Chapter 5

Modification of clay using ILs

Mechanistic outlook on thermal degradation of 1,3-dialkyl imidazolium ionic liquids and organoclays

Eapen Thomas, Deepthi Thomas, Kunduchi Periya Vijayalakshmi* and Benny Kattikanal George
Abstract

Sodium montmorillonite clay (MMT-Na\(^+\)) was modified using cation exchange reaction of Na\(^+\) with \([C_n\text{MIm}]^+\). The modification was followed using FTIR analysis, improved d-spacing in XRD, CHN analysis and TG analysis. The cation exchange efficiency was 60 - 64\%. The modified clay showed decrease in thermal stability with respect to increase in alkyl chain length complimenting the theoretical prediction. The decomposition product of C\(_4\text{MIm}/\text{MMT}\) was identified using pyrolysis GC-MS and activation energy was calculated using FWO method. The predicted carbene mechanism was established by identifying 1-butyl-3-methylimidazol-2-ylidine using \(^{13}\)C NMR spectroscopy.

5.1 Introduction

Awad et al. for the first time in 2004, used 1-alkyl-3-methylimidazolium based ionic liquid for clay modification. The modified, 1-ethyl-3-methylimidazolium montmorillonite clay (C\(_2\text{MIm}/\text{MMT}\)) showed an improved basal spacing of 1.2 Å and thermal stability with onset temperature (5 % weight loss, T\(_{5\%}\)) of 325 °C. Later, Ding et al. [2006] used 1-methyl-3-tetradecylimidazolium modified clay (C\(_{14}\text{MIm}/\text{MMT}\)) with increased d-spacing of 7.5 Å, as a filler (5 wt %) for polyolefin-clay composite and observed an improvement in thermal stability of composite material (T\(_s\) = 484 °C) over neat polypropylene (T\(_s\) = 318 °C). Table 5.1 shows the reported 1-alkyl-3-methylimidazolium modified MMT clays (C\(_n\text{MIm}/\text{MMT}\)) with d-spacing values. In reported C\(_n\text{MIm}/\text{MMT}\) systems, TGA data was used for organic content estimation [Ha et al. 2009; Huang et al. 2010; Yalcinkaya et al. 2014] and multiple maximum decomposition temperatures due to side chain degradation and adsorbed IL in unwashed clays were reported [Lv et al. 2015; Montano et al. 2017]. Only few literatures gives a quantitative information on thermal stability of C\(_n\text{MIm}/\text{MMT}\) [Awad et al. 2004; Reinert et al. 2012].

The initial studies were focused on the use of C\(_n\text{MIm}/\text{MMT}\) as a filler for polymer-clay nanocomposites [Ding et al. 2006; Kim et al. 2006; Ha et al. 2009]. Various applications and modification process of C\(_n\text{MIm}/\text{MMT}\) are shown in Table 5.1.
<table>
<thead>
<tr>
<th>CnMIm/MMT</th>
<th>d-spacing increase (Å)</th>
<th>Application</th>
<th>Method/ References</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2MIm/MMT</td>
<td>1.2</td>
<td>Thermal degradation studies</td>
<td>Aq. suspension of MMT and IL mixture stirred for 5 h at 60 °C. [Awad et al. 2004]</td>
</tr>
<tr>
<td>C14MIm/MMT</td>
<td>7.5</td>
<td>Polyolefin clay nano-composites</td>
<td>Magnetic stirring for 5 h at 50 °C. [Ding et al. 2006]</td>
</tr>
<tr>
<td>C3MIm/MMT</td>
<td>0.9</td>
<td>Polypropylene clay nano-composites/</td>
<td>Stirring at 80 °C for 6 h. [Kim et al.2006; Ha et al. 2009]</td>
</tr>
<tr>
<td>C4MIm/MMT</td>
<td>2.0</td>
<td>Clay-supported chloro-aluminate ionic liquid catalyst</td>
<td>Stirring at 80 °C for 5 h. [Huang et al. 2010]</td>
</tr>
<tr>
<td>C6MIm/MMT</td>
<td>1.6</td>
<td>Adsorption of ILs on to MMT</td>
<td>Agitation at 55 °C for 30 min. [Reinert et al. 2012]</td>
</tr>
<tr>
<td>C8MIm/MMT</td>
<td>1.7</td>
<td>Electrically conducting thin film</td>
<td>Mixing MMT and IL in the weight ratio 1:10. [Takahashi et al. 2012]</td>
</tr>
<tr>
<td>C12MIm/MMT</td>
<td>2.5</td>
<td>Chromatographic applications</td>
<td>Stirring overnight. [Yalcinkaya et al. 2014]</td>
</tr>
<tr>
<td>C16MIm/MMT</td>
<td>4.0</td>
<td>Ionic liquids in Ca-MMT for chromate removal</td>
<td>Shaken for 24 h at 150 rpm. [Li et al. 2014]</td>
</tr>
<tr>
<td>C16MIm/MMT</td>
<td>8.2</td>
<td>IL concentration on process of intercalation</td>
<td>Centrifuged for 60 min at 150 rpm. [Wu et al. 2014]</td>
</tr>
<tr>
<td>C16MIm/MMT</td>
<td>2.1</td>
<td>Removal of amaranth dye</td>
<td>Stirring overnight. [Lawal et al. 2015]</td>
</tr>
<tr>
<td>C16MIm/MMT</td>
<td>4.0</td>
<td>Ionic liquids in Ca-MMT</td>
<td>Shaken on a reciprocal shaker at 150 rpm for 24 h. [Lv et al. 2015]</td>
</tr>
<tr>
<td>C16MIm/MMT</td>
<td>8.5</td>
<td>Thermal degradation of organoclay</td>
<td>Probe sonication for 15 min. [Eapen et al. 2016 (This Thesis)]</td>
</tr>
<tr>
<td>C16MIm/MMT</td>
<td>2.2</td>
<td>Perchlorate removal from water</td>
<td>Probe sonication for 15 min. [Eapen et al. 2016 (This Thesis)]</td>
</tr>
<tr>
<td>C16MIm/MMT</td>
<td>6.4</td>
<td>Extraction of low-polarity organic compounds from water</td>
<td>Stirred for 1 h at room temperature. [Ladino et al. 2016]</td>
</tr>
<tr>
<td>C16MIm/MMT</td>
<td>1.9</td>
<td>Functionalization of MMT with ILs</td>
<td>Stirred for 1 h at room temperature. [Montano et al. 2017]</td>
</tr>
<tr>
<td>C16MIm/MMT</td>
<td>8.5</td>
<td>Removal of chloramphenicol from water</td>
<td>Mixed on a shaker table at 150 rpm for 24 h. [Sun et al. 2017]</td>
</tr>
</tbody>
</table>
Processing of CₙMIm/MMT involves time consuming stirring methods with or without heating (Table 5.1). Wu et al. [2014] studied the effect of IL concentration on efficiency of clay intercalation and observed no further improvement in d-spacing above 5000 ppm concentration of IL. Ladino et al. [2016] studied the effect of counter anion on IL intercalation in MMT clay by selecting ILs with Br⁻, OH⁻ and BF₄⁻ anions and no significant changes in d-spacing (± 0.3 Å) were observed.

In this work, the proposed ILs viz. C₄MIm/MMT, C₆MIm/MMT and C₁₆MIm/MMT for clay modification, together with unexplored 1-decyl-3-methylimidazolium modified MMT (C₁₀MIm/MMT) were prepared using a probe sonication method with the lowest processing time (15 min.) reported. Thermal stability of prepared CₙMIm/MMT was compared quantitatively with commercial alkyl ammonium clays for 1 % decomposition (T₁%) and 50 % decomposition (T₅₀%). The conformation of [CₙMIm]⁺ inside the clay gallery was analysed using Raman spectroscopy and the microstructural environment of CₙMIm/MMT is also depicted. Thermal decomposition mechanism of C₄MIm/MMT was established using pyrolysis GC-MS analysis, ¹³C NMR analysis and computational studies.

5.2 Experimental section

5.2.1 Materials

Sodium montmorillonite clay (MMT-Na⁺), Cloisite 10A, Cloisite 15A, Cloisite 20A and Cloisite 25A from Southern Clay Products, Inc., USA; 1-butyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium tetrafluoroborate and 1-decyl-3-methylimidazolium chloride from Otto Chemie, India; Methanol from Fisher Scientific, India; 1-hexyl-3-methylimidazolium chloride and 1-hexadecyl-3-methylimidazolium chloride synthesized were used for clay modification.

5.2.2 Modification of clay

Aqueous suspension of MMT-Na⁺ in distilled water (2%) was prepared by sonicating for 10 minutes using Hielscher-UIP1000hd probe sonicator at amplitude of 80 %. To this IL diluted in methanol was added and the exchange reactions were carried out by sonicating for 15 minutes. It was allowed to settle and filtered. The residue was repeatedly (5–8 times) washed with distilled water until no chloride traces were detected with silver nitrate solution. The residue (CₙMIm/MMT) was dried at room
temperature for 4 h and then at 100 °C for 2 hour under vacuum. Table 5.2 shows the
list of modified clays.

**Table 5.2** Modifier and abbreviations for modified clays.

<table>
<thead>
<tr>
<th>Modifier/cation</th>
<th>Modified clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-butyl-3-methylimidazolium</td>
<td>C₄MIm/MMT</td>
</tr>
<tr>
<td>1-hexyl-3-methyl imidazolium</td>
<td>C₆MIm/MMT</td>
</tr>
<tr>
<td>1-decyl-3-methyl imidazolium</td>
<td>C₁₀MIm/MMT</td>
</tr>
<tr>
<td>1-hexadecyl-3-methylimidazolium</td>
<td>C₁₆MIm/MMT</td>
</tr>
</tbody>
</table>

**5.3 Results and discussion**

**5.3.1 FTIR analysis**

Figure 5.1 shows the FTIR spectrum of C₁₆MIMCl, MMT-Na⁺ and C₁₆MIm/MMT. In [C₁₆MIM]⁺[Cl]⁻, The peaks at 3154, 3083 and 3048 cm⁻¹ were due to the aromatic C-H stretching vibrations of imidazolium ring. Strong absorption bands in the region 2800-3000 cm⁻¹ represent alkyl C-H stretching vibrations. Peaks at 1574 cm⁻¹ and 1466 cm⁻¹ are due to C=C and C=N vibrations respectively. Presence of water is confirmed from the peaks at 3462 and 1634 cm⁻¹. In MMT-Na⁺, The stretching signals for the silicon-oxygen and aluminum-oxygen bonds are observed at 1047 cm⁻¹ and 915 cm⁻¹ respectively. The bands at 1636 cm⁻¹ and 3630 cm⁻¹ are assigned to absorbed water, while peak at 3430 cm⁻¹ is assigned to the stretching of hydroxyl group. The modification of MMT-Na⁺ is clearly evident in C₁₆MIm/MMT from the appearance of peaks characteristic of [C₁₆MIM]⁺[Cl]⁻.

![Figure 5.1 FTIR spectra of [C₁₆MIM]⁺[Cl]⁻, MMT-Na⁺ and C₁₆MIm/MMT.](image_url)
5.3.2 XRD analysis

XRD analysis was performed to observe the basal spacing between layers after exchanging sodium ions with the imidazolium cation (Figure 5.2). X-ray diffraction pattern of MMT-Na$^+$ exhibits 001 peak centred at $2\theta = 7.30^\circ$ corresponding to a basal d-spacing of 12.09 Å. For the modified clays, the characteristic peak of the clay was shifted to lower 2$\theta$ value leading to an increase of the interlayer spacing. This shift is a clear signature of the intercalation of the imidazolium cation between the layers of MMT. The d-spacing values of modified clays are shown in Figure 5.2.

![XRD spectra of MMT-Na$^+$, C$_4$MIm/MMT, C$_6$MIm/MMT, C$_{10}$MIm/MMT and C$_{16}$MIm/MMT. The d-spacing values are shown as inset.]

<table>
<thead>
<tr>
<th>Clay</th>
<th>d-spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMT-Na$^+$</td>
<td>12.09</td>
</tr>
<tr>
<td>C$_4$MIm/MMT</td>
<td>13.64</td>
</tr>
<tr>
<td>C$_6$MIm/MMT</td>
<td>13.97</td>
</tr>
<tr>
<td>C$_{10}$MIm/MMT</td>
<td>14.38</td>
</tr>
<tr>
<td>C$_{16}$MIm/MMT</td>
<td>18.55</td>
</tr>
</tbody>
</table>

5.3.3 Sodium estimation

Table 5.3 shows the sodium content in MMT-Na$^+$ and modified clays. The ion exchange efficiency was calculated from the amount of Na$^+$ exchanged on clay modification. An ion exchange efficiency of 60-63 % was observed in modified clays.

<table>
<thead>
<tr>
<th>Clay</th>
<th>Na (%)</th>
<th>Na exchanged (%)</th>
<th>Ion exchange efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMT-Na$^+$</td>
<td>3.03</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C$_4$MIm/MMT</td>
<td>1.12</td>
<td>1.91</td>
<td>63</td>
</tr>
<tr>
<td>C$_6$MIm/MMT</td>
<td>1.21</td>
<td>1.82</td>
<td>60</td>
</tr>
<tr>
<td>C$_{10}$MIm/MMT</td>
<td>1.11</td>
<td>1.92</td>
<td>63</td>
</tr>
<tr>
<td>C$_{16}$MIm/MMT</td>
<td>1.12</td>
<td>1.91</td>
<td>63</td>
</tr>
</tbody>
</table>
5.3.4 CHN analysis

1-alkyl-3-methylimidazolium cation with general formula $[\text{C}_{n+4}\text{H}_{2n-1}\text{N}_2]^+$ in modified clays were estimated using CHN analysis (Table 5.4). The total \%(C+H+N) gave the organic content in modified clays.

Table 5.4 CHN analysis of modified clays.

<table>
<thead>
<tr>
<th>Clay</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>Total (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_4\text{MIm/MMT}$</td>
<td>7.9</td>
<td>1.4</td>
<td>2.2</td>
<td>11.5</td>
</tr>
<tr>
<td>$\text{C}_6\text{MIm/MMT}$</td>
<td>9.3</td>
<td>1.9</td>
<td>2.0</td>
<td>13.2</td>
</tr>
<tr>
<td>$\text{C}_{10}\text{MIm/MMT}$</td>
<td>14.0</td>
<td>2.4</td>
<td>2.2</td>
<td>18.6</td>
</tr>
<tr>
<td>$\text{C}_{16}\text{MIm/MMT}$</td>
<td>20.1</td>
<td>3.4</td>
<td>2.1</td>
<td>25.6</td>
</tr>
</tbody>
</table>

5.3.5 Thermal stability of clays

Thermal stability of clays were analysed using TG from room temperature to 600 °C. MMT-Na$^+$ has a mass loss of 2.6 % between 500 and 600 °C assigned to the loss of condensation water of silanol groups on the clay mineral surface (Figure 5.3).

Figure 5.4 shows the TG/DTG curves for $\text{C}_4\text{MIm/MMT}$, $\text{C}_6\text{MIm/MMT}$, $\text{C}_{10}\text{MIm/MMT}$, $\text{C}_{16}\text{MIm/MMT}$ and commercial alkyl ammonium modified clays. The temperature for 1 % decomposition ($T_{1\%}$) and 50 % decomposition ($T_{50\%}$) are shown in Table 5.5. Among selected $\text{C}_n\text{MIm/MMT}$ clays, $\text{C}_4\text{MIm/MMT}$ showed maximum $T_{1\%}$ of 423 °C and the stability decreased with increase in alkyl chain length to 266 °C for $\text{C}_{16}\text{MIm/MMT}$. The $T_{50\%}$ also showed similar trend. Thermal stability of $[\text{C}_n\text{MIm}]^+$ followed the same trend predicted using computed HOMO-LUMO gap.
Figure 5.4 TG/DTG curves for C_nMIm/MMT clays and commercial alkylammonium modified clays.
Cloisite 25A showed the highest thermal stability among selected alkylammonium modified clays with $T_{1\%}$ of 214 °C. The $T_{1\%}$ of $C_{16}$MIm/MMT showed an increase of 52 °C than Cloisite 25A. All $C_n$MIm/MMT clays showed higher thermal stability than conventional alkyl ammonium clays (Table 5.5).

**Table 5.5** Thermal stability of $C_n$MIm/MMT clays and Cloisite clays. The d-spacing values are also shown.

<table>
<thead>
<tr>
<th>Clay</th>
<th>$T_{1%}$</th>
<th>$T_{50%}$</th>
<th>d-spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_4$MIm/MMT</td>
<td>423</td>
<td>467</td>
<td>13.64</td>
</tr>
<tr>
<td>$C_6$MIm/MMT</td>
<td>307</td>
<td>425</td>
<td>13.97</td>
</tr>
<tr>
<td>$C_{10}$MIm/MMT</td>
<td>290</td>
<td>411</td>
<td>14.38</td>
</tr>
<tr>
<td>$C_{16}$MIm/MMT</td>
<td>266</td>
<td>396</td>
<td>18.55</td>
</tr>
<tr>
<td>Cloisite 10A</td>
<td>181</td>
<td>284</td>
<td>19.20</td>
</tr>
<tr>
<td>Cloisite 15A</td>
<td>208</td>
<td>317</td>
<td>31.50</td>
</tr>
<tr>
<td>Cloisite 20A</td>
<td>154</td>
<td>318</td>
<td>24.20</td>
</tr>
<tr>
<td>Cloisite 25A</td>
<td>214</td>
<td>321</td>
<td>18.60</td>
</tr>
</tbody>
</table>

*Figure 5.5* Raman spectra of $C_4$MIm/MMT and $C_{16}$MIm/MMT. The deconvoluted spectrum is shown in inset.

### 5.3.6 Raman spectral analysis

Figure 5.5 shows the Raman spectrum of $C_{16}$MIm/MMT and $C_4$MIm/MMT. Peak position and intensities of $-CH_2$ indicates the conformational state and local environment of imidazolium ionic liquids. Higher intensity for $-CH_2$ asymmetric stretching (2878 cm$^{-1}$) than symmetric stretching (2847 cm$^{-1}$) indicates a trans
conformer [Prokhorov et al. 2005]. C_{16}MIm/MMT possess -CH$_2$ asym. (2883 cm$^{-1}$) and sym. (2848 cm$^{-1}$) stretching with peak intensities 0.74 and 0.19 respectively, the value of 3.9 for intensity ratio of asymmetric to symmetric confirms trans conformation for [C$_{16}$MIm]$^+$ inside the clay gallery. In C$_4$MIm/MMT, -CH$_2$ asymmetric stretching appears at 2912 cm$^{-1}$ and symmetric stretching at 2873 cm$^{-1}$ with peak intensities 0.56 and 0.45 respectively. All modified clays showed higher intensity for -CH$_2$ asymmetric stretching than symmetric stretching and exist as trans conformer (Table 5.6). A shift in peak position was observed as the alkyl chain length increased.

**Table 5.6** Conformation analysis of [C$_n$MIm]$^+$ inside the clay gallery.

<table>
<thead>
<tr>
<th>C$_n$MIm/MMT</th>
<th>-CH$_2$- sym str.</th>
<th>-CH$_2$- asym str.</th>
<th>$I_{asym}/I_{sym.}$</th>
<th>Conformation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peak position (cm$^{-1}$)</td>
<td>Intensity</td>
<td>Peak position (cm$^{-1}$)</td>
<td>Intensity</td>
</tr>
<tr>
<td>C$_4$MIm/MMT</td>
<td>2873</td>
<td>0.45</td>
<td>2912</td>
<td>0.56</td>
</tr>
<tr>
<td>C$_6$MIm/MMT</td>
<td>2867</td>
<td>0.74</td>
<td>2906</td>
<td>0.86</td>
</tr>
<tr>
<td>C$_{10}$MIm/MMT</td>
<td>2856</td>
<td>0.50</td>
<td>2903</td>
<td>0.51</td>
</tr>
<tr>
<td>C$_{16}$MIm/MMT</td>
<td>2848</td>
<td>0.19</td>
<td>2883</td>
<td>0.74</td>
</tr>
</tbody>
</table>

5.3.7 **Thermal decomposition of C$_4$MIm/MMT**

Pyrolysis GC-MS analysis was done to identify the decomposition products of C$_1$MIm/MMT (Figure 5.6). The decomposition products were 1-butene (m/z = 56) and methylimidazole (m/z = 82).

**Figure 5.6** Pyrogram of C$_4$MIm/MMT at 600 °C.

The possible reactions were analyzed using computational method, B3LYP at 6-311+G(d,p) level of DFT (Figure 5.7). From the model of MMT-Na$^+$ given in Figure 5.7 (a), it is clear that the ions in the interlayer gallery face SiO$_4$ tetrahedral unit as their immediate neighbour [Cadars et al. 2012]. In C$_4$MIm/MMT (Figure 5.7 (b)), sodium ions are replaced by [C$_4$MIm]$^+$ cation. Considering the possible CH/O–Si interactions
from [C₄MIm]⁺ to the clay, the use of the anionic moiety Si(OH)₃O⁻ to model the decomposition reaction of [C₄MIm]⁺ in the clay is proposed. [C₄MIm]⁺[Si(OH)₃O]⁻ ion pair is found to be marginally higher in energy (9.1 kJ/mol) than the neutral complex of imidazole-2-ylidene–Si(OH)₄ (Figure 5.7(e)). Therefore the DFT results suggest that the intercalated imidazolium cations can easily form the 1-butyl-3-methylimidazole-2-ylidene through a barrier less pathway.

![Figure 5.7](image)

**Figure 5.7** (a) Model structure of MMT-Na⁺, (b) C₄MIm/MMT, (c-h) Optimized structures of species involved in decomposition of C₄MIm/MMT with transition state and energy profile.
The singlet carbenes thus formed on heating can undergo elimination reactions involving β hydrogen shift from the butyl substituent at N1 to the carbenic centre followed by bond breaking at the quaternary nitrogen. Such a transition state was located in the DFT analysis with single imaginary frequency corresponding to the bond shifting process which is shown in Figure 5.7(g). The activation energy for the decomposition was 195.6 kJ/mol (Figure 5.7(h)) and the reaction is exothermic by 39.9 kJ/mol. The summarized decomposition mechanism is shown in Scheme 5.1. Anions with high basicity is capable of deprotonating imidazolium cation at C2 position, resulting in the formation of neutral carbon bases with nucleophilic singlet carbenes that are stabilized by the two neighbouring nitrogen atoms at the carbenic centre.

Scheme 5.1 Mechanism of C₄MIm/MMT decomposition through 1-butyl-3-methylimidazole-2-ylidene route.

The formation of carbene from [C₄MIm]⁺ cation on heating was confirmed by the NMR analysis of C₄MImCl in D₂O solvent in presence of colloidal silica. Colloidal silica is 30 % suspension of SiO₂ in water, which contains –SiOH species similar to the model compound Si(OH)₃O⁻ used in DFT study. ¹³C NMR spectra of C₄MImCl and C₄MImCl with colloidal silica heated at 90 °C for 5 minutes are shown in Figure 5.8. The additional NMR signal observed at 187.64 ppm is attributed to singlet carbene carbon in imidazolium ring.
Figure 5.8 $^{13}$C NMR spectrum of (a) $[C_4\text{MIm}]^+\text{Cl}^-$ in D$_2$O and (b) $[C_4\text{MIm}]^+\text{Cl}^-$ with colloidal silica in D$_2$O after heating.

Pyrolysis GC-MS analysis of C$_6$MIm/MMT, C$_{10}$MIm/MMT and C$_{16}$MIm/MMT also showed 1-methylimidazole and alkene as major product, in addition side chain decomposition products were also observed.

5.4 Conclusions

Modification of MMT-Na$^+$ was achieved with the lowest processing time of 15 minutes using a probe sonication method. The modification was confirmed using FTIR analysis, improved d-spacing in XRD, CHN analysis and TG analysis. The amount of $[C_n\text{MIm}]^+$ inside the clay gallery was quantified using CHN analysis. The cation exchange efficiency was estimated to be 60 - 63% from sodium estimation and CHN analysis. The $C_n$MIm/MMT showed improved thermal stability than conventional alkyl ammonium modified clays. $C_{16}$MIm/MMT with d-spacing of 18.55 Å and $T_{1%}$ of 266
°C is proposed as a replacement for Cloisite 25A with d-spacing of 18.65 Å and T$_{1\%}$ of 214 °C. For the first time the thermal degradation of ionic liquid modified clay was elucidated using DFT and experimentally rationalized using Pyrolysis GC-MS and $^{13}$C-NMR experiments. The predicted carbene mechanism was established by identifying 1-butyl-3-methylimidazol-2-ylidene using $^{13}$C NMR spectroscopy. The experimental results on stability of [C$_n$MIm]$^+$ cations were in parallel to the theoretical studies described in chapter 3.
Chapter 6

Perchlorate removal from water using IL modified clay

1,3-Dialkylimidazolium modified clay sorbents for perchlorate removal from water

Lapen Thomas, Krishnan G. Rekha, Soundiraraju Bhuvaneswari, Kunduchi P. Vijayakrishna and Benny K. Georgo
Abstract

C$_n$MIm/MMT was used for perchlorate adsorption from water. MMT-Na$^+$ showed negligible adsorption whereas C$_n$MIm/MMT showed an increase in adsorption with increase in chain length of the exchanged cation. C$_{16}$MIm/MMT showed the highest adsorption of 15.6 mg/g from 1000 ppm perchlorate solution at pH = 2 and contact time of 15 min. The adsorption followed the Freundlich isotherm with pseudo second order kinetics. The d-spacing of C$_{16}$MIm/MMT (18.55 Å) decreased to 13.70 Å on perchlorate adsorption and observed a conformational change in [C$_{16}$MIm]$^+$ inside the clay gallery from trans to gauche, suggesting the possible formation of [C$_{16}$MIm]$^+$[ClO$_4^-$] inside the clay gallery. The adsorbed clays were regenerated by heating to 175 ± 5 °C in air and 95 % regenerability was observed.

6.1 Introduction

Perchlorate ion detected in soil, water and food originates mainly from different salts used in solid propellants for rockets and oxidizer components in various military and industrial processes [Kannan et al. 2009; Kosaka et al. 2007; Ye et al. 2012; Chitrakar et al. 2012]. Perchlorates are highly soluble in water and it enters human body through drinking water or food chain and causes hypothyroidism by interfering with the ability of the thyroid gland to process iodine [Urbansky 1998; Wolff 1998]. The persistent and toxic nature of perchlorates with its unusual physical and chemical properties makes it difficult to remove. Different methods like adsorption, ion-exchange, membrane methods, biological treatment, chemical reduction, electrochemical reduction and so on were studied and a reliable, repeatable, recyclable system is yet to be established for perchlorate removal from water [Rekha et al. 2017; Srinivasan and Sorial 2009; Parette and Cannon 2005; Luo et al. 2016; Kim et al. 2011; Komarneni et al. 2010; Seliem et al. 2010, 2011, 2013; Hutchison and Zilles 2015].

Among alternatives for perchlorate removal, ion-exchange is apparently the most efficient method. However, it is costly and not efficient to deal with small concentration of perchlorate in water. Adsorption methods are promising and widely studied method for perchlorate removal. The first choice for adsorption, virgin activated carbon, was not effective for perchlorate adsorption, however surface modification made it comparative to ion exchange [Parette and Cannon 2005]. Considering the
availability, low cost and thermal stability, clays were studied for perchlorate removal but no improvements were observed. The use of organoclays to 'selective' uptake of perchlorate from water marked the changing phase in terms of perchlorate removal systems [Chitrakar et al. 2012; Kim et al. 2011; Komarneni et al. 2010; Seliem et al. 2010, 2011, 2013; Wu et al. 2016]. Alkyl ammonium and alkyl pyridinium modified clays were extensively used for perchlorate removal and no regenerable system was reported.

Luo et al. [2015, 2016] used benzyloctadecyldimethylammonium modified and hexadecylpyridinium modified montmorillonite clay to achieve perchlorate removal efficiency of 0.90 and 0.09 mmol/g respectively. Kim et al. [2011] used octadecyltrimethylammonium, dodecyltrimethylammonium and hexadecyltrimethylammonium modified clays with perchlorate uptake of 0.07, 0.02 and 0.04 mmol/g respectively. Seliem et al. [2011] used commercially available clays, Cloisite 10A, Cloisite 15A and Cloisite 20A for perchlorate removal with 0.26, 0.16 and 0.09 mmol/g perchlorate uptake efficiency respectively. Bagherifam et al. [2014] used hexadecylpyridinium modified montmorillonite clay and achieved perchlorate removal of 1.11 mmol/g. Al-pillared montmorillonite by Komarneni et al. [2013] showed perchlorate removal capacity of 0.01 mmol/g.

In this work, a new class of modified clays using thermally stable 1-alkyl-3-methylimidazolium based ILs with varying chain lengths were explored for perchlorate removal from water. The adsorption mechanism, isotherms, kinetics and regeneration studies are reported.

6.2 Methodology
6.2.1 Materials
Sodium montmorillonite, MMT-Na$^+$ from Southern Clay Products, Inc., USA, Hydrochloric acid (purity > 36-38 %) from Merck, C$_6$MIm/MMT, C$_8$MIm/MMT, C$_{10}$MIm/MMT, C$_{16}$MIm/MMT and ammonium perchlorate AR (99.9 %) prepared in house were used.

6.2.2 Perchlorate adsorption studies
0.5 g of C$_n$MIm/MMT was dispersed in 25 mL each of 50, 100, 250, 500 and 1000 mg/L perchlorate solution and the mixture was equilibrated at 30 °C for 1, 2, 5, 10, 15, 30, 60, 120 and 180 min. using a shaker. After equilibration, the suspension was
centrifuged and the solution was analysed for perchlorate content using Ion Chromatograph (IC). The experiment was repeated with different pH from 2 to 8. The amount of sorbed perchlorate per gram of clay was calculated using eqn. 6.1,

\[
ClO_4^- (\text{mg/g}) = \frac{(C_i - C_e)V}{m} \quad --- (6.1)
\]

where, \(C_i\) is the initial perchlorate solution concentration, \(V\) is the volume of perchlorate solution, \(m\) is the weight of adsorbent in g and \(C_e\) is the concentration of perchlorate after adsorption calculated from IC analysis.

### 6.2.3 Kinetic studies

The experiments were conducted at pH = 2 and various time intervals, viz. 1, 2, 5, 10, 15, 30 and 60 min. The experimental data were fitted with pseudo-first order (eqn. 6.2), pseudo-second order (eqn. 6.3) and intra-particle diffusion process (eqn. 6.4),

\[
\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad --- (6.2)
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad --- (6.3)
\]

\[
q_t = k_p t^{1/2} + C \quad --- (6.4)
\]

where \(q_e\) and \(q_t\) are the amount of perchlorate (mg/g) adsorbed at equilibrium and time \(t\) (min) respectively. The first order rate constant, \(k_1\) is obtained from the slope of the log \((q_e - q_t)\) versus \(t\) plot. \(k_2\) is the second order rate constant obtained from the plot of \(t/q_t\) versus \(t\). \(k_p\) is the rate constant of intra-particle diffusion determined from the slope of \(q_t\) versus \(t^{1/2}\) plot. The value of \(C\) relates to the thickness of the boundary layer. Larger the intercept, greater is the boundary layer effect [Vimonses et al. 2009]. If the plot passes through the origin (\(C = 0\)), the intra-particle diffusion is regarded as the only rate controlling step [Demiral and Gunduzoglu 2010].

### 6.2.4 Isotherm studies

It is essential to establish the most suitable adsorption equilibrium correlation for reliable prediction of adsorption parameters and quantitative comparison. Langmuir model (eqn. 6.5) (based on the assumption that monolayer adsorption on a homogeneous adsorbent takes place with no interacting forces between adsorbed
molecules) and heterogeneous models, viz. Freundlich (eqn. 6.6) and Tempkin (eqn. 6.7) were used to fit the adsorption of perchlorate onto modified clay,

\[
\text{Langmuir model} \quad \frac{c_e}{q_e} = \frac{1}{Q_0 b} + \frac{c_e}{Q_0} \quad --- \ (6.5)
\]

\[
\text{Freundlich model} \quad \log q_e = \log k_F + \frac{1}{n} \log C_e \quad --- \ (6.6)
\]

\[
\text{Tempkin model} \quad q_e = B_l N + B_l N_c \quad --- \ (6.7)
\]

where \(C_e\) (mg/L) is the concentration of perchlorate solution at equilibrium, \(q_e\) (mg/g) is the amount of perchlorate adsorbed per unit mass of the adsorbent at equilibrium and \(Q_0\) (mg/g) is the amount of adsorbate at complete coverage, which gives the maximum adsorption capacity and \(b\) (L/mg) is the Langmuir constant reflecting the energy of adsorption. \(k_F\) is the Freundlich constant, \(n\) is a constant related to energy of adsorption and its magnitude is an indication of the favourability of adsorption. \(A\) and \(B\) are the Tempkin constants.

6.2.5 Computational method

Geometries of gaseous ion pairs were optimized at B3LYP level of density functional theory using 6-311+G(d,p) basis set as implemented in Gaussian 09. BSSE corrected binding energy for the ion-pairs ([RMIIm][X]) was calculated using eqn. (6.8).

\[
[RMIIm]^+ + [X]^- \leftrightarrow [RMIIm]^+[X]^- \quad --- \ (6.8)
\]

6.2.6 Regeneration

The perchlorate adsorbed clays were regenerated by heating at different temperatures; 170, 175, 180 and 190 °C. The % regenerability was analysed by comparing the perchlorate adsorption efficiency of regenerated clay and parent modified clay.

6.2.7 Instrumental

Perchlorate was estimated using a Dionex model ICS 2000 Ion Chromatograph (IC) equipped with AS16 column, AG16 Guard column, ASRS 300 Suppressor column and a conductivity detector using 35 mM NaOH as eluent with a flow rate of 1 mL/min. Chromeleon chromatographic software was used for the data analysis. XRD analysis
was done using Bruker D8 Discover diffractometer. CHN analysis using Perkin Elmer 2400 CHNS analyzer with thermal conductivity detector. Thermal analysis using TA instruments SDT Q600 TGA from room temperature to 600 °C at a heating rate of 10 °C/min. in nitrogen atmosphere for modified clay and in air for regeneration study and Raman spectral studies using WiTec alpha 300R confocal Raman microscope were also done.

6.3 Results and discussion

6.3.1 Effect of solution pH on adsorption

Figure 6.1 shows the variation of adsorption capacity of modified clays with pH. pH was limited to 8 due to the enhanced solubility of clay in alkaline medium [McBride 1994]. Higher rate of adsorption was observed at lower pH and pH = 2 was selected for experiment. At low pH levels H⁺ ions dominate the surface of the clay. Perchlorate ions with negative charge at low pH results in electrostatic attraction with the positive charge on the clay resulting in an increased adsorption at the surface.

![Figure 6.1 Effect of pH on perchlorate adsorption using C\textsubscript{16}MIm/MMT.](image)

When pH is increased, the excess of OH⁻ ions present in the solution lead to competition of adsorption sites with perchlorate ions which results in lower adsorption. If there is still significant amount adsorbed onto modified clay surface at higher pH values, it can be attributed to chemisorption [Lawal and Moodley 2015]. From Figure 6.1, at pH = 8, higher perchlorate adsorption capacity is retained (11.3 mg/g) by C\textsubscript{16}MIm/MMT suggest chemisorption.
6.3.2 Effect of contact time

The effect of contact time on adsorption at room temperature (303 K) was studied at various time intervals from 1 to 180 min. Figure 6.2 shows the perchlorate adsorption by C\textsubscript{16}MIm/MMT. Maximum adsorption was observed at 15 min. and equilibrium was reached. Lower equilibration time is advantageous in its practical applications.

![Figure 6.2 Effect of contact time on perchlorate adsorption using C\textsubscript{16}MIm/MMT.](image)

6.3.3 Effect of perchlorate concentration

Adsorption studies were done using different concentrations of perchlorate solutions from 50 mg/L to 1000 mg/L and the adsorption increased linearly ($R^2 = 0.98$) with increasing concentrations of perchlorate solutions (Figure 6.3).

![Figure 6.3 Effect of initial concentration on adsorption using C\textsubscript{16}MIm/MMT.](image)

Table 6.1 d-spacing of clay and its adsorption capacity ($q_e$).

<table>
<thead>
<tr>
<th>Clay</th>
<th>d-spacing (Å)</th>
<th>$q_e$ (mg/g)</th>
<th>d-spacing after ClO$_4^-$ adsorption (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMT-Na$^+$</td>
<td>12.09</td>
<td>0.1</td>
<td>12.10</td>
</tr>
<tr>
<td>C$_4$MIm/MMT</td>
<td>13.64</td>
<td>0.7</td>
<td>13.08</td>
</tr>
<tr>
<td>C$_6$MIm/MMT</td>
<td>13.97</td>
<td>1.1</td>
<td>13.43</td>
</tr>
<tr>
<td>C$_{10}$MIm/MMT</td>
<td>14.38</td>
<td>12.4</td>
<td>14.20</td>
</tr>
<tr>
<td>C$_{16}$MIm/MMT</td>
<td>18.55</td>
<td>15.6</td>
<td>13.70</td>
</tr>
</tbody>
</table>

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6.3.4 Perchlorate adsorption by CₙMIm/MMT

Adsorption studies were carried out using MMT-Na⁺, C₄MIm/MMT, C₆MIm/MMT, C₁₀MIm/MMT and C₁₆MIm/MMT with 1000 mg/L perchlorate solution at pH = 2 and contact time of 15 min. The adsorption capacity (qₑ) and d-spacing of clays before and after adsorption are tabulated in Table 6.1. The value of qₑ showed the same trend as d-spacing of modified clays; MMT-Na⁺ < C₄MIm/MMT < C₆MIm/MMT < C₁₀MIm/MMT < C₁₆MIm/MMT (Table 6.1). C₁₆MIm/MMT showed maximum perchlorate adsorption of 15.6 mg/g (0.16 mmol/g) of clay. d-spacing of C₁₆MIm/MMT decreased from 18.55 Å to 13.70 Å on adsorption of perchlorate (Figure 6.4) with composition unchanged while all other modified clays showed negligible change (Table 6.1). The increased adsorption of perchlorate with increasing d-spacing is attributed to the enhanced access of perchlorate ions on to the clay surface.

![XRD spectra of C₁₆MIm/MMT and perchlorate adsorbed C₁₆MIm/MMT (C₁₆MIm/MMT-ClO₄)](image)

Raman spectroscopy was used for conformational analysis to account for the decreased d-spacing on adsorption by measuring the intensity of symmetric (2847 cm⁻¹) and asymmetric (2878 cm⁻¹) stretching vibrations of methylene groups present [Prokhorov et al. 2005]. Trans conformer shows higher intensity for asymmetric stretching than symmetric stretching and in gauche conformer symmetric stretching is reported to possess higher intensity. Figure 6.5 shows the Raman spectra of C₁₆MImCl, C₁₆MIm/MMT and C₁₆MIm/MMT-ClO₄ with intensity of methylene stretching vibrations. C₁₆MIm/MMT showed an increase in intensity ratio of asymmetric to symmetric stretching vibrations, suggesting more of trans conformer. The C₁₆MIm/MMT-ClO₄ showed a decrease in intensity ratio of asymmetric to symmetric C-H stretching vibrations compared to C₁₆MIm/MMT, an indication of change in
conformation from trans to gauche. This accounts for the large decrease (4.85 Å) in d-spacing observed for C\textsubscript{16}MIm/MMT on perchlorate adsorption. The analysis reveals the possibility of formation of a new ion pair, [C\textsubscript{16}MIm]\textsuperscript{+}[ClO\textsubscript{4}]\textsuperscript{-} within the clay layer between imidazolium cation and perchlorate anion. From the Figure 6.5, it is clear that the CH\textsubscript{2} stretching pattern in free ionic liquid [C\textsubscript{16}MIm]\textsuperscript{+}[Cl]\textsuperscript{-} and newly formed ion pair within the clay layers are comparable.

<table>
<thead>
<tr>
<th>IL/Clay</th>
<th>I\textsubscript{sym.}</th>
<th>I\textsubscript{asym.}</th>
<th>I\textsubscript{asym.}/I\textsubscript{sym.}</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C\textsubscript{16}MIm]\textsuperscript{+}[Cl]\textsuperscript{-}</td>
<td>0.66</td>
<td>0.80</td>
<td>1.21</td>
</tr>
<tr>
<td>C\textsubscript{16}MIm/MMT</td>
<td>0.19</td>
<td>0.74</td>
<td>3.89</td>
</tr>
<tr>
<td>C\textsubscript{16}MIm/MMT-ClO\textsubscript{4}</td>
<td>0.95</td>
<td>0.99</td>
<td>1.04</td>
</tr>
</tbody>
</table>

Figure 6.5 Raman spectra of [C\textsubscript{16}MIm]\textsuperscript{+}[Cl]\textsuperscript{-}, C\textsubscript{16}MIm/MMT and C\textsubscript{16}MIm/MMT-ClO\textsubscript{4}.

The table shows the intensity of C-H str. vibrations.

The [C\textsubscript{16}MIm]\textsuperscript{+}[ClO\textsubscript{4}]\textsuperscript{-} ion-pair formation possibility was studied using B3LYP/6-311+G(d,p) method. [C\textsubscript{16}MIm]\textsuperscript{+}[Si(OH)\textsubscript{3}O]\textsuperscript{-} represent the model structure of C\textsubscript{16}MIm/MMT used for computational studies as depicted in Figure 6.6, where the [C\textsubscript{16}MIm]\textsuperscript{+} represent the intercalated imidazolium cation and [SiO\textsubscript{4}H\textsubscript{3}]\textsuperscript{-} represent the anionic clay layer. C\textsubscript{16}MIm/MMT in acidic medium (pH = 2) weakens the cation clay layer interaction due to the presence of excess H\textsuperscript{+} ions, which is supported by the increase in C2H\textsubscript{2}O bond distance from 1.476 Å to 2.077 Å in the optimized model structures given in Figure 6.6(a) and 6.6(b) respectively. The free imidazolium cations
thus generated on acidification, can also interact with perchlorate anions to form 1-hexadecyl-3-methylimidazolium perchlorate, \([C_{16}\text{MIm}]^+\text{[ClO}_4^-]\) (Figure 6.6(c) as substantiated by Raman spectroscopic analysis.

![Figure 6.6](image)

**Figure 6.6** Optimized structures of species involved in perchlorate adsorption mechanism, (a) \([C_{16}\text{MIm}]^+\text{[Si(OH)}_3\text{O}]^\text{-}\), (b) \([C_{16}\text{MIm}]^+\text{[Si(OH)}_4\text{]}\) and (c) \([C_{16}\text{MIm}]^+\text{[ClO}_4^-]\).

![Figure 6.7](image)

**Figure 6.7** Raman spectra of \([C_{16}\text{MIm}]^+\text{[ClO}_4^-]\), \(C_{16}\text{MIm}/\text{MMT-ClO}_4\) and \(C_{16}\text{MIm}/\text{MMT}\).
The $[\text{C}_{16}\text{MIm}]^+[\text{ClO}_4^-]$ ion-pair formation inside the clay gallery was further confirmed by comparing the Raman spectra of $\text{C}_{16}\text{MIm/MMT}$ and $\text{C}_{16}\text{MIm/MMT-ClO}_4^-$ with $[\text{C}_{16}\text{MIm}]^+[\text{ClO}_4^-]$ (Figure 6.7). $[\text{C}_{16}\text{MIm}]^+[\text{ClO}_4^-]$ was synthesized using reported procedure by Wang et al. [2014]. The characteristic peak of perchlorate anion at 931 cm$^{-1}$ is seen in Raman spectra of $[\text{C}_{16}\text{MIm}]^+[\text{ClO}_4^-]$ (Figure 6.7). Clay shows a characteristic vibration of Si-O$_b$-Si at 705 cm$^{-1}$ (O$_b$- bridging oxygen atoms that connects the SiO$_4$ tetrahedra which makes up the layers in clay). Raman spectra of $\text{C}_{16}\text{MIm/MMT-ClO}_4^-$ shows the presence of characteristic peaks due to Si-O$_b$-Si and ClO$_4^-$ with a peak shift. i.e. the peak due to Si-O$_b$-Si at 705 cm$^{-1}$ shifted to 701 cm$^{-1}$ indicating the change in inter gallery spacing and the peak due to ClO$_4^-$ at 931 cm$^{-1}$ is downshifted to 929 cm$^{-1}$. This further confirms the formation of $[\text{C}_{16}\text{MIm}]^+[\text{ClO}_4^-]$ in the clay gallery.

### 6.3.5 Adsorption kinetics

![Image of Raman spectra and graphs](image.png)

*Figure 6.8* (a) Pseudo-first order model (b) Pseudo-second order model and (c) Intra-particle diffusion model for perchlorate uptake by $\text{C}_{16}\text{MIm/MMT}$. 

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Pseudo-second order and intra-particle diffusion models were best fitted for perchlorate adsorption with $R^2 = 0.99$. The pseudo-second order linear plot (Figure 6.8) suggests that the rate limiting step is chemisorption including valence force through sharing and exchange of electrons between ClO$_4^-$ and modified MMT [Ho 2006]. In Figure 6.8 (c), the intercept not passing through the origin ($C \neq 0$) suggests that intra-particle diffusion is not the rate controlling step [Demiral and Gunduzoglu 2010]. The conformational change and thereby fluidic property observed may be the reason for higher correlation of intra-particle diffusion kinetics.

6.3.6 Adsorption isotherm study

The experimental data were fitted in eqn. 6.5 - 6.7 and adsorption isotherms were plotted. Freundlich adsorption describes the most favourable adsorption process with $R^2 = 0.98$ (Figure 6.9). The value of $n > 1$ in Freundlich adsorption isotherm indicates a favourable adsorption process and $1/n = 0.54$, a value below unity implies chemisorption [Haghseresht and Lu 1998].

![Figure 6.9](image.png)

Figure 6.9 (a) Langmuir plot (b) Freundlich plot and (c) Tempkin plot for perchlorate uptake by C$_{16}$MIm/MMT.
6.3.7 Regeneration studies

The formation of HClO₄ on heating C₁₆MIm/MMT-ClO₄ was analysed using B3LYP/6-311+G(d,p) method due to the presence of excess H⁺ ions (pH = 2) during adsorption process. Figure 6.10 shows the optimized structure of [C₁₆MIm]⁺[HClO₄]. The C2H⁺O bond distance in [C₁₆MIm]⁺[HClO₄] (2.183 Å) was higher than [C₁₆MIm]⁺[ClO₄⁻] (2.007 Å). The binding energy for [C₁₆MIm]⁺[Si(OH)₃O]⁻ (409.8 kJ/mol) and [C₁₆MIm]⁺[ClO₄⁻] (337.3 kJ/mol) suggest imidazolium cation-silicate interaction is much stronger than the imidazolium cation-perchlorate interaction. Hence, on thermal activation of the perchlorate adsorbed system, reversal of cation interaction from perchlorate to silicate is feasible with the elimination of HClO₄. The peak decomposition temperature of HClO₄ was 173 ºC from TG/DTG analysis (Figure 6.10(b)).

![Figure 6.10](image-url)

(a) [C₁₆MIm]⁺[HClO₄]

(b) TG/DTG curve of HClO₄ in air.

Thermal regeneration of perchlorate adsorbed clays were done at different temperatures from 170 to 190 ºC (Table 6.2). The initial C₁₆MIm/MMT perchlorate adsorption of 15.6 mg/g is taken as 100 % (Cycle-I) and it is compared with perchlorate adsorption after regeneration at different temperatures (Cycle-II). Maximum
regenerability of 95% was achieved at 175 °C. This confirms the regeneration mechanism proposed using computational studies, where the H+ ions accelerated the elimination of HClO₄ by weakening the imidazolium cation-perchlorate bonding. Above 175 °C regeneration capacity decreased due to initiation of alkyl chain degradation of intercalated imidazolium cation.

Table 6.2 Regeneration of modified clays at different temperatures.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Regeneration (adsorption capacity in %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cycle-I</td>
</tr>
<tr>
<td>170</td>
<td>100</td>
</tr>
<tr>
<td>175</td>
<td>100</td>
</tr>
<tr>
<td>180</td>
<td>100</td>
</tr>
<tr>
<td>190</td>
<td>100</td>
</tr>
</tbody>
</table>

4. Conclusions

1-alkyl-3-methylimidazolium modified clays were used for perchlorate adsorption from water. C₁₆MIm/MMT with maximum d-spacing showed highest adsorption and the conformational changes associated with adsorption were studied using Raman spectroscopy. Experimental data fitted with different adsorption isotherms and kinetic models revealed Freundlich adsorption and pseudo second order kinetics for the adsorption process. On thermal activation 95% regeneration of clay was observed at 175 °C and regeneration mechanism involving perchloric acid removal was proposed based on DFT studies. The organoclay prepared represents a potential adsorbent for perchlorate with advantage of very low contact time and regenerability of the system.
Chapter 7

PVDF- IL modified clay nanocomposite

PVDF-ionic liquid modified clay nanocomposites: Phase changes and shish-kebab structure

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Abstract

Crystalline behaviour of PVDF nanocomposite with 1-alkyl-3-methylimidazolium modified montmorillonite clay was analyzed. The phase change from $\alpha$ to $\beta$ increased with alkyl chain length of the organic modifier in the filler, 1-alkyl-3-methylimidazolium clay, and maximum conversion (99%) was observed for PVDF-1-hexadecyl-3-methylimidazolium modified clay composite with 2% loading. The phase conversion was evident from X-ray diffraction, DSC analysis and improved electrical properties. AFM analysis of PVDF-1-butyl-3-methylimidazolium montmorillonite clay composite (PVDF-C4) showed a shish-kebab structure while pristine PVDF and all other composites showed spherulite structures. Computational studies revealed that the extended chain $\alpha$-phase forms the 'shish', the back bone and folded chain $\beta$-phase forms the 'kebab'. This was further supported by the superior mechanical properties for PVDF-C4 composite. Present work shows that introducing ionic liquid modified MMT-clay within the PVDF matrix enables nucleation of electroactive $\beta$ phase and the presence of equal content of $\alpha$ to $\beta$ can leads to the formation of self reinforced shish-kebab structures in PVDF.

7.1 Introduction

Poly(vinylidene fluoride) (PVDF) is a semi-crystalline polymer known for its electrical properties [Kawai 1969; da-Silva et al. 2014; Wang et al. 2009]. Among the polymorphs of PVDF viz., $\alpha$-phase (TGTG’ conformation), $\beta$-phase (TTT), $\gamma$-phase (T3GT3G’) and $\delta$-phase (two TGTG’ chains parallel), PVDF exists mainly in the stable non-polar $\alpha$-phase along with polar $\beta$-phase (Figure 7.1) [Bohlen and Bolton 2014; Lovinger 1981]. $\beta$-phase is responsible for electrical properties and finds wide application in polymer sensors, actuators, etc., [Zhu et al. 2012; Lee et al. 2004; Khanna et al. 2004; Martins et al. 2012]. Several methodologies were adopted to improve the $\beta$-phase in PVDF such as melt crystallization under high pressure from solution [Rinaldo and Borges 2008], fast quenching from the melt [Ke et al. 2014], uniaxial or biaxial stretching of PVDF film [Sajkiewicz et al. 1999; Li et al. 2014; Gebrekrstos et al. 2016; Satyanarayana and Bolton 2012], addition of nanofillers [Byelov et al. 2008; Huo et al. 2004; Patil et al. 2010; Fillery et al. 2012] etc.
The most convenient and vast studied method to improve the $\beta$-phase is the nanofiller addition since it acts as nucleation sites and thus influencing crystallization kinetics and final morphology of the polymer. Nanofillers with high aspect ratio are beneficial for large electric break down field and permittivity [Fillery et al. 2012]. The combined effects of addition of particles and the shear have been suggested to yield an increase in the number of active nuclei, increasing crystallization rates higher than their individual contribution [Byelov et al. 2008; Huo et al. 2004]. Nanofillers with stronger chain-particle interaction and retarding the relaxation of extended chains are known to form "shish-kebab" structure with molecular orientation composed of an extended chain crystal called 'shish' and folded chain crystal called 'kebab' [Patil et al. 2010]. Shish-kebab structures are important as it shows improved mechanical property and thermal stability.

Various PVDF nanocomposites were studied using BaTiO$_3$ [Dang et al. 2010; Hao et al. 2015], TiO$_2$ [Li et al. 2009] silver nanoparticles [Manna et al. 2006 ; Audoit et al. 2015] copper oxide nanoparticles [Dutta et al. 2015], CoFe$_2$O$_4$ nanoparticles [Martins et al. 2012], carbon nanotubes [Sharma et al. 2015; Kim et al. 2009; Mandal and Nandi 2011; Yu et al. 2014, Zhao et al. 2009], graphene or graphene oxide [Layek et al. 2010; Achaby et al. 2012; Maity et al. 2015], ionic liquids [Wang et al. 2012; Xing et al. 2013; Okada et al. 2015; Mejri et al. 2015], clay and organically modified clays, [Wang et al. 2015; Priya et al. 2002; Dillon et al. 2006; Buckley et al. 2006; Patro et al. 2008] etc. Organically modified clays were preferred over pristine clay as fillers due to its better dispersion with polymers. The trend of PVDF to crystallize in the
β-phase is higher in organically modified clays [Patro et al. 2008], however few reports indicate that electrically active γ-phase also can be nucleated in the presence of organoclays [Martins et al. 2014; Ince-Gunduz et al. 2010; Lopes et al. 2011]. It was suggested that the matching of crystal lattice of the clay with that of the β-phase of PVDF is probably responsible for the formation and stabilization of the β-phase.

In this work, C₆MIm/MMT was used for PVDF-clay nanocomposite preparation. The effect of alkyl chain length of IL cation on the crystallization behaviour and orientation of PVDF structure was investigated. Xing et al. [2013] used ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate for PVDF modification and more of γ-phase was observed. The colloidal crystallization of PVDF (46 % α-phase and 54 % amorphous phase) in presence of ionic liquid, 1-ethyl-3-methylimidazolium nitrate by Okada et al. [2015] resulted in partial conversion to β-phase (32 %). Mejri et al. [2015] reported the effect of ionic liquid anion and cation on the properties of PVDF/ionic liquid blends and observed that the average size of the spherulites depend on both the anion and cation (spherulite size increases with chain length of cation for a specific anion). Lopes et al. [2013] reported the nucleating effect of MMT on the crystallization of PVDF, incorporation of MMT fillers resulted in increased number of spherulites with decreased spherulite size. All reported PVDF-clay composites describe crystallization into spherulite morphology [Sencadas et al. 2011; Xing et al. 2013; Lopes et al. 2013].

7.2 Experimental section

7.2.1 Materials

PVDF (CAS No. 24937-79-9, product No.44080) from Alfa Aesar and HPLC grade N,N'-Dimethylacetamide (DMAc) from Spectrochem were used for the preparation of casting solution. Distilled water was used in coagulation bath as non solvent.

7.2.2 Nanocomposite preparation

PVDF-clay nanocomposite films were prepared by phase inversion method using MMT-Na⁺, C₄MIm/MMT, C₆MIm/MMT, C₁₀MIm/MMT and C₁₆MIm/MMT. PVDF powder was dried at 100 °C for 2 hour prior to processing. Clay (1, 2, 3 and 5 wt % w.r.t PVDF) were dispersed in 50 mL DMAc by bath sonication (10 min.) and the clay dispersions were maintained at 50 °C using a water bath. 5 g PVDF powder was
added to the clay dispersion, the mixture was stirred for 30 min. and the solution was kept at room temperature for 24 hours. PVDF–clay nanocomposite films were casted on a glass plate using doctor blade (set at 30 rotations for films of ~100 micron thickness) and the casted films on glass plate was immersed in water (T=25 °C). Selection of coagulation bath (water) temperature was based on report by Buonomenna et al. [2007]. Films peeled off from the glass plates were washed thoroughly with water to remove any solvent traces present and dried at 100 °C for 2 hour in an air oven. Table 7.1 shows the list of PVDF-clay composites.

Table 7.1 List of clays and PVDF-clay composites.

<table>
<thead>
<tr>
<th>Clay</th>
<th>PVDF-clay composite</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMT-Na⁺</td>
<td>PVDF-MMT</td>
</tr>
<tr>
<td>C₄MIm/MMT</td>
<td>PVDF-C4</td>
</tr>
<tr>
<td>C₆MIm/MMT</td>
<td>PVDF-C6</td>
</tr>
<tr>
<td>C₁₀MIm/MMT</td>
<td>PVDF-C10</td>
</tr>
<tr>
<td>C₁₆MIm/MMT</td>
<td>PVDF-C16</td>
</tr>
</tbody>
</table>

7.2.3 Instrumental

PVDF films were characterized using Perkin Elmer Spectrum GX FTIR spectrometer in ATR mode in the wavelength region 4000-550 cm⁻¹ with a spectral resolution of 4 cm⁻¹. For systems containing α and β–phases, the relative fraction of the β-phase, F(β), was calculated from FTIR spectra by measuring the absorbance at 763 cm⁻¹ (CF₂ bending and skeletal bending, Aₐ) and 840 cm⁻¹ (CH₂ rocking mode, Aₐ) respectively using Eqn.7.1 [Salimi and Yousefi 2004].

$$F(\beta) = \frac{A_{\beta}}{\left(\frac{k_{\beta}}{k_{\alpha}}\right) A_{\alpha} + A_{\beta}} \quad \text{... (7.1)}$$

where, Aₐ and Aₐ are the absorbance of the peaks corresponding to α and β respectively in the FTIR spectrum. The absorption coefficients of α-phase (kₐ) and β-phase (kₐ) were 6.1 x 10⁴ cm²/mol and 7.7 x 10⁴ cm²/mol respectively.

XRD studies were carried out using Bruker D8 Discover diffractometer with 20 ranges between 10-30°. Thermal stability of PVDF-clay nanocomposite films were studied using TA Instruments SDT Q600 TGA from room temperature to 600 °C at a heating rate of 10 °C/min. in nitrogen atmosphere. Percentage crystallinity of PVDF in the nanocomposite films were determined using TA Q20 Differential Scanning Calorimeter (DSC) by heating at a rate of 5 °C/min. from room temperature to 200 °C.
in nitrogen atmosphere and followed by cooling at the same rate to obtain the crystallization peak. Percentage crystallinity, \( X_c \) (%) of PVDF was calculated from its enthalpy of crystallization (\( \Delta H_c \)) using Eqn. 7.2.

\[
X_{c}(\%) = \frac{\Delta H_c}{\Delta H_p} \times 100 \quad \ldots (7.2)
\]

where, \( \Delta H_p = 104.7 \text{ J/g} \), heat of fusion for 100 % crystalline PVDF [Thakur et al. 2011].

Morphology was studied using AFM in contact mode using Agilent 5500 scanning probe microscope. FESEM was performed using a Carl Zeiss, Supra 55 model field emission scanning electron microscope with an acceleration voltage of 15 kV to evaluate the morphology and microstructure. Mechanical properties of PVDF-modified clay composites were measured using UTM INSTRON 5569 in tensile mode with cross head speed of 50 mm/min. and gauge length of 80 mm. At least 3 samples of each type of films were tested as per ASTM D-882. Capacitance of the films were measured using TEGAM 3550 LCR meter at temperature of 23 °C ± 2 °C and relative humidity of 60 % ± 5 % at 1 KHz frequency using ASTM D-257 method.

The activation energy (\( E_a \)) for thermal decomposition of PVDF and PVDF-clay nanocomposites were studied using Coats-Redfern method. First order reaction and random nucleation (F1 function) is generally used for thermal degradation kinetic study of nanocomposite films. The Coats-Redfern for F1 function is given as,

\[
\ln \left( \frac{-\ln (1 - \alpha)}{T^2} \right) = \ln \frac{AR}{bE_a} - \frac{E_a}{RT} \quad \ldots (7.3)
\]

where, \( E_a \) is the activation energy for decomposition, \( A \) is the pre-exponential factor, \( R \) is the universal gas constant, \( b \) is the heating rate (10 °C/min.), \( \alpha \) is the degree of conversion and \( T \) is the maximum decomposition temperature (K) corresponding to each \( \alpha \). The plot of \( \ln \left( \frac{-\ln (1 - \alpha)}{T^2} \right) \) versus \( 1/T \), result in a linear plot whose slope gives the value of activation energy.

**7.2.4 Computational studies**

PVDF was constructed using 'build polymer' tool in Materials Studio 4.0 (Accelrys Inc.) software with single chain of PVDF in \( \alpha \)-phase or \( \beta \)-phase [Accelrys 2006; Wang et al. 2010]. Amorphous cell calculation was done using the polymer
consistent force field (PCFF), Ewald electrostatic summation with accuracy = 0.0001 kcal/mol and temperature = 298 K with 20 monomer units.

7.3 Results and discussion

7.3.1 Phase changes

Organically modified clays facilitate the formation of β-phase in PVDF composites. In this study highly stable imidazolium cations were used as clay modifier and the phase transformation with increasing alkyl chain length was quantified using FTIR spectroscopy. Figure 7.2 shows the FTIR spectra of pristine PVDF, PVDF-C16 and C_{16}MIm/MMT in the spectral range of 1800 to 600 cm\(^{-1}\). The characteristic peaks of the α-phase occur at 763, 974 and 1181 cm\(^{-1}\). In β-phase (TTT) and γ-phase (T3GT3G'), due to the similar polymer chain conformation the absorption bands appear at similar wave numbers [Boccaccio et al. 2002]. The β-phase is associated with absorptions at 840 and 1275 cm\(^{-1}\). The quantification of γ-phase has been more difficult, as exclusive FTIR bands (776, 833 and 1234 cm\(^{-1}\)) corresponding to the γ-phase appear as shoulders [Martins et al. 2014].

![Figure 7.2 FTIR spectra of pristine PVDF, PVDF-C16 and C_{16}MIm/MMT.](image)
In C\textsubscript{16}MIm/MMT, the characteristic imidazolium ring absorption peak is at 1171 cm\(^{-1}\). The peak at 1181 cm\(^{-1}\) corresponding to CF\textsubscript{2}-CH\textsubscript{2} stretching vibration in pristine PVDF was shifted to 1171 cm\(^{-1}\) in PVDF-C16, suggesting the specific interaction of PVDF chains with the imidazolium ring in the cation. CF\textsubscript{2}-CH\textsubscript{2} bending vibration at 871 cm\(^{-1}\) in PVDF was shifted to 878 cm\(^{-1}\) in PVDF-C16. These results suggest that the β-phase formation was driven through the coulombic interaction between the imidazolium cations in the clay interface and the negatively polarized CF\textsubscript{2} groups in PVDF.

In PVDF-modified clay composites, the relative fraction of β-phase was calculated from FTIR absorption spectra using Eqn.1 assuming that the crystalline phase content of the polymer is either in the α or β-phase, with no or small traces of γ-phase. The variation of β-phase in PVDF with MMT-Na\textsuperscript{+} and C\textsubscript{n}MIm/MMT were represented graphically in Figure 7.3. The relative fraction of β-phase in pristine PVDF (0.43) was increased to 0.99 in PVDF-C16. PVDF-MMT showed a relative β-phase of 0.57 and PVDF-C4 showed equal proportion of both phases (α=0.49 and β=0.51). Due to the high surface to volume ratio of nanofillers, the interfacial interactions between the nanofiller and the polymer matrix increases in general. Higher conversion to β-phase in PVDF-C16 is attributed to the maximum d-spacing of C\textsubscript{16}MIm/MMT (18.55 Å) which enhance the interaction of PVDF with imidazolium cation. The phase conversion was constant above 2 % filler, IL modified clay and 2 % IL modified clay was used for PVDF-clay composite preparation in this study.

**Figure 7.3** Variations of α and β-phase content in PVDF with the addition of MMT and C\textsubscript{n}MIm/MMT. Error bars are shown for the selected chart series with 1 % value.
The phase change was further studied using XRD and the XRD spectra of PVDF, PVDF-MMT and PVDF-C16 are given in Figure 7.4. For PVDF films, the peaks corresponding to the 2\(\theta\) values of 18.1, 18.7 and 20.3\(^\circ\) are assigned to the diffraction in (100), (020), and (201) planes, belong to \(\alpha\)-phase. On addition of MMT-Na\(^+\) clay, intensity of peak corresponding to \(\alpha\)-phase decreases and a merged broad peak is observed at \(2\theta = 20.7\(^\circ\), corresponding to (110) reflection of \(\beta\)-phase. In PVDF-C16, the broad peak at 21.3\(^\circ\) refers to the sum of the diffraction in (110) and (200) planes characteristic of \(\beta\)-phase.

Figure 7.5 DSC heating and cooling curve for (a) PVDF and (b) PVDF-C16.
The enthalpy change associated with α to β-phase change was estimated using DSC analysis. DSC heating and cooling curves of PVDF and PVDF-C16 are shown in Figure 7.5. The enthalpy changes for crystallization were calculated using eqn. 7.2. Addition of modified clay in PVDF results in lowering of enthalpy of crystallization and percentage crystallinity (Table 7.2). An increase in crystallization temperature was also observed on addition of modified clay filler in PVDF (Table 7.2), which is also an indication for the formation of β-phase as reported by Patro et al. [2008].

**Table 7.2** Crystallization temperature ($T_c$), enthalpy of crystallization ($\Delta H_c$) and percentage crystallinity ($X_c$ using eqn.7.2) of PVDF clay nanocomposite films.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Film</th>
<th>$T_c$ (°C)</th>
<th>$\Delta H_c$ (J/g)</th>
<th>$X_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PVDF</td>
<td>132</td>
<td>39.87</td>
<td>38.1</td>
</tr>
<tr>
<td>2</td>
<td>PVDF-MMT</td>
<td>137</td>
<td>32.99</td>
<td>31.5</td>
</tr>
<tr>
<td>3</td>
<td>PVDF-C4</td>
<td>141</td>
<td>30.53</td>
<td>29.2</td>
</tr>
<tr>
<td>4</td>
<td>PVDF-C6</td>
<td>143</td>
<td>29.69</td>
<td>28.4</td>
</tr>
<tr>
<td>5</td>
<td>PVDF-C10</td>
<td>144</td>
<td>28.12</td>
<td>26.9</td>
</tr>
<tr>
<td>6</td>
<td>PVDF-C16</td>
<td>145</td>
<td>16.60</td>
<td>15.8</td>
</tr>
</tbody>
</table>

### 7.3.2 Electrical properties

In PVDF, β-phase having an all trans conformation as shown in Figure 7.1 is responsible for its electrical properties. The electrical properties are likely to increase with the β-phase content. Figure 7.6 shows the variation of capacitance with increasing β content in PVDF films. The capacitance of PVDF with relative β fraction of 0.43 was 45.1 pF and showed an increase of 36.4 % (61.5 pF) in PVDF-C16 (β fraction = 0.99). A linear plot with $R^2 = 0.95$ suggests the dependence of electrical properties on β-phase content.

![Figure 7.6](image.png)

*Figure 7.6* Plot of capacitance of PVDF-clay nanocomposite at 1 KHz with β-phase content. Error bars are shown for the selected chart series with 3 % value.
7.3.3 Molecular orientations

The change in molecular orientation was studied using AFM technique (Figure 7.7). The texture aspect ratio (Str) of the surface was calculated from the image to find the structural orientation. AFM images of pristine PVDF, PVDF-C6, PVDF-C10 and β-phase rich PVDF-C16 films possessed spherulite morphology with isotropic nature (Str = 0.77) and are devoid of oriented molecular structure. The spherulite morphology of PVDF was transformed to shish-kebab in PVDF-C4 due to stress induced during crystallinity change (Str = 0.58). Stress induced in PVDF-C4 is evident from the equal proportion of α-phase (0.49) and β-phase (0.51) estimated from FTIR analysis.

FESEM images of pristine PVDF and PVDF/clay nanocomposites are shown in Figure 7.8. FESEM images show a uniform distribution of C₆MIm/MMT within the polymer matrix with porous microstructure. PVDF-C4 (Figure 7.8c) showed a difference in microstructure complimenting the formation of shish-kebab as revealed in

Figure 7.7 Topography images of (a) pristine PVDF, (b) PVDF-C4 and (c) PVDF-C16 (left) with motifs (right).
the AFM images shown in Figure 7.7. The EDX spectra of PVDF-C16 (Figure 7.8f) confirms the presence of C, F (from PVDF) and Si (from MMT) which serves as an evidence for the exfoliation of clay in PVDF. The dispersion of C$_{16}$MIm/MMT in PVDF-C16 was confirmed using EDX analysis at various sites.

![Figure 7.8](image)

**Figure 7.8** FESEM images of (a) pristine PVDF, (b) PVDF-MMT, (c) PVDF-C4, (d) PVDF-C6 and (e) PVDF-C16 at scale bar = 200 nm, and 50 Kx magnification, (f) EDX spectra of PVDF-C16.

Nagasawa *et al.* [1974] used polyethylene to study the mechanism of shish-kebab formation and observed that gradual and undisturbed cooling of polyethylene solution resulted in single crystals while gradual cooling with ultrasonication produced shish-kebab structures. The methodology followed in this work was also similar to the reported studies with ultrasonication and undisturbed cooling. PVDF-clay composite was prepared by bath sonication for 10 min. at 50 °C and kept at room temperature for 24 hours before casting the film. In PVDF-clay composites, unlike the reported mechanism, the interplay of phase changes and molecular orientation was observed as
evidenced from the AFM imaging. The ratio of two dominant phases in PVDF, $\alpha$ and $\beta$ in the mixture has a great importance in the formation of its final morphology. The shish-kebab formation was further supported by computational studies and improved mechanical properties.

7.3.4 Computational studies

The polymer chain was constructed with 20 repeating units initially and observed a linear structure for $\alpha$-phase and a bent structure for $\beta$-phase as shown in Figure 7.9. As the number of repeating VDF units in $\beta$-phase was increased, with 160 repeating units the folded chain is converted to a circle, (Figure 7.9c) whereas $\alpha$-phase remained as linear molecule under similar condition.

![Figure 7.9](image)

**Figure 7.9** Structure of PVDF (a) $\alpha$-phase with 20 repeating units (b) $\beta$-phase containing 20 repeating units, (c) $\beta$-phase containing 160 repeating units and (d) Penning's model for shish-kebab structure.

Equal ratio of $\alpha$-chains and $\beta$-chains results in a symmetrical shish-kebab structure as explained by Penning's model. Alternatively, extended chain ' $\alpha$-phase' forms the shish, the back bone and folded chain ' $\beta$-phase' forms the kebab. Among the studied PVDF-clay composites, only PVDF-C4 falls in this category and shows shish-kebab structure as evidenced in the AFM analysis. PVDF containing 20 monomer units of both $\alpha$-phase and $\beta$-phase were used to construct the amorphous cell (Figure 7.10). The $\alpha$-phase was lower in energy by 9.06 kJ/mol than $\beta$-phase.
Figure 7.10 Optimized Structure of PVDF using amorphous cell with dimensions (Å) 12.9 x 12.9 x 12.9 (a) $\alpha$-phase and (b) $\beta$-phase containing 20 monomer units.

7.3.5 Mechanical properties

The shish-kebab formation in polymers leads to improved mechanical properties, especially elongation as evident from the Penning's model. Mechanical properties of pristine PVDF and PVDF-clay composites are listed in Table 7.3. PVDF-C4 showed 8% improvement in tensile strength, 77% improvement in elongation and 17% improvement in modulus than pristine PVDF film. The toughness of the polymer calculated as area under the stress-strain curve, also showed 117% improvement for PVDF-C4 than pristine PVDF. This clearly supports the shish-kebab formation in PVDF-C4 nanocomposites. PVDF-MMT, PVDF-C6, PVDF-C10 and PVDF-C16 showed an increase in modulus and decrease in elongation, tensile strength and toughness as similar to reported PVDF-functionalized multiwalled carbon nanotube composite by Mandal et al. [2011].

Table 7.3 Mechanical properties of pristine PVDF film and PVDF-clay composites.

<table>
<thead>
<tr>
<th>Film</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation (%)</th>
<th>Modulus (MPa)</th>
<th>Toughness (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF</td>
<td>2.21 ± 0.02</td>
<td>5.6 ± 0.6</td>
<td>108 ± 3</td>
<td>9.2</td>
</tr>
<tr>
<td>PVDF-MMT</td>
<td>1.66 ± 0.04</td>
<td>4.4 ± 0.5</td>
<td>109 ± 5</td>
<td>5.4</td>
</tr>
<tr>
<td>PVDF-C4</td>
<td>2.40 ± 0.06</td>
<td>9.9 ± 0.7</td>
<td>126 ± 6</td>
<td>20.1</td>
</tr>
<tr>
<td>PVDF-C6</td>
<td>1.50 ± 0.10</td>
<td>4.7 ± 0.5</td>
<td>113 ± 6</td>
<td>5.9</td>
</tr>
<tr>
<td>PVDF-C10</td>
<td>1.62 ± 0.10</td>
<td>5.1 ± 0.6</td>
<td>113 ± 5</td>
<td>6.1</td>
</tr>
<tr>
<td>PVDF-C16</td>
<td>1.72 ± 0.10</td>
<td>5.2 ± 0.6</td>
<td>115 ± 5</td>
<td>7.2</td>
</tr>
</tbody>
</table>
### 7.3.6 Thermal properties

Thermal stability of PVDF decreased on addition of modified clay filler, an evidence for the phase conversion. The interaction of CH$_2$-CF$_2$ with the imidazolium ring leads to lower thermal stability (10 to 23 °C). Figure 7.11 shows the TG/DTG curves of pristine PVDF, PVDF-C4 and PVDF-C16. The peak decomposition temperature ($T_d$) for pristine PVDF was 480 °C and PVDF-C16 showed the lowest thermal stability (457 °C) among the studied PVDF-clay nanocomposites (Table 7.4). The results agree with the lower degradation temperatures of PVDF-nanocomposites reported by Manna et al. [2006].

![Figure 7.11 TG and DTG curves of pristine PVDF, PVDF-C4 and PVDF-C16.](image)

PVDF-C4 with $T_d$ of 470 °C showed higher thermal stability than PVDF-MMT ($T_d = 467$ °C) and all other nanocomposites. The higher stability of PVDF-C4 is due to its oriented and self reinforced structural features. Dutta et al. [2015] reported an $E_a$ of 545.6 kJ/mol for pristine PVDF and a comparable value of 524.2 kJ/mol is obtained in the present work. Coats-Redfern plot for pristine PVDF is shown in Table 7.4. Generally the activation energy of thermal decomposition of polymer composites decreases with addition of fillers [Kar et al. 2015]. The same trend is followed here with exception to PVDF-C4 (Table 7.5) due to self reinforced shish-kebab structure.
### Table 7.4 Activation energy of PVDF by Coats-Redfern method.

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>$T$ (°C)</th>
<th>$T$ (K)</th>
<th>$1000/T$</th>
<th>$\ln[{-\ln(1-\alpha)/T^2}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>461.83</td>
<td>734.83</td>
<td>1.3609</td>
<td>-15.4496</td>
</tr>
<tr>
<td>0.2</td>
<td>469.32</td>
<td>742.32</td>
<td>1.3471</td>
<td>-14.7195</td>
</tr>
<tr>
<td>0.3</td>
<td>473.59</td>
<td>746.59</td>
<td>1.3394</td>
<td>-14.2620</td>
</tr>
<tr>
<td>0.4</td>
<td>476.54</td>
<td>749.54</td>
<td>1.3341</td>
<td>-13.9106</td>
</tr>
<tr>
<td>0.5</td>
<td>478.9</td>
<td>751.90</td>
<td>1.3300</td>
<td>-13.6117</td>
</tr>
<tr>
<td>0.6</td>
<td>481.04</td>
<td>754.04</td>
<td>1.3262</td>
<td>-13.3383</td>
</tr>
<tr>
<td>0.7</td>
<td>483.21</td>
<td>756.21</td>
<td>1.3224</td>
<td>-13.0710</td>
</tr>
<tr>
<td>0.8</td>
<td>485.72</td>
<td>758.72</td>
<td>1.3180</td>
<td>-12.7874</td>
</tr>
<tr>
<td>0.9</td>
<td>489.35</td>
<td>762.35</td>
<td>1.3117</td>
<td>-12.4388</td>
</tr>
</tbody>
</table>

$E_a$ (kJ/mol) = -slope x R  
$E_a$ = 524.2 kJ/mol

### Table 7.5 Peak decomposition temperature ($T_s$) and $E_a$ for thermal decomposition of pristine PVDF and PVDF-modified clay composites.

<table>
<thead>
<tr>
<th>Film</th>
<th>$T_s$ (°C)</th>
<th>$E_a$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF</td>
<td>480</td>
<td>524.2</td>
</tr>
<tr>
<td>PVDF-MMT</td>
<td>467</td>
<td>382.8</td>
</tr>
<tr>
<td>PVDF-C4</td>
<td>470</td>
<td>711.9</td>
</tr>
<tr>
<td>PVDF-C6</td>
<td>458</td>
<td>283.3</td>
</tr>
<tr>
<td>PVDF-C10</td>
<td>458</td>
<td>264.1</td>
</tr>
<tr>
<td>PVDF-C16</td>
<td>457</td>
<td>232.0</td>
</tr>
</tbody>
</table>

### 7.4 Conclusions

The microstructural changes induced in PVDF by ionic liquid modified clay was investigated in the present study. Enhancement of electro active $\beta$-phase crystallization was observed with increased alkyl chain length of the organic modifier, 1-alkyl-3-methylimidazolium cations in the nanoclay. The PVDF-C4 composite with a self
reinforced shish-kebab structure showed superior mechanical properties and retained the thermal stability of pristine PVDF. This work reports a way to prepare PVDF/organoclay composites with enhanced electrical and mechanical properties by adjusting the alkyl chain length of the ionic liquid which offers potential applications in the field of sensors, actuators and batteries.
Chapter 8

Summary and future perspectives
8.1 Summary

The main objectives and the outcomes of the thesis are shown below:

- Design of imidazolium based energetic ionic liquids using computational chemistry tools.
  Thermochemistry of a variety of imidazolium based ILs were predicted accurately using quantum chemical computational studies. The computed heats of formation of all the EILs of 1-ethyl-3-methylimidazolium cation and tetrazolide derivatives, dicyanamide, triazolide, dinitrotriazine, and dinitramide as anions were higher than that of hydrazine. Considering ILs with a suitable oxidizer as a binary monopropellant, Isp of different EILs with varying concentration of HAN was computed. Among the 12 imidazolium based EILs studied, [C2MIm]+[dtrz]−, [C2MIm]+[dn]− and [C2MIm]+[NO2Otz]− provided the best energetic performance in combination with HAN proposing the title compounds as potential green substitute for hydrazine.

- Structural studies of ionic liquids using computational methods for organic modification of clay.
  1-alkyl-3-methylimidazolium ILs were proposed as a replacement for alkyl ammonium salts in clay modification for high temperature applications. Screening of ILs for cation exchange with MMT-Na+ was done based on computed parameters like HOMO-LUMO energy gap for stability studies, Mulliken charge analysis and MK charge analysis for charge contribution to electrostatic and hydrogen bonding interactions. The stability of [CnMIm]+ cations were assessed based on HOMO-LUMO energy gap (ΔE*). ΔE* shows drastic decrease in stability after [C4MIm]+ (ΔE*= 6.7 eV). This change in stability is attributed to shift in HOMO from imidazolium ring to alkyl chain after C4. Chain length of [CnMIm]+ in this study is limited to C16 for thermally stable IL modified organoclay (ΔE* > 4 eV). ΔE* analysis illustrates higher stability for [CnMIm]+[BF4]− (6.8 eV) than [CnMIm]+[Cl]− (4.1 eV). In [CnMIm]+[BF4]−, HOMO is diffused between BF4− and imidazolium ring and shifted to N2-alkyl group on increasing chain length beyond C14, where as HOMO is located on the Cl− anion irrespective of the N2-alkyl chain length in [CnMIm]+[Cl]−. Compiling all results, [C4MIm]+, [C6MIm]+ and [C16MIm]+ based ILs were selected for experimental studies.
Synthesis of ionic liquids and experimental validation of predicted properties. Ionic liquids selected for clay modification, \( [C_6\text{MIm}]^+[\text{Cl}]^ - \) and \( [C_{16}\text{MIm}]^+[\text{Cl}]^ - \) were synthesized with 95% yield. The effect of anion on thermal stability of ILs were established using \( [C_4\text{MIm}]^+[\text{Cl}]^ - (T_s = 284 \, ^\circ\text{C}) \) and \( [C_4\text{MIm}]^+[\text{BF}_4^-] \) \( (T_s = 427 \, ^\circ\text{C}) \), and conform to the computed parameters based on HOMO-LUMO energy gap. The decomposition products identified using pyrolysis GC-MS and transition states using DFT method established the higher reactivity of \( [C_4\text{MIm}]^+[\text{Cl}]^ - \) over \( [C_4\text{MIm}]^+[\text{BF}_4^-] \) as predicted from the charge transfer analysis. The non-dependency of alkyl chain length on stability of ILs were confirmed by analysing \( [C_4\text{MIm}]^+[\text{Cl}]^ - \), \( [C_6\text{MIm}]^+[\text{Cl}]^ - \) and \( [C_{16}\text{MIm}]^+[\text{Cl}]^ - \). Modification of MMT-Na\(^+\) with IL was achieved with the lowest processing time of 15 minutes using probe sonication method. The modification was confirmed using FTIR analysis, improved d-spacing in XRD, CHN analysis and TG analysis. The \( C_n\text{MIm/MMT} \) showed improved thermal stability than conventional alkyl ammonium modified clays. \( C_{16}\text{MIm/MMT} \) with d-spacing of 18.55 Å and \( T_{1\%} \) of 266 °C is proposed as a replacement for Cloisite 25A with d-spacing of 18.65 Å and \( T_{1\%} \) of 214 °C. Thermal degradation mechanism of ionic liquid modified clay was elucidated using DFT and experimentally rationalized using pyrolysis GC-MS and \(^{13}\text{C} \) NMR experiments. For the first time, the predicted carbone mechanism was established by identifying 1-butyl-3-methylimidazol-2-ylidine using \(^{13}\text{C} \) NMR spectroscopy. The experimental results were conforming to the theoretical studies.

Application of ionic liquid modified clay in the removal of perchlorate ion from water. 1-alkyl-3-methylimidazolium modified clays were used for perchlorate adsorption from water. \( C_{16}\text{MIm/MMT} \) showed highest adsorption of perchlorate ions (15.6 mg/g of clay) and the conformational changes associated with adsorption were studied using Raman spectroscopy. Experimental data fitted with different adsorption isotherms and kinetic models revealed Freundlich adsorption and pseudo second order kinetics for the adsorption process. On thermal activation 95% regeneration of clay was observed at 175 °C and regeneration mechanism involving perchloric acid removal was proposed based on DFT studies. The organoclay prepared represents a potential adsorbent for perchlorate with advantage of very low contact time and regenerability of the system.
➢ Preparation and property evaluation of IL modified clay nanocomposites.

The microstructural changes induced in PVDF by ionic liquid modified clay was investigated. Enhancement of electro active β-phase crystallization was observed with increased alkyl chain length of the organic modifier, 1-alkyl-3-methylimidazolium cations in the nanoclay. The PVDF-C4 composite with a self reinforced shish-kebab structure showed superior mechanical properties and retained the thermal stability of pristine PVDF. This work reported a way to prepare PVDF/organoclay composites with enhanced electrical and mechanical properties by adjusting the alkyl chain length of the ionic liquid which offers potential applications in the field of sensors, actuators and batteries.

8.2 Future perspectives

The present investigations extend ample scope for further investigations and future developments, especially to realize ionic liquid based green propellant in space application. Synthesis and characterization of long chain ionic liquid C_{16}MImCl provides, scope for their application as surfactant/soft template in polymerization reactions. The initial studies using C_{16}MImCl as a soft template for copolymerization of aniline and pyrrole resulted in uniform spherical particles with particle size less than 40 nm. AFM images of copolymer of aniline and pyrrole (APC) with and without C_{16}MImCl are shown in Figure 8.1. This opens a promising route for APC synthesis with improved property, especially for sensor application. The use of IL modified clays as thermally stable filler for preparation of different polymer composites are also appealing.

![Figure 8.1](image)

**Figure 8.1** Topography images of (a) APC and (b) APC in presence of [C_{16}MIm]^+[Cl]^-.
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List of Awards

1. "Innovative idea award-2016" from Vikram Sarabhai Space Centre, Thiruvananthapuram for designing "Ionic liquid based green monopropellant for space application".

Mr. Eapen Thomas and Dr. Vijayalakshmi K. P. receiving Innovative Idea Award-2016 from Chairman, ISRO in presence of Director, VSSC.

2. Best paper award, National conference on advanced technologies for material processing and diagnostics, Kochi, September 18-20, 2014,
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  M.Sc., (Analytical Chemistry)  
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- Navodaya Vidyalaya, Kottayam  
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  78.7%  
  2001

RESEARCH TOPIC

**Imidazolium based ionic liquids: Computational studies, synthesis and applications**

**Research highlights**

- Structural and conformational studies of ionic liquids (ILs) using Gaussian 09 and Materials Studio 4.0 software
- Modeled a new ionic liquid as high energetic propellant for future space application- Awarded “ISRO INNOVATIVE IDEA AWARD -2016”
- Synthesis of novel ILs and extensive characterization using vibrational and NMR spectroscopy and Gas chromatography-mass spectrometry
- Explored applications of ILs: (a) IL modified clay for anionic contaminant removal from water, (b) IL modified clay for polymer nanocomposites

PUBLICATIONS

International Journals: 5
National and International conferences: 8

PROFESSIONAL EXPERIENCES

Vikram Sarabhai Space Centre, Indian Space Research organization  
Feb ‘13- present  
Research fellow

Synthite Industries Limited, Cochin  
Nov ‘08- Feb ‘13  
Junior Scientist

- Analysis of processed, in-process and finalized products by keeping in view the relevant quality standards to be met for food applications
CORE COMPETENCIES

- Computational chemistry
- Chromatography
- Spectroscopy
- Method development and validation

INSTRUMENTS HANDLED

- HPLC
- GC
- FTIR spectrometer
- FTNMR
- UV-Vis-NIR spectrometer
- Pyrolysis GC-MS
- Thermogravimetry
- AAS

PROFESSIONAL AFFILIATIONS

- Life time member of High Energy Materials Society of India.

COMPUTER SKILLS

- Software packages:
  - Technical: Gaussian 09, Material studio 5.0, NASA chemical equilibrium with applications software, ChemCraft, GaussView, ChemOffice, Origin Pro
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ADDITIONAL SKILLS

- Good at technical writing and documenting
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REFERENCES

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