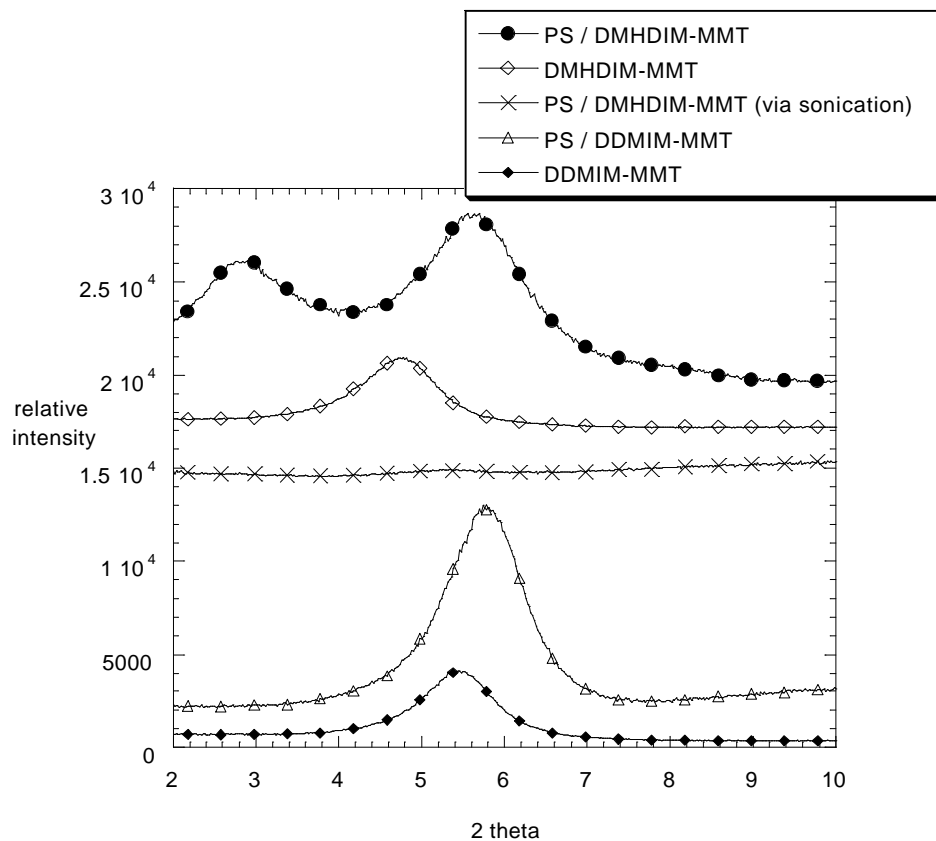
Figure 6. XRD of: PS/DMHDIM-MMT (95:5) prepared via extrusion, DMHDIM-MMT, PS/DMHDIM-MMT (95:5) prepared via sonication in toluene solution, PS/DDMIM-MMT (95:5) prepared via extrusion, and DDMIM-MMT.
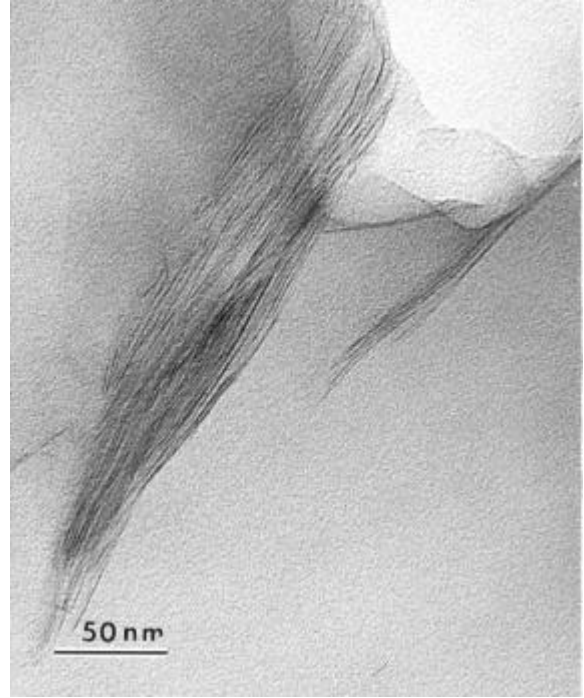
Figure 7. TEM of DDMIM-MMT/PS (95:5)
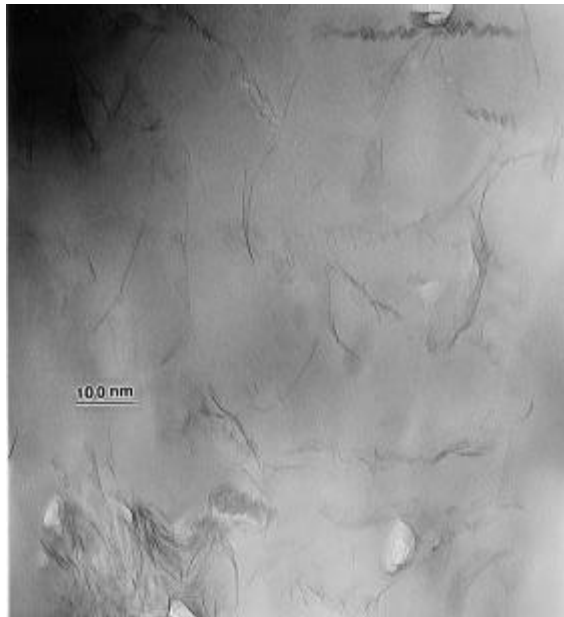


Figure 8. TEM of DMHDIM-MMT/PS (95:5)



Figure 9.TEM of DMHDIM-MMT/PS  (95:5) prepared by solution blending.

We also melt blended PA-6 with DMHDIM-MMT. Here, we obtained    fully exfoliated nanocomposites. In these experiments, also done in a mini-extruder, four different processing conditions were evaluated to find the best conditions. The TEM of these samples are shown in Figure 11 through Figure 14. From these images it is apparent that the DMHDIM-MMT exfoliated in the PA-6 matrix, however it is difficult to differentiate which processing condition produced the best nanocomposite. The XRD data shown in Figure 10, might lead one to conclude that the sample processed at $250^{o}C$ for 2 min is the best since no peak is observed, however there may be other reasons, aside from exfoliation, for the lack of order, and hence lack of a low angle peak. The samples processed longer and, or at higher temperature do show a low angle peak shifted to larger d-spacings relative to the DMHDIM-MMT. The TEM images of these samples clearly show the majority of the MMT exfoliated in the PA-6 matrix, therefore the low angle peaks ($3^{o}$ to $4^{o}$ two-theta) may represent only a minor fraction of the MMT in the nanocomposites, or they may also be higher order reflections of a 001 peak, which is not observed. Utilizing a quantitative NMR method, recently developed by VanderHart[10], we have further characterized these PA-6 MMT nanocomposites. This NMR method focuses on measurement of the proton longitudinal relaxation rates ($T_{1H}$) of the nanocomposites. The shorter the $T_{1H}$ the better the mixing of the MMT in the PA-6. The data for these samples is shown in Table 4 . From the NMR data it appears the sample processed at $250^{o}C$ for 5 min is the most homogeneous.
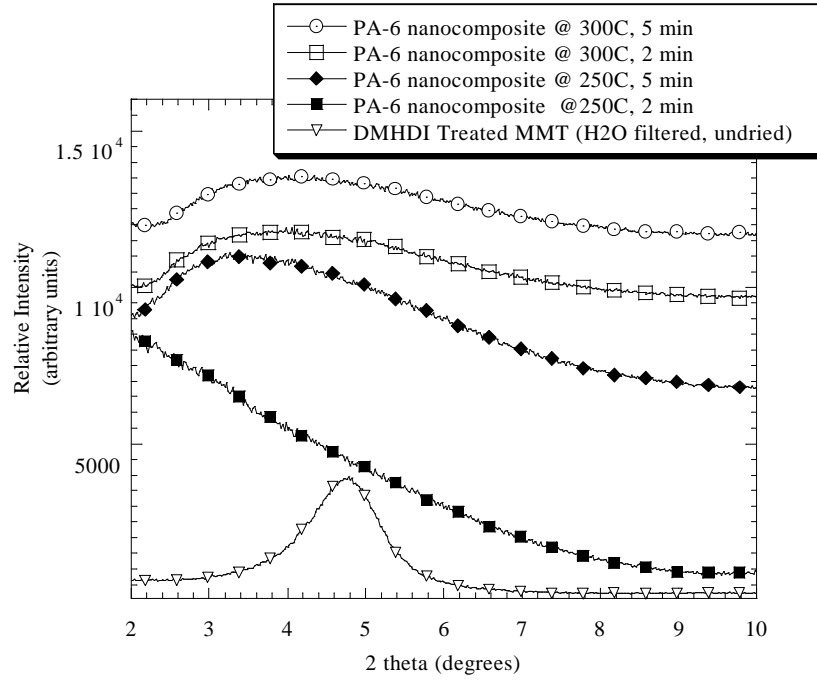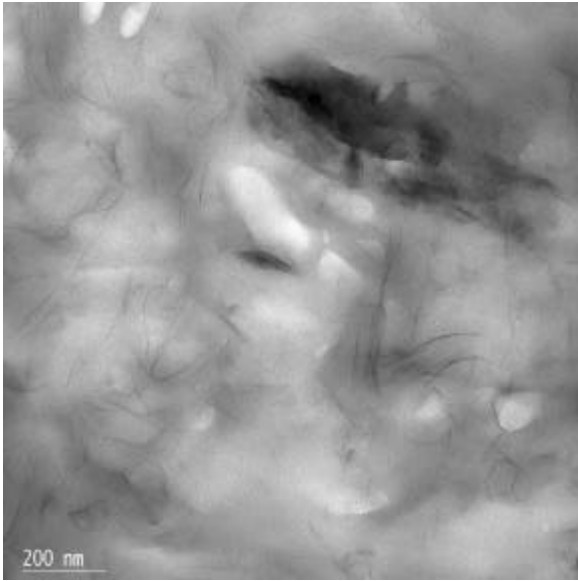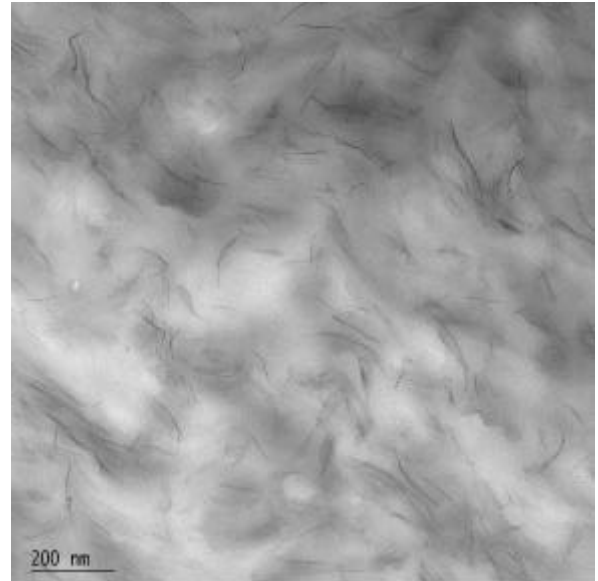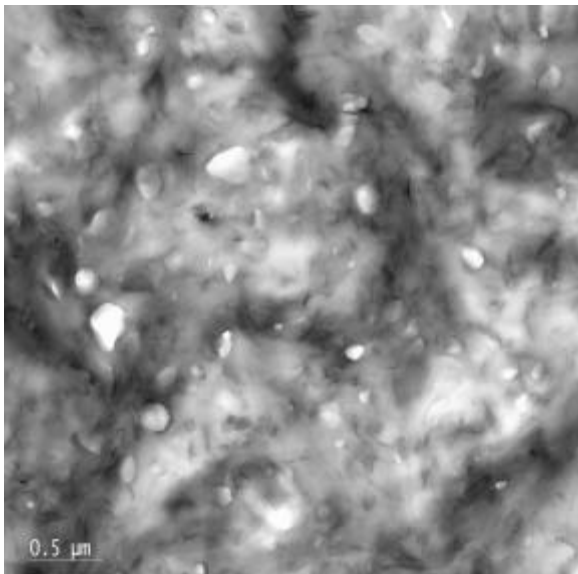
Figure 10. XRD of DMHDIM-MMT and DMHDIM-MMT/PA-6 (95:5) processed at 4 different conditions.
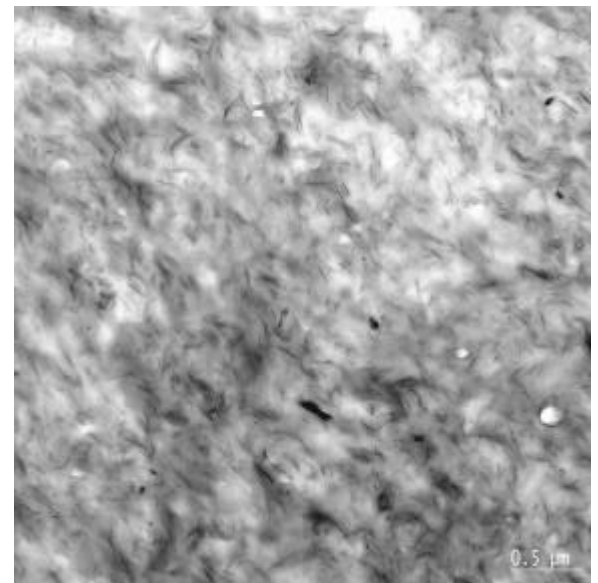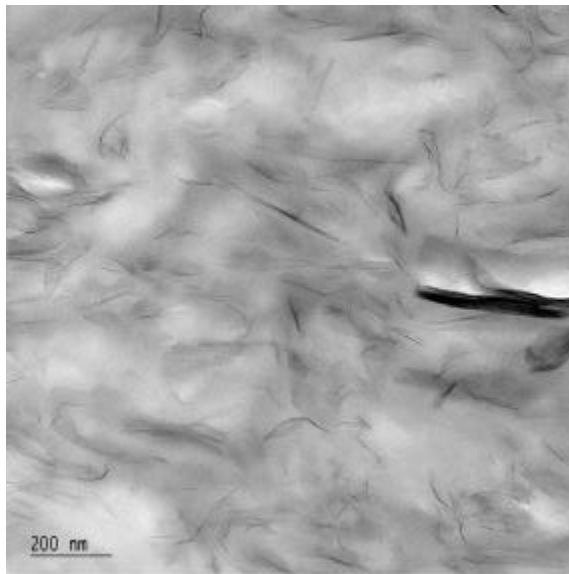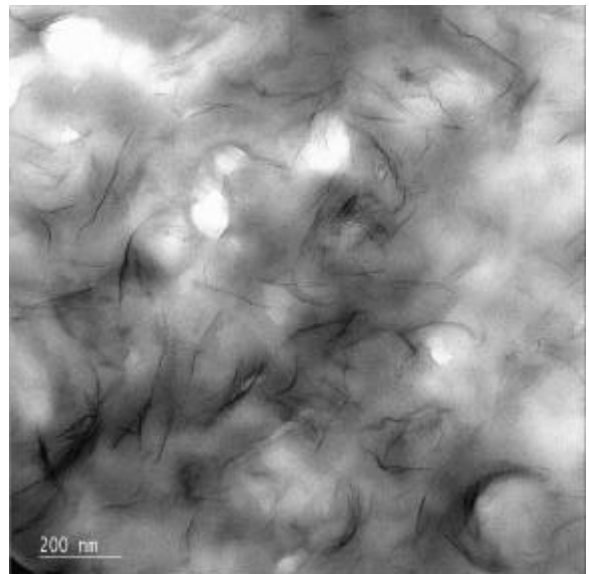
A



A



B



B

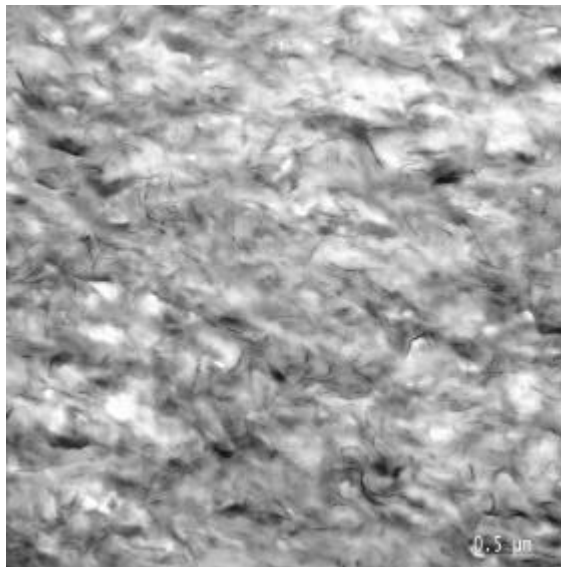Figure 11 A and B: TEM of DMHDIM-MMT/PA-6 (95:5) processed at 250 ?C for 2 min.

Figure 12 A and B: TEM of DMHDIM-MMT/PA-6 (95:5) processed at 250 ?C for 5 min.
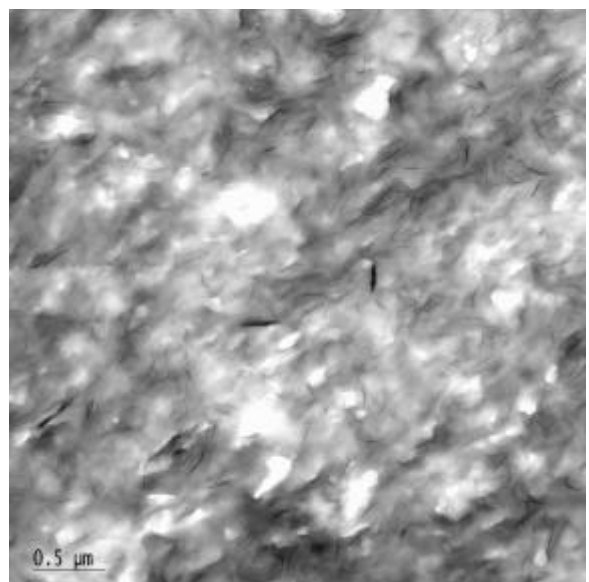
A



B

Figure 13 A and B: TEM of DMHDIM-MMT/PA-6 (95:5) processed at 300 ?C for 2 min.



A



B

Figure 14 A and B: TEM of DMHDIM-MMT/PA-6 (95:5) processed at 300 ?C for 5 min.

Table 4. NMR data for PA-6 and various MMT nanocomposites.

| PA-6 and PA-6 nanocomposites | $T_1^H$ (ms) |
|---|---|
| DMHDIM-MMT/PA-6 at 250 ?C / 2 min | 361 |
| DMHDIM-MMT/PA-6 at 250 ?C / 5 min | 343 |
| DMHDIM-MMT/PA-6 at 300 ?C / 2 min | 388 |
| DMHDIM-MMT/PA-6 at 300 ?C / 5 min | 381 |
| Pure PA-6* | 529 |
| Medium exfoliation of MMT in PA-6* | 400 |
| Very good exfoliation MMT in PA-6* | 327 |

*Results from previous publications.[10]

The physical, thermal and flammability properties of these imidazolium treated MMT nanocomposites are in the process of being characterized. Furthermore, we are also exploring the use of trialkylimidazolium-treated layered-silicates for preparing nanocomposites with other resins with procesing temperatures, or curing temperatures above 250 $^o$C (PET, cyanate esters, etc.).

## CONCLUSIONS

This work has demonstrated the superior thermal stability of trialkylimidazolium treated layered silicates. The hexadecyl functionalized imidazolium (DMHDIM-MMT) shows excellent compatibility with PA-6, and hence forms high quality PA-6/MMT nanocomposites. The DMHDIM-MMT also forms fairly good quality mixed intercalated and exfoliated nanocomposites with PS. Additional efforts to explore the use of IM-treated layered silicates will possibly show them to be useful for the preparation of nanocomposites from thermoplastic polymers with high processing temperatures and for thermoset polymers with high cure temperatures.

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