PROCESSING, STRUCTURE PROPERTY RELATIONSHIPS IN POLYMER LAYER DOUBLE HYDROXIDE MULTIFUNCTIONAL NANOCOMPOSITES

Sunny Minister Ogbomo, M.S.

Dissertation Prepared for the Degree of

DOCTOR OF PHILOSOPHY

UNIVERSITY OF NORTH TEXAS

August 2009

APPROVED:

Nandika Anne D’Souza, Major Professor
Mohammad A. Omary, Committee Member
Witold Brostow, Committee Member
Nigel Shepherd, Committee Member
Thomas Scharf, Committee Member
Richard F. Reidy, Interim Chair of the Department of Materials Science and Engineering
Michael Monticino, Dean of the Robert B. Toulouse School of Graduate Studies

Layer double hydroxide (LDH) or hydrotalcites or anionic clays are layered nanomaterials that have been used for many years. Their structure coupled to the potential for anion exchange lends them effective in engineering multifunctional properties. The underlying parameters driving the properties of the multifunctional nanocomposites are host polymer physical and chemical structure, interaction between the filler and the matrix and dispersion of the nanofiller. Thus, the plan of work is designed to address these issues. The basis for nanofiller dispersion and its impact on thermal and mechanical properties is established through investigation of an amorphous polymer (polystyrene) (PS) processed by in-situ polymerization coupled to an LDH that is both delaminated and undelaminated prior to introduction in the styrene monomer. The potential for flame retardance from LDH nanocomposites and the introduction of a third metal cation is examined through semi-crystalline linear density polyethylene (LDPE) and acrylonitrile butadiene styrene (ABS) polymers. Finally, medical application potential is examined through a semicrystalline polylactic acid (PLLA)-LDH nanocomposite that has been functionalized with ibuprofen. It was observed that the mechanism for the flame retardancy was due to the structure of the char formed during combustion, which enables the char to thermally insulate the polymer and inhibit the formation and escape of volatiles during combustion. For
medical applications, it was found that the hybrids reduced cell proliferation, and the amount of cell reduction was related to ibuprofen release.
Copyright 2009

by

Sunny Minister Ogbomo
ACKNOWLEDGMENTS

First and foremost, my gratitude goes to the Lord Jesus Christ, the Almighty God who provided me with his mercy, grace, courage and determination to accomplish this work. “…all things work together for good to those who love God…” Rom 8:28.

My profound and sincere gratitude goes to my major advisor, Prof. Nandika Anne D’Souza for her many advice, guidance, direction and support during my program. Many other people contributed to the successful completion of this work and I am very grateful to my academic committee members, Profs. Witold Brostow, Mohammad Omary, Nigel Shepherd and Thomas Scharf for their guidance, advice, encouragement and suggestion. It has been an honor and privilege for me to have you all on my committee.

My special thanks goes to Prof. D’Souza’s group, my laboratory fellow and friends, Dr. Ali Shaito, Divya Kosuri, Koffi Dagnon, Shailesh Vidhate, Sandeep Manandhar and Emmanuel Ogunsona for their friendship and support. I would like to thank Dr. Mickey Richardson and Sriram Ambadapadi, my mentors in layer double hydroxide for their encouragement and efforts during my time with them at chemistry department. I am also indebted to David Garrick for his assistance in TEM work.

Finally, this work would never be possible without the support of my wife, Joan, and my children, Efosa, Iziegbe, Joshua and Caleb who stayed with me during many of my darkest hours. I am deeply indebted to you all for your patience, love, companionship, encouragement and understanding.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENTS</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
</tr>
<tr>
<td>CHAPTER</td>
</tr>
<tr>
<td>1. GENERAL INTRODUCTION AND BACKGROUND</td>
</tr>
<tr>
<td>1.1 Matrix Polymers</td>
</tr>
<tr>
<td>1.1.1 Polystyrene</td>
</tr>
<tr>
<td>1.1.2 Acrylonitrile Butadiene Styrene</td>
</tr>
<tr>
<td>1.1.3 Polylactic Acid</td>
</tr>
<tr>
<td>1.1.4 Polyethylene</td>
</tr>
<tr>
<td>1.2 Layer Double Hydroxide (LDH)</td>
</tr>
<tr>
<td>1.2.1 Synthesis of LDH</td>
</tr>
<tr>
<td>1.2.2 LDH Characterization</td>
</tr>
<tr>
<td>1.2.2.1 Metals and C, H, N Analysis</td>
</tr>
<tr>
<td>1.2.2.2 Fourier Transform Infrared (FTIR) Analysis</td>
</tr>
</tbody>
</table>
1.2.2.3 Wide Angle X-ray Diffraction (WAXD) Analysis ..................................................... 21

1.3 Polymer-LDH nanocomposites ................................................................. 23

1.4 Preparation of Polymer Nanocomposites .............................................. 25

1.4.1 In-situ Polymerization for Polystyrene Nanocomposites ......................... 26

1.4.2 Melt Blending ...................................................................................... 28

1.4.3 Spin Casting ....................................................................................... 29

1.4.4 Compression Molding ........................................................................ 29

1.5 Characterization of Polymer Nanocomposites ...................................... 29

1.5.1 X-ray Diffraction Spectroscopy (XRD) ........................................... 29

1.5.2 Scanning Electron Spectroscopy (SEM) ........................................ 30

1.5.3 Fourier Transform Infrared Spectroscopy (FTIR) .................................. 30

1.5.4 Transmission Electron Spectroscopy (TEM) ....................................... 31

1.5.5 Thermogravimetric Analysis (TGA) .................................................. 31

1.5.6 Dynamic Mechanical Analysis (DMA) ............................................. 32

1.6 Multi-functional Nanocomposites ............................................................ 32

1.6.1 Flame Retardancy ............................................................................. 33

1.6.2 Drug Delivery .................................................................................... 35

1.7 Dissertation Overview ............................................................................. 37

1.8 Conclusions ............................................................................................ 38

1.9 References ............................................................................................... 40
2. IN-SITU POLYSTYRENE-LDH NANOCOMPOSITES: EFFECTS OF POLYMERIZATION AND LDH DELAMINATION ON NANOCOMPOSITE DISPERSION AND MECHANICAL PERFORMANCE ................................................................. 45

2.1 Introduction ............................................................................. 45

2.2 Experimental ........................................................................ 48

2.2.1 LDH Preparation and Delamination ................................. 48

2.2.2 Synthesis of LDH-NO$_3$/PS Nanocomposites from Bulk Polymerization .......................................................... 49

2.2.3 Synthesis of LDH-ST/PS Nanocomposites from Bulk Polymerization .......................................................... 49

2.2.4 Synthesis of LDH-STH/PS Nanocomposites from Solution Polymerization ................................................... 50

2.2.5 Synthesis of LDH-STH/PS Nanocomposites from Bulk Polymerization .................................................... 51

2.3 Characterization ...................................................................... 52

2.3.1 LDH Characterization .......................................................... 52

2.3.1.1 Metals and C, H, N Analysis of LDHs .... 52

2.3.1.2 Fourier Transform Infrared (FTIR) Analysis ......................... 52

2.3.1.3 Wide Angle X-ray Diffraction (WAXD) Analysis ................. 52

2.3.1.4 Transmission Electron Microscopy (TEM) Analysis ............. 52

2.3.2 PS/LDH Nanocomposites ................................................. 53

2.3.2.1 Dispersion ........................................................................ 53

2.3.2.2 Thermal Analysis .............................................................. 54
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3.2.3</td>
<td>Mechanical properties</td>
<td>54</td>
</tr>
<tr>
<td>2.4</td>
<td>Results and Discussion</td>
<td>55</td>
</tr>
<tr>
<td>2.4.1</td>
<td>X-ray Diffraction Spectroscopy (XRD) and Elemental Analysis</td>
<td>55</td>
</tr>
<tr>
<td>2.4.2</td>
<td>Transmission Electron Spectroscopy, (TEM)</td>
<td>68</td>
</tr>
<tr>
<td>2.4.3</td>
<td>Ultraviolet (UV) Spectra Analysis</td>
<td>80</td>
</tr>
<tr>
<td>2.4.4</td>
<td>Fourier Transform Spectroscopy (FTIR)</td>
<td>81</td>
</tr>
<tr>
<td>2.4.5</td>
<td>Differential Scanning Calorimeter Analysis (DSC)</td>
<td>88</td>
</tr>
<tr>
<td>2.4.6</td>
<td>Dynamic Mechanical Analysis (DMA)</td>
<td>94</td>
</tr>
<tr>
<td>2.4.7</td>
<td>Thermo-gravimetric Analysis (TGA)</td>
<td>105</td>
</tr>
<tr>
<td>2.5</td>
<td>Conclusions</td>
<td>115</td>
</tr>
<tr>
<td>2.6</td>
<td>References</td>
<td>119</td>
</tr>
<tr>
<td>3.</td>
<td>ABS-LDH NANOCOMPOSITES: FLAME RETARDANCY, MECHANICAL AND LOW TEMPERATURE PERFORMANCE</td>
<td>121</td>
</tr>
<tr>
<td>3.1</td>
<td>Introduction</td>
<td>121</td>
</tr>
<tr>
<td>3.2</td>
<td>Experimental</td>
<td>124</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Materials</td>
<td>124</td>
</tr>
<tr>
<td>3.2.2</td>
<td>Preparation of the LDH-Nitrate</td>
<td>125</td>
</tr>
<tr>
<td>3.2.3</td>
<td>Preparation of LDH-PTS</td>
<td>125</td>
</tr>
<tr>
<td>3.2.4</td>
<td>Preparation of the ABS/LDH Composites</td>
<td>125</td>
</tr>
<tr>
<td>3.3</td>
<td>Characterization</td>
<td>126</td>
</tr>
</tbody>
</table>
3.3.1 LDH Characterization........................................ 126

3.3.1.1 Metals and C, H, N Analysis of LDH ..... 126

3.3.1.2 Fourier Transform Infrared (FTIR) Analysis
................................................................. 126

3.3.1.3 Wide Angle X-ray Diffraction (WAXD)
Analysis................................................... 126

3.3.1.4 Scanning Electron Microscopy (SEM) ... 127

3.3.2 ABS/LDH Nanocomposites......................... 127

3.3.2.1 Dispersion ........................................ 127

3.3.2.2 Interaction ........................................ 128

3.3.2.3 Thermal Analysis................................. 128

3.1.1.1.Flammability Test ................................. 128

3.4 Results & Discussion................................. 129

3.4.1 Elemental and XRD Analysis of LDH-PTS .... 129

3.4.2 X-ray Diffraction Spectroscopy ................. 131

3.4.3 Fourier Transform Spectroscopy ................. 134

3.4.4 Differential Scanning Calorimetry ............... 135

3.4.5 Dynamic Mechanical Analysis .................. 137

3.4.6 Thermogravimetry Spectrometry ............... 141

3.4.7 Flame Retardancy (UL-94) ....................... 142

3.4.8 Scanning Electron Microscopy .................. 147

3.4.9 Transmission Electron Microscopy ............. 148

viii
3.5 Conclusions................................................................. 150
3.6 References................................................................. 152

4. POLYETHYLENE-LDH NANOCOMPOSITES: FLAME
RETARDANCY AND MECHANICAL PERFORMANCE........... 153

4.1 Introduction............................................................... 153

4.2 Experimental............................................................. 159

4.2.1 Materials .............................................................. 159

4.2.2 Synthesis of Mg₂NiAl(OH)₆C₇H₈SO₃.2H₂O...... 159

4.2.3 Preparation of LDH/LDPE Nanocomposites ...... 160

4.3 Characterization.......................................................... 160

4.3.1 LDH Characterization Techniques: .................. 160

4.3.1.1 Metals and C, H, N Analysis of LDH ..... 160

4.3.1.2 Fourier Transform Infrared (FTIR) Analysis
........................................................................... 161

4.3.1.3 Wide Angle X-ray Diffraction (WAXD)
Analysis.......................................................... 161

4.3.2 LDPE/LDH Nanocomposites......................... 161

4.3.2.1 Dispersion ............................................... 161

4.3.2.2 Thermal Analysis .................................... 162

4.3.2.3 Mechanical Properties............................. 162

4.3.2.4 Flammability Test ................................... 163

4.4 Results and Discussion ............................................. 163

4.4.1 Elemental and X-Ray Diffraction Analysis ...... 163
4.4.2 Differential Scanning Calorimetry ...................... 167
4.4.3 Optical Microscopy ............................................. 169
4.4.4 Thermo-gravimetric Analysis ............................. 170
4.4.5 Flame Retardancy Testing ................................. 171
4.4.6 Morphological Analysis of Char ......................... 174
4.4.7 Scanning Electron Microscopy ........................... 176
4.4.8 Mechanical Properties ........................................ 177

4.5 Conclusions .......................................................... 180

4.6 References ............................................................. 180

5. POLY (L-LACTIC ACID)-LDH NANOCOMPOSITES: DRUG
RELEASE AND DECREASED TOXICITY ............................. 182

5.3 Introduction ........................................................... 182

5.4 Experimental .......................................................... 184

5.4.1 Materials ........................................................... 184

5.4.2 Preparation of Zn-Al LDH Nitrate ....................... 184

5.4.3 Preparation of Zn-Al LDH Ibuprofen ................. 185

5.4.4 Preparation of PLLA/LDH Ibu Nanocomposites 185

5.5 Characterization ...................................................... 186

5.5.1 LDH Characterization .......................................... 186

5.5.1.1 Metals and C, H, N Analyses of LDH Ibu....
.............................................................................. 186

5.5.1.2 Fourier Transform Infrared (FTIR) Analysis
.............................................................................. 186

x
5.5.1.3 Wide Angle X-ray Diffraction (WAXD) Analysis.............................. 186

5.5.2 PLLA/LDH Nanocomposites........................................ 187

5.5.2.1 Dispersion .......................................................... 187

5.5.2.2 Thermal analysis ................................................. 187

5.5.2.3 Mechanical Properties........................................ 188

5.5.2.4 Biofunctionalities............................................... 189

5.6 Results and Discussion .................................................. 190

5.6.1 Structural Characterization ...................................... 190

5.6.2 Dispersion of the LDH Ibu in PLLA Matrix ............ 193

5.6.3 Thermal Stability ..................................................... 196

5.6.4 Thermal Transitions ............................................... 199

5.6.5 Thermo-mechanical and Mechanical Properties. 202

5.6.6 Reduction in Cell Proliferation and Release Profile of Ibuprofen ..................................................... 205

5.7 Conclusions........................................................................ 209

5.8 References........................................................................ 210

6. CONCLUSIONS..................................................................... 212

6.1 References........................................................................ 215
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Polystyrene properties and values</td>
<td>6</td>
</tr>
<tr>
<td>1.2</td>
<td>ABS properties and values.</td>
<td>7</td>
</tr>
<tr>
<td>1.3</td>
<td>PLLA properties and values</td>
<td>9</td>
</tr>
<tr>
<td>1.4</td>
<td>PE properties and values</td>
<td>10</td>
</tr>
<tr>
<td>1.5</td>
<td>Summary of nanocomposites investigated</td>
<td>38</td>
</tr>
<tr>
<td>2.1</td>
<td>XRD data of LDH-NO$_3$ and LDH-ST.</td>
<td>56</td>
</tr>
<tr>
<td>2.2</td>
<td>Comparison of observed and estimated element contents (weight percent) in the</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>as-prepared and as-exfoliated LDH-STH.</td>
<td></td>
</tr>
<tr>
<td>2.3</td>
<td>$d$ spacing and crystallite size of LDH NO$_3$ and it nanocomposites with PS.</td>
<td>57</td>
</tr>
<tr>
<td>2.4</td>
<td>XRD data of LDH-ST and its nanocomposites with PS from bulk polymerization.</td>
<td>60</td>
</tr>
<tr>
<td>2.5</td>
<td>Comparing XRD data of pure ZnO to LDH-STH.</td>
<td>66</td>
</tr>
<tr>
<td>2.6</td>
<td>DSC of pure PS and LDH-NO3/PS nanocomposites from bulk polymerization.</td>
<td>89</td>
</tr>
<tr>
<td>2.7</td>
<td>DSC of pure PS and LDH-STH/PS nanocomposites from solution polymerization.</td>
<td>92</td>
</tr>
<tr>
<td>2.8</td>
<td>DSC of pure PS and LDH-STH/PS nanocomposites from bulk polymerization.</td>
<td>93</td>
</tr>
<tr>
<td>2.9</td>
<td>Thermo-mechanical properties of pure PS and its nanocomposites from solution</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>polymerization.</td>
<td></td>
</tr>
<tr>
<td>2.10</td>
<td>Thermo-mechanical properties of pure PS and its nanocomposites with LDH-STH</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>from bulk polymerization.</td>
<td></td>
</tr>
<tr>
<td>Section</td>
<td>Title</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>-----------------------------------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>2.11</td>
<td>Summary of the results of various nanocomposites with PS and LDHs.</td>
<td>117</td>
</tr>
<tr>
<td>3.1</td>
<td>Comparison of observed and estimated elemental content for LDH sample</td>
<td>129</td>
</tr>
<tr>
<td>3.2</td>
<td>XRD data for LDH-NO₃ and LDH-PTS.</td>
<td>130</td>
</tr>
<tr>
<td>3.3</td>
<td>Some representative XRD data of LDH and LDH/ABS composites</td>
<td>133</td>
</tr>
<tr>
<td>3.4</td>
<td>DSC data for pure ABS and composites</td>
<td>137</td>
</tr>
<tr>
<td>3.5</td>
<td>Storage modulus (E’) of pure ABS and its composites with LDH</td>
<td>141</td>
</tr>
<tr>
<td>3.6</td>
<td>UL-94 data for pure ABS and LDH composites</td>
<td>144</td>
</tr>
<tr>
<td>4.1</td>
<td>Comparison of observed and estimated elemental content for LDH sample</td>
<td>162</td>
</tr>
<tr>
<td>4.2</td>
<td>XRD patterns of LDH showing the characteristics of the different reflectance peaks</td>
<td>163</td>
</tr>
<tr>
<td>4.3</td>
<td>XRD patterns of LDH and the nanocomposites: effect of LDH addition on the (110) peak</td>
<td>165</td>
</tr>
<tr>
<td>4.4</td>
<td>Detailed information obtained from DSC thermal analysis of LDPE and its composites</td>
<td>167</td>
</tr>
<tr>
<td>4.5</td>
<td>TGA data for LDPE and LDH nanocomposites</td>
<td>170</td>
</tr>
<tr>
<td>4.6</td>
<td>Mechanical properties</td>
<td>178</td>
</tr>
<tr>
<td>5.1</td>
<td>WAXD characteristic peaks of LDH Ibu</td>
<td>193</td>
</tr>
<tr>
<td>5.2</td>
<td>Effect of PLLA on the (003) reflection peak of LDH Ibu showing intercalated structure</td>
<td>193</td>
</tr>
<tr>
<td>5.3</td>
<td>Thermal properties of the cooling and second heating of PLLA and PLLA/LDH Ibu nanocomposites.</td>
<td>200</td>
</tr>
<tr>
<td>5.4</td>
<td>Mechanical properties of PLLA and PLLA/LDH Ibu nanocomposites showing an increase in modulus and ultimate tensile strength but decrease in strain to failure.</td>
<td>204</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figures</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>3</td>
</tr>
<tr>
<td>1.2</td>
<td>4</td>
</tr>
<tr>
<td>1.3</td>
<td>5</td>
</tr>
<tr>
<td>1.4</td>
<td>7</td>
</tr>
<tr>
<td>1.5</td>
<td>8</td>
</tr>
<tr>
<td>1.6</td>
<td>10</td>
</tr>
<tr>
<td>1.7</td>
<td>12</td>
</tr>
<tr>
<td>1.8</td>
<td>21</td>
</tr>
<tr>
<td>1.9</td>
<td>22</td>
</tr>
<tr>
<td>1.10</td>
<td>23</td>
</tr>
<tr>
<td>1.11</td>
<td>25</td>
</tr>
<tr>
<td>2.1</td>
<td>56</td>
</tr>
<tr>
<td>2.2</td>
<td>58</td>
</tr>
<tr>
<td>2.3</td>
<td>59</td>
</tr>
<tr>
<td>2.4</td>
<td>61</td>
</tr>
<tr>
<td>2.5</td>
<td>62</td>
</tr>
</tbody>
</table>

1.1 Structure of an amorphous polymer
1.2 Structure of crystalline and amorphous polymer
1.3 Structure of polystyrene
1.4 Structure of ABS
1.5 Structure of PLLA
1.6 Structure of PE
1.7 Schematic of LDH structure. Between the layers are the anions and water, [Figure taken from Applied Clay Science 36 (2007), 103-121]
1.8 FTIR of LDH-NO₃ compared with LDH-ST
1.9 XRD pattern of aged 2:1 Zn-Al LDH NO₃
1.10 Schematic determining the tilting angle
1.11 Schematic of phase separation, intercalation and exfoliation
2.1 XRD patterns of LDH-NO₃, LDH-ST and LDH-STH
2.2 XRD pattern of pure PS, LDH-NO₃ and its nanocomposites with PS from bulk polymerization
2.3 Schematic of the delamination processes from (A) monolayer LDH-ST, to (B) bilayer LDH-STH, and to (C) delaminated sheet in LDH/PS nanocomposite
2.4 XRD patterns of LDH-ST/PS nanocomposites from bulk polymerization
2.5 Low angle XRD patterns of LDH-ST/PS nanocomposites from bulk polymerization
2.6 XRD patterns of the LDH-STH/PS nanocomposites from bulk polymerization. 62
2.7 Low angle XRD patterns of LDH-STH/PS and its nanocomposites from bulk polymerization. 63
2.8 High angle XRD patterns of LDH-STH and its nanocomposites with PS from bulk polymerization. 64
2.9 Comparing ZnO and LDH-STH sample. 65
2.10 Schematic of the delamination processes under in situ solution polymerization. 67
2.11 XRD patterns of the LDH-STH/PS nanocomposites from solution polymerization. 68
2.12 TEM image of 1LDH-NO$_3$/PS nanocomposites from bulk polymerization. 69
2.13 TEM image of 3LDH-NO$_3$/PS nanocomposites from bulk polymerization. 69
2.14 TEM image of 5LDH-NO$_3$/PS nanocomposites from bulk polymerization. 70
2.15 TEM image of 7LDH-NO$_3$/PS nanocomposites from bulk polymerization. 70
2.16 TEM of 1%ZnO/PS nanocomposites from bulk polymerization. 71
2.17 TEM image of LDH-ST. 72
2.18 TEM image of LDH-STH. 72
2.19 TEM image 1LDH-ST and its nanocomposites with PS from bulk polymerization. 73
2.20 TEM image 3LDH-ST and its nanocomposites with PS from bulk polymerization. 73
2.21 TEM image 5LDH-ST and its nanocomposites with PS from bulk polymerization. 74
2.22 TEM image of 1LDH-STH/PS from solution polymerization. 75
2.23 TEM image of 3LDH-STH/PS from solution polymerization. 76
2.24 TEM image of 5LDH-STH/PS from solution polymerization. 76
2.25 TEM image of 1LDH-STH/PS nanocomposite from bulk polymerization. ........ 78
2.26 TEM image of 3LDH-STH/PS nanocomposite from bulk polymerization. .... 78
2.27 TEM image of 5LDH-STH/PS nanocomposite from bulk polymerization. .... 79
2.28 TEM images of 7LDH-STH/PS nanocomposite from bulk polymerization. .... 79
2.29 Uv-vis spectra of pure PS, ZnO, LDH-ST, LDH-STH, 1, 3, 5, and 7LDH-STH/PS nanocomposites, (pure ZnO was purchased from Fisher Scientific ACS). ........ 80
2.30 FTIR of LDH-NO$_3$ and its nanocomposites with pure PS from bulk polymerization. ........................................................................................................ 81
2.31 FTIR of LDH-NO$_3$, LDH-ST and LDH-STH. ........................................ 83
2.32 FTIR of pure PS and its nanocomposites with LDH-ST from bulk polymerization. ........................................................................................................ 84
2.33 FTIR of LDH-STH and its nanocomposites with PS from solution polymerization. ........................................................................................................ 85
2.34 FTIR of pure PS and its nanocomposites with LDH-STH from bulk polymerization. ........................................................................................................ 87
2.35 DSC thermograms of pure PS and its LDH-NO$_3$/PS nanocomposites from bulk polymerization. ........................................................................................................ 88
2.36 DSC of pure PS and its nanocomposites with LDH-ST from bulk polymerization. ........................................................................................................ 90
2.37 DSC thermograms of pure PS and its nanocomposites from solution polymerization. ........................................................................................................ 91
2.38 DSC thermograms of pure PS and its nanocomposites with LDH-STH from bulk polymerization. ........................................................................................................ 92
2.39 Storage modulus (E') of pure PS and nanocomposites with LDH-NO$_3$ from bulk polymerization. ........................................................................................................ 95
2.40 Loss modulus (E'') of pure PS and its nanocomposites from bulk polymerization. ........................................................................................................ 96
2.41 Tan delta (δ) of pure PS and its nanocomposites with LDH-NO₃ from bulk polymerization. ................................................................. 97

2.42 Storage modulus (E’) of pure PS and its nanocomposites with LDH-ST bulk polymerization. ................................................................. 98

2.43 Tan delta (δ) of pure PS and its nanocomposites with LDH-ST from bulk polymerization. ................................................................. 99

2.44 Storage modulus (E’) of pure PS and its nanocomposites from solution polymerization. ................................................................. 100

2.45 Loss modulus (E”) of pure PS and its nanocomposites from solution polymerization. ................................................................. 101

2.46 Tan delta (δ) of pure PS and its nanocomposites from solution polymerization. 101

2.47 Storage modulus (E’) of pure PS and its nanocomposites with LDH-ST/PS from bulk polymerization. .................................................. 102

2.48 Loss modulus (E”) of pure PS and its nanocomposites from bulk polymerization. ................................................................. 103

2.49 Tan delta (δ) of pure PS and its nanocomposites from bulk polymerization. 104

2.50 TGA of pure PS, LDH-NO₃ and its nanocomposites with PS from bulk polymerization. ................................................................. 105

2.51 DTG of pure PS, LDH-NO₃ and its nanocomposites with PS from bulk polymerization. ................................................................. 106

2.52 TGA and DTG of LDH-ST................................................................. 108

2.53 TGA and DTG of LDH-STH................................................................. 109

2.54 TGA of pure PS and LDH-ST/PS nanocomposites from bulk polymerization. ................................................................. 110

2.55 TGA of pure PS and the LDH-STH/PS nanocomposites from solution polymerization. ................................................................. 112

2.56 TGA of pure PS and LDH-STH/PS nanocomposites from bulk polymerization. ................................................................. 113
<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.57</td>
<td>DTG of PS and LDH-STH/PS nanocomposites from bulk polymerization. ..... 114</td>
</tr>
<tr>
<td>3.1</td>
<td>XRD of LDH-NO₃ and LDH-PTS. ................................................................. 129</td>
</tr>
<tr>
<td>3.2</td>
<td>Schematic of orientation of LDH-PTS. ...................................................... 131</td>
</tr>
<tr>
<td>3.3</td>
<td>XRD patterns of LDH, ABS and composites. .............................................. 132</td>
</tr>
<tr>
<td>3.4</td>
<td>FT-ATR spectra for LDH, ABS and composites. .......................................... 134</td>
</tr>
<tr>
<td>3.5</td>
<td>DSC curves for LDH, ABS and composites. ............................................... 136</td>
</tr>
<tr>
<td>3.6</td>
<td>Storage modulus (A), loss modulus (B) and tan delta (C) of pure ABS and composites. ................................................................. 140</td>
</tr>
<tr>
<td>3.7</td>
<td>TGA curves for LDH, ABS and composites. .............................................. 141</td>
</tr>
<tr>
<td>3.8</td>
<td>Digital photographs of burning characteristics of the sample during flame testing for (a) ABS, (b) 10LDH, (c) 30LDH and (d) 60LDH composites. ...................... 143</td>
</tr>
<tr>
<td>3.9</td>
<td>Char from flame testing for (a) ABS, (b) 10LDH, (c) 30LDH and (d) 60LDH composites. ................................................................. 144</td>
</tr>
<tr>
<td>3.10</td>
<td>Burning rate of ABS and LDH/ABS composites. ........................................ 146</td>
</tr>
<tr>
<td>3.11</td>
<td>SEM of LDH-PTS. ..................................................................................... 147</td>
</tr>
<tr>
<td>3.12</td>
<td>TEM morphology of OsO₄ stained LDH/ABS composites (10, 30 and 60 LDH/ABS) corresponding to A and B, C and D, and E and F, respectively. Note rubber phases with different spherical sizes in (B, D and F images). .......... 149</td>
</tr>
<tr>
<td>4.1</td>
<td>Typical structure of LDH. ........................................................................ 155</td>
</tr>
<tr>
<td>4.2</td>
<td>XRD of LDH-NO₃ and LDH-PTS-Ni. ............................................................. 163</td>
</tr>
<tr>
<td>4.3</td>
<td>XRD patterns of LDPE and LDH nanocomposites. ......................................... 165</td>
</tr>
<tr>
<td>4.4</td>
<td>DSC heating and cooling scan of LDPE and composites. ............................. 166</td>
</tr>
<tr>
<td>4.5</td>
<td>Optical images of the microstructures of (a, b, c and d) for 5, 15, 30 and 60% LDH, respectively, in LDPE matrix showing the formation of LDH agglomerates in PE matrix. ................................................................. 168</td>
</tr>
</tbody>
</table>
4.6 TGA curves of pure LDPE and blends with LDH ................................................. 169
4.7 Char formation during HB 94 flame testing ....................................................... 171
4.8 Samples of 60LDH before (a, b) and before and after flame test, respectively. . 172
4.9 Microstructure of char after flame test for LDH (a, b and c) 15, 30 and 60 wt% with LDPE, respectively .......................................................... 174
4.10 SEM of (a, b, c and d) for 5, 15, 30 and 60% LDH, respectively, in LDPE matrix showing the formation of LDH agglomerates in PE matrix ... 175
4.11 Dependence of linear burn rate on weight % of LDH nanocomposites .......... 176
4.12 Young modulus and strain at break ................................................................. 177
5.1 Chemical structure of ibuprofen ................................................................. 191
5.2 WAXD pattern of neat LDH NO₃, neat LDH Ibu, neat PLLA and PLLA/LDH Ibu nanocomposites with different LDH Ibu loadings ....................................... 192
5.3 TEM micrograph of PLLA/1LDH Ibu nanocomposites ................................. 194
5.4 TEM micrograph of PLLA/3LDH Ibu nanocomposites ................................. 195
5.5 TEM micrograph of PLLA/5LDH Ibu nanocomposites ................................. 195
5.6 TGA traces of neat Ibu, neat LDH Ibu, neat PLLA, and PLLA/LDH Ibu nanocomposites .............................................................. 196
5.7 DTG traces of neat Ibu, neat LDH Ibu, neat PLLA, and PLLA/LDH Ibu nanocomposites .............................................................. 197
5.8 DSC traces for the second heating of neat PLLA and its nanocomposites showing the effect of the LDH Ibu on the glass transition, cold crystallization and melting temperature ........................................... 199
5.9 DSC traces for the cooling of neat PLLA and its nanocomposites indicating the slight crystallization promoting effect of the LDH Ibu ......................... 200
5.10 Storage modulus E’ (solid markers) and loss factor tan δ (open markers) curves of the virgin PLLA and PLLA/LDH Ibu nanocomposites showing increase in E’ and a slight shift to the lower temperatures of tan δ peak .................................. 203
5.11 Tensile testing results for neat PLLA and PLLA/LDH Ibu nanocomposites showing an increase in UTS and Young’s modulus and decrease in strain to failure with increased LDH Ibu concentration................................................... 204

5.12 LDH Ibu blended PLLA films reduced SMC proliferation. Cells were cultured on glass vials (control), PLLA, PLLA/LDH Ibu, PLLA/Ibu, LDH Ibu, or Ibu samples with Ibu concentrations of 1%, 3% and 5%. Cell proliferation was estimated using DNA assays as described in the material and method section (n=4, *significantly difference compared to PLLA, p<0.05)......................................... 206

5.13 Percent cumulative drug release curves of PLLA modified with 1 wt% Ibu, 1LDH Ibu, 3LDH Ibu, and 5LDH Ibu. ............................................................ 207
CHAPTER 1
GENERAL INTRODUCTION AND BACKGROUND

Layer double hydroxides (LDH) offer a highly surface active platform that enable multifunctional properties in the resultant composite. As an example, for many years, halogenated flame retardants, for example, tetrabromobisphenol A, have been used for fire protection and extinguishing with the purpose of protecting human life, health and property.\(^1\) Due to the chemical stability of the halogenated flame retardant these compounds have a tendency to accumulate and spread in the environment. Some new environmental friendly non-halogen flame retardants have been synthesized and characterized. Other functionalities needed from polymers are limited toxicity in medical applications.

Deployments of LDH into polymer matrices to produce nanocomposites are facilitated via in situ polymerization or melt blending. Thus, the nature of matrix, the processing method and nature of the clay treatment affect the properties of the material. For nanocomposites, the extent of dispersion influences properties. These in turn are affected by the clay surfactant treatment.

In this chapter, the following are reviewed:

1. Matrices utilized for this study
2. Layer double hydroxides: synthesis and characterization
3. Flame retardancy and medical application of polymer nanocomposites
1.1 Matrix Polymers

Polymers are long chain molecules that are characterized based on their thermal response or structure. Based on thermal response they can be thermoplastics (soften on heating) or thermosets (once reacted do not remelt). Based on their structure they are categorized as amorphous, semi-crystalline or network polymers. Finally, more recently, there has been consideration to the source of the polymer material to categorize the polymers. Polymers can thus be categorized based on petroleum non-renewable or plant based renewable resources.

Thermoplastic materials can be melted or deformed at high temperatures. This property makes them suitable for many applications because they can be readily molded into different shapes or films and hardened. In addition, they can be remolded by applying heat, a process which is essentially reversible. Examples of thermoplastics materials are polyethylene, polystyrene, acrylonitrile butadiene styrene. Thermoplastics can be grouped into three main matrices which are amorphous, semi-crystalline and crystalline. On the other hand, thermosets have cross-linked structures. They are solid after curing. Examples are epoxy resin, vulcanized rubber and Bakelite. The characteristics of this polymer are that they cannot be remolded on heating and under high temperature they can decompose or degrade. This material is well suited for many applications such as in high impact strength, corrosion and water resistant and creep resistant applications. Elastomers also consist of cross-linked capable of forming a loosely bound network. They can randomly coil when unstretched and are capable of undergoing stretching. This results in polymer chains being less random. At ambient
temperatures, most elastomers are soft and deformable. They are therefore classified as rubber-like materials. The molecules are prevented from moving past each other and entangled. They cannot be caused to melt because of the presence of crosslink. Examples of elastomers are natural rubber, polyisoprene, polybutadiene.

Based on their structure, polymers can be amorphous, semi-crystalline, thermosets or network. Amorphous polymers have no long range order (Figure 1.1). They do not crystallize and are therefore non-crystalline. Materials in this category do not have systematic and regular arrangement of atoms.

Figure 1.1 Structure of an amorphous polymer.

The XRD patterns of amorphous polymers consist of diffuse halos instead of the sharp peaks that are characteristics of crystalline materials. Amorphous polymers have glass transition temperature (\(T_g\)), but have no melting temperature. The \(T_g\) represents the temperature of transition from the glassy state to rubbery state. With no crystallites, the polymer flows above this temperature. The \(T_g\) value is usually reduced by the addition of moderate amounts of plasticizers like toluene and sometimes the \(T_g\) is affected by the addition of small amounts of plasticizers. There is no segmental motion at temperatures
below $T_g$ and dimensional changes are the result of the polymer’s primary valence bonds. Polystyrene considered in this dissertation is an amorphous polymer.

Polymers are not 100% crystalline due to their long chain nature. Slow cooling can cause an increase in the amount of crystallinity because there is sufficient time for the chains to align themselves into a more ordered structure. However, under normal conditions, completely crystalline polymers do not exist. A combination of methods such as XRD and DSC can be used to determine the extent of crystallinity. Examples of highly crystalline polymers are high density polyethylene (HDPE), isotactic polypropylene and polytetrafluoroethylene. Semi-crystalline polymers consist of both the amorphous and crystalline phase (Figure 1.2). At the melting temperature, the ordered regions disintegrate and become disordered. Most materials can be ductile and can bend without breaking. Semi-crystalline materials have a crystalline region in amorphous matrix.

![Figure 1.2 Structure of crystalline and amorphous polymer.](image)

The advantage of these materials is that they blend the crystalline strength with the amorphous flexibility. This dissertation focuses on thermoplastic polymers. We now provide the properties of the individual polymers.
1.1.1 Polystyrene

Polystyrene is a thermoplastic material widely used for a variety of applications. It is a vinyl polymer and consists of long chain hydrocarbon and phenyl rings (Figure 1.3). They are produced from a free radical polymerization from the styrene monomer.

\[
\begin{array}{c}
\text{CH}_2-\text{C-CH} \quad \text{H} \\
\text{H} \quad \text{H} \\
\text{H} \quad \text{H} \\
\text{H} \quad \text{H} \\
\end{array}
\]

Polystyrene

Figure 1.3 Structure of polystyrene.

The pure solid polystyrene is brittle, colorless and transparent while the extruded type is white and made of polystyrene beads. The pendant bulky constituents in polystyrene distort the linear arrangement inherent of the chains next to each other thereby preventing it from crystallizing under the condition.\(^6\) Polystyrene can also be blended with rubber to produce another useful styrene rubber material.\(^2\) This material has reduced tensile strength and modulus, increased toughness that sustains high impact (Table 1.1).
Table 1.1 Polystyrene properties and values.\textsuperscript{7-10}

<table>
<thead>
<tr>
<th>Polystyrene properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Index of refraction</td>
<td>1.592 K(^{-1})</td>
</tr>
<tr>
<td>Heat deflection temperature</td>
<td>90 °C</td>
</tr>
<tr>
<td>Solubility parameter</td>
<td>9,100 (kPa(^{1/2}))</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.04</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>41,000 kPa</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>2.5</td>
</tr>
<tr>
<td>Glass transition temperature</td>
<td>95 °C</td>
</tr>
<tr>
<td>Density</td>
<td>1.050 g/cm(^3)</td>
</tr>
</tbody>
</table>

1.1.2 Acrylonitrile Butadiene Styrene

Acrylonitrile butadiene styrene (ABS) is a copolymer consisting of acrylonitrile, butadiene, and styrene (Figure 1.4). ABS is made as a graft by polymerizing styrene and acrylonitrile (SAN) in the presence of butadiene polymer backbone. The graft may be blended with ratio of acrylonitrile having 15-30%, styrene 40-60% and butadiene 5-30%. Several changes to the proportions can be made in order to improve the impact resistance, toughness and heat resistance leading to a wide variety of ABS.
Acrylonitrile monomer can be obtained from ammonia and propylene while the butadiene is produced from the catalytic dehydrogenation of normal butane and the styrene monomer is produced from dehydrogenation of ethyl benzene. With the strength and rigidity of acrylonitrile and styrene coupled with the toughness of the polybutadiene

Table 1.2 ABS properties and values.\textsuperscript{6,11}

<table>
<thead>
<tr>
<th>ABS copolymer</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>1.20 g/cm\textsuperscript{3}</td>
</tr>
<tr>
<td>Surface hardness</td>
<td>RR96</td>
</tr>
<tr>
<td>Melting temperature</td>
<td>210 °C</td>
</tr>
<tr>
<td>UL 94 Flammability</td>
<td>HB-5VA</td>
</tr>
<tr>
<td>Oxygen index</td>
<td>30%</td>
</tr>
<tr>
<td>Glass transition</td>
<td>105-115 °C</td>
</tr>
<tr>
<td>Dielectric constant 1kHz</td>
<td>3.26</td>
</tr>
</tbody>
</table>
this copolymer has many uses. Some of the advantages of ABS is its excellent impact strength, stiffness and dimensional stability as well as the ease at which this material can be machined for various fabrication but its disadvantage is it extreme flammability (Table 1.2). Random copolymers of styrene and butadiene with amounts of styrene tend to be amorphous and transparent.

1.1.3 Polylactic Acid

Polylactic acid (PLLA) is a renewable bio-based biodegradable/compostable thermoplastic polymer. PLLA, aliphatic eco-friendly polyester that can undergo enzymatic or hydrolytic degradation and is used in many applications such in the sutures, stent, drug delivery devices, and in tissue engineering (Figure 1.5 and Table 1.3). PLLA can also be formed into blown films, injected molded objects and coatings.

\[
\text{Polylactic acid}
\]

Figure 1.5 Structure of PLLA.

PLLA can be synthesized from the fermentation of corn, sugar cane, sugar beat, and potato and also by ring-opening polymerization of lactides or condensation polymerization of all stereoisomers of lactic acid monomers. The racemic mixture (D and L) polymerization gives the poly-DL-lactic acid (PDLLA) known to be amorphous. But we can control the D and L enantiomers by stereospecifically using catalyst to obtain the
L enantiomers, the poly(l-lactic) acid (PLLA) which is crystalline.\textsuperscript{12} PLLA can be crystallized by slow cooling, annealing it above the $T_g$, or strain crystallized.\textsuperscript{13} Despite extensive studies of PLLA, their crystallization behavior is still not completely understood. Depending on the processing conditions, PLLA can crystallize in three different forms, $\alpha$, $\beta$, $\gamma$ forms. Crystallization of PLLA from the melt or from solution under normal conditions results in its most common polymorph, the $\alpha$ form.\textsuperscript{14} One disadvantage of PLLA is relatively poor abrasion resistance. Table 1.3 gives some properties of PLLA and its values.

Table 1.3 PLLA properties and values.\textsuperscript{15,16}

<table>
<thead>
<tr>
<th>Polylactic acid</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>1.24g/cm$^3$</td>
</tr>
<tr>
<td>Glass transition temperature</td>
<td>57 °C</td>
</tr>
<tr>
<td>Melting temperature</td>
<td>175 °C</td>
</tr>
<tr>
<td>Amorphous grade</td>
<td>Transparent</td>
</tr>
</tbody>
</table>

1.1.4 Polyethylene

Polyethylene (PE) is the most common polymer in the world (Figure 1.6 and Table 1.4). It is a thermoplastic material consisting of long chains of the ethylene monomer.
Essentially, two hydrogen atoms are connected to each carbon atom linked together by a double bond. Several classes of PE are available; some of them include the ultra high molecular weight polyethylene (UHMWPE), ultra low molecular weight polyethylene (ULMWPE), high density polyethylene (HDPE), linear low density polyethylene (LLDPE) and low density polyethylene (LDPE). The LDPE has a density of 0.912 g/cm$^3$. PE is widely used for most containers and commercial plastics films such as

**Table 1.4 PE properties and values.$^{17-19}$**

<table>
<thead>
<tr>
<th>Polyethylene</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>0.910-0.940 g/cm$^3$</td>
</tr>
<tr>
<td>Percent crystallinity</td>
<td>60-70%</td>
</tr>
<tr>
<td>Crystalline melting temperature</td>
<td>110-120 °C</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>0.91</td>
</tr>
<tr>
<td>Elongation</td>
<td>100%</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>5,515 kPa</td>
</tr>
</tbody>
</table>
plastic bags and films wrap. Its long chains and high degree of branching gives its unique and desirable properties. Some other properties as well as its values are stated in Table 1.4.

1.2 Layer Double Hydroxide (LDH)

Layered double hydroxides (LDH) (Figure 1.7) or hydrotalcite-like, hydrotalcite-type, are anionic clays with the general formula \([M^{II}_{1-x}M^{III}_x(OH)_2]^+[A^{n-}]_{x/n}yH_2O\).\(^{20,21}\) Here, \(M^{II}\) are divalent metals such as \(Zn^{2+}\), \(Mg^{2+}\), \(Ca^{2+}\), etc and \(M^{III}\) represents trivalent metal cations such as \(Al^{3+}\), \(Mn^{3+}\), \(Cr^{3+}\), etc, and \(A\) is a \(n\)-valent anions. The value of \(x\) range between 0.25 and 0.33.\(^{22,23}\) These materials are of Brucite-type \(M(OH)_2\) octahedral layers. The \(M^{2+}\) occupy alternate layers of octahedral sites while \(OH^-\) are hexagonally close packed in which the metal ions, for example \(Zn^{2+}\) is six-coordinated to \(OH^-\) to form an infinite 2D layers. To compensate for the net positive charge on the basal hydroxide layers, \(A^{n-}\) are intercalated into the interlayer domain with water. The basal spacing in brucite is 0.48 nm and the presence of carbonate anions and water contribute to the interlayer distance of 0.77 nm in LDH.\(^{24}\) The most naturally occurring clay material is known as hydrotalcite and has a general formular \(Mg_6Al_2(OH)_{16}CO_3.4H_2O\). This was the first known materials discovered in Sweden in 1842.\(^{25}\) The fascinating thing about LDH is that there is the flexibility as to the selection of the nature of the cations as well as the interlayer anions. The anions in LDH are exchangeable with other anions; this property along with the fact that they can also be pillard makes LDH increasingly useful for several applications.
A wide variety of anions can be present in the interlayer domains in addition to the water molecules. Therefore, there is no limit to the nature of anions in the LDH as long as there are no side reactions by way of the anions abstracting the metal ions from the hydroxide surfaces. Anions commonly used are:

(i) Inorganic anions such as halides (X⁻), CO₃²⁻, NO₃⁻, etc

(ii) Organic carboxylates, dicarboxylates, etc

(iii) Polymeric polyvinylsulfonate, polyaniline, etc

(iv) Complexes, such as CoCl₄²⁻, etc

(v) Medicinal and biochemical anions, such as ibuprofen, DNA, etc

A comparable list of preference for anions is represented below:
Thus, the nitrate LDH are commonly used as precursor for exchange reactions and in the case of the carbonate, exchange is difficult. The major problem in LDH is the contamination of the pure LDH with CO$_2$ as carbonates are easily intercalated. Therefore, a CO$_2$-free atmosphere is normally encouraged if carbonation is to be eliminated.$^{20}$ Within the hydroxide layers, a wide range of divalent and trivalent cations can be used. Commonly used divalent metals are Mg$^{2+}$, Fe$^{2+}$, Co$^{2+}$, Ni$^{2+}$, etc, while for trivalent metals, they are Al, Cr$^{3+}$, Fe$^{3+}$, Co$^{3+}$, etc. It is instructive to note that the requirement is that an ionic radius should be closed to 0.0720 nm of Mg$^{2+}$.

1.2.1 Synthesis of LDH

There are several methods for the synthesis of LDH. The most commonly used method is by direct synthesis,$^{26}$ this route involves nucleating and growing the metal hydroxide layer by mixing an aqueous solution containing the salts of two metal ions with the desired anion and in the presence of a sodium hydroxide. In this method, nitrate or chloride salts are often used because of the low preference of LDH towards anions.$^{27}$ A major disadvantage of using this method is that entering anion must have high affinity for hydroxide layers or else there will be the formation of contaminating salts with the constituent’s cations. An alternative method of preparation is via co-precipitation.$^{28,29}$ This method is more reliable and it provides elegant synthetic route to preparation of inorganic LDH and organo-inorganic hybrid. In this method, a mixed metals salt containing both M$^{2+}$ and M$^{3+}$ are placed in a reaction flask after which a calculated
amount of deionized water is added to form a solution and followed by stirring. Then a co-addition of a 50% NaOH is added to maintain constant pH under dry N₂. This is necessary to eliminate CO₂ because it often results in the formation of CO₃²⁻ in solution when it comes in contact with alkaline solution. Hydrothermal treatment can be applied to the resulting gel and such process improves the crystallinity of the material.³⁰,³¹ Other methods also used are the sol-gel technique,³³ memory effect or rehydration method³⁴ and so on.

Miyata and Kumura³⁵ were the first group who performed an exchange reaction with acetate anion and also in a study involving aliphatic carboxylate anion with LDH observed that the sebacate anion with its long axis oriented perpendicularly to the hydroxide layers in a monolayer arrangement. Chibwe and Jones³⁶ reported interlayer spacing’s of 18.8 Å consistent with that obtained by Miyata and his group and this result was from MgAl-LDH sebacate anion prepared using coprecipitation method.³⁷ However, a change in value in the interlayer spacing has been observed and the differences probably resulting from the additional water particle as well as to change in the packing of the alkyl chains. But Carlino and Hudson³⁸ attributed the changes to a fluctuation of the angle of orientation of the sebacate dianion with respect to the hydroxyl layer surface. In a related studies, Meyn et al.³⁹ observed an interlayer spacing increase and they went on and found a linear relationship exist between the observed interlayer spacing and the chain length of linear aliphatic dicarboxylates. Following co-precipitation route in synthesis of series of LDH with dicarboxylate anions, Raki et al.⁴⁰ obtained an analogous linear relationship.
The formation of a vertical bilayer arrangement with a linear monocarboxylate anion is possible because the interlayer of LDH has two ionic surfaces to which the carboxylate anion group can easily attach to. Thus there will be bilayer arrangement with the alkyl chains of the anions aligned from end to end or alternatively interleaved. Furthermore, the anion may also be made to incline at an angle from the normal to the layers. In a study of alkyl sulfate anions with LDH by Kopka et al.\textsuperscript{41} they observed that the alkyl sulfate anions adopt monolayer arrangements between the hydroxide layers. An almost perpendicular orientation of the alkyl chains was proposed but quite different from orientation after drying the sample, the sulfate anion chains oriented at an angle 56° to the surface of the hydroxide layers. Clearfield et al.\textsuperscript{42} performed a comparative study with dodecyl sulfate anion using two anion exchanges in a co-precipitation method. Three different interlayer spacing reflecting three different interlayer arrangement of the anion were reported. They attributed some of these arrangements to monolayer as well as bilayer arrangement in which the dodecylsulfate anion is position at an angle of approximately 40° to the surface of the hydroxide layers. A related result illustrating that the layer structure is extremely well-ordered has been reported by Meyn et al.\textsuperscript{39} for an LDH alkanesulfonates. Because these anions are a mixture of different isomers, the sulfonate anion group were said to be positioned at different carbon atoms along the alkyl chain. They attributed their result that the alkanesulfonates in a bilayer arrangement adopt a U-shaped conformation.

A study involving an anion exchange material with dibasic functionalities was carried out by Franklin et al.\textsuperscript{43} They reported the formation of three distinct phases with
use of phenolate and sulfonate anion derivatives in ZnAl-LDH and found that with only the sulfonate anion used the interlayer LDH spacing gave a result quite different from that having divalent anion (the sulfonates and phenolate anion). It was gathered that the different interlayer spacing’s indicated that the guest molecules occupies two distinct conformations within the interlayer. There is a growing interest in the synthesis of organo LDH hybrid materials for various nanopolymeric compounds for diverse applications in recent years. In this direction, Tanaka et al.\textsuperscript{44} prepared an LDH via exchange reaction and then performed an in situ polymerization with acrylate anions. The product was characterized by physicochemical means and results indicated a poorly crystalline material. Following a similar procedure, Sugahara et al.\textsuperscript{45} reported the preparation of LDH polyacrylonitrile by an in situ polymerization route of a CuCr-LDH polyaniline. The preparation and characterizations of polyacrylate, polyvinylsulfonate and polystyrenesulfonate has been carried out by Oriakhi et al.\textsuperscript{46} The polymer materials were obtained from co-precipitation of the organo-LDH anion in a basic solution containing the dissolved and reported interlayer spacing’s of between 12.0 and 21.6 Å indicating incorporation of the polymer. They proposed a bilayer arrangement of the anionic polymers. An analogous route was developed by Messersmith and Stupp.\textsuperscript{47} They integrated polymer between the hydroxides layer after intercalating water soluble organohybrid into the LDH material and poor crystallinity was reported to be the case of the material property.

1.2.2 LDH Characterization

A variety of techniques have been used for characterization of LDH.
1.2.2.1 Metals and C, H, N Analysis

To determine the metals ratio in LDH, atomic absorption spectroscopy (AAS) is used. The principles is based on the fact that metallic element absorbs light energy at a specific wavelength characteristics of that elements. An acidic solution 5% HNO$_3$ containing the element to be tested is usually passed through either air/acetylene or N$_2$O/acetylene burner head which reduces the ions to atoms. The energy emitted by the element lamp is absorbed by the same element passing through the flame; all other elements will therefore not absorb this particular energy.

Finally, to get the experimental formula and compare it to that predicted by stoichiometry, we do elemental analysis. With this technique we can determine the amount of CHN in a material. In elemental analysis, the sample which has been under combustion convert C, H and N to their respective gaseous stage which is after separation in a column by a carrier gas estimated by thermal conductivity changes. It is usually a desired practice to be able to determine the amount of CO$_3^-$ from the LDH nominal molecular formular. Thus we can determine if material has been intercalated or delaminated with the relative amounts present in the analysis. A typical determination is carried as follows:

Zn$_2$Al(OH)$_6$ C$_{18}$H$_{35}$O$_2$.C$_{16}$H$_{34}$

Molecular weight = 769.70 g

% C

No. of carbon in the molecule = 18+16 = 34
Weight of total carbon = 12 x 34 = 408 g

Theoretical weight% of carbon = \( \frac{408 \times 100}{769.70} = 53.00 \% \)

% N

No. of nitrogen in the molecule = 1

Weight of total nitrogen = 14.0067 x 1 = 14.0067 g

Theoretical weight% of nitrogen = \( \frac{14.0067/100}{769.7} = 1.81 \% \)

% H:

No. of hydrogen in the molecule = 6+35+34 = 75

Weight of total hydrogen = 1.008 x 75 = 75.6 g

Theoretical weight% of hydrogen = \( \frac{75.6x100}{769.7} = 9.82 \% \)

<table>
<thead>
<tr>
<th>( \text{Zn}<em>2\text{Al(OH)}<em>6 \text{C}</em>{18}\text{H}</em>{35}\text{O}<em>2\text{C}</em>{16}\text{H}_{34} )</th>
<th>Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>53.00</td>
</tr>
<tr>
<td>H</td>
<td>9.82</td>
</tr>
<tr>
<td>N</td>
<td>1.66</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Theoretical</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>52.62</td>
<td>8.91</td>
</tr>
<tr>
<td>0.44</td>
<td></td>
</tr>
</tbody>
</table>

Now the AAS calculations:

LDH-stearate sample

[\( \text{Al}^{3+} \)] = 40.64 ppm
\[ [\text{Zn}^{2+}] = 0.7855 \text{ ppm} \]

\[
\text{Al (in mg)} = \left( \frac{40.64 \text{mg}}{L} \right) \left( 0.05 \text{ L} \right) = 2.032 \text{ mg Al}
\]

AAS reading * volume of LDH sample solution

\[
\text{Zn (in mg)} = \left( \frac{0.7866 \text{mg}}{L} \right) \left( \frac{0.05 L}{0.000206L} \right) \left( 0.05 \text{ L} \right) = 9.546 \text{ mg Zn}
\]

AAS reading * dilution factor * volume of LDH sample solution

\[
\frac{2.032 \text{mg Al}}{26.98 \text{mg / mol Al}} = 0.0753 \text{ mol Al}
\]

\[
\frac{Zn}{Al} = \frac{0.165}{0.0834} = 1.94
\]

\[
\frac{9.546 \text{mg Zn}}{65.39 \text{mg / mol Zn}} = 0.146 \text{ mol Zn}
\]

To find the percent of each metal, divide the amount of mg per metal by the amount of mg of LDH weighed out for AAS:

\[
\text{Al} = \frac{2.032 \text{mg Al}}{71.32 \text{mg LDH}} \times 100\% = 2.85\% \text{ Al}
\]

\[
\text{Zn} = \frac{9.546 \text{mg Zn}}{71.32 \text{mg LDH}} \times 100\% = 13.38\% \text{ Zn}
\]

**Theoretical Calculations**

\[
\text{Al} = \frac{26.98 \text{mg Al}}{769.7 \text{mg LDH}} \times 100\% = 3.50\% \text{ Al}
\]

where 769.7 is the formula weight of the total LDH stearate hexadecane
Zn = \frac{130.74 \text{mgZn}}{769.7 \text{mgLDH}} \times 100\% = 16.9\% \text{Zn}

1.2.2.2 Fourier Transform Infrared (FTIR) Analysis

Fourier transform infrared spectroscopy (FT-IR) is another technique for characterizing LDH especially for functional group identification. Functional groups like CO$_3^–$, NO$_3^–$, SO$_4^{2–}$, OH, etc, can be observed. For example, the carboxylate gives strong symmetric and anti-symmetric stretching bands at 1400 and 1560 cm$^{-1}$, respectively. Similarly, acid carbonyl group absorbs strong vibration in the 1700 cm$^{-1}$ region. The hydroxyl stretching and water bending modes occurs at around 3000 and 3700 cm$^{-1}$ and below 1000 cm$^{-1}$ we can find the metal oxide of the LDH occurring, therefore, it is also used to identify the metallic component of LDH. Typically, for an aged ZnAl-LDH material, a sharp absorption peaks is found at 425 cm$^{-1}$ while in the case of age MgAl-LDH, it is 444-455 cm$^{-1}$. Thus, we can essentially distinguish the age from the freshly prepared material where the peaks may not be visible.$^{49}$ Other peaks that are commonly observed are the NO$_3^–$ peak occurring at 720-750 cm$^{-1}$ and 1384 cm$^{-1}$ and CO$_3^–$ around 670-690 cm$^{-1}$, 850-880 cm$^{-1}$ and 1350-1380 cm$^{-1}$. Typically, as in the Figure 1.8, most of the nitrate absorption band disappears after the nitrate LDH was functionalized with stearate (ST). The IR absorption peaks at 2908 cm$^{-1}$ and 2844 cm$^{-1}$ represent C-H stretching vibrations, and peaks at 1478 cm$^{-1}$ and 720 cm$^{-1}$ corresponds to the bending and rocking of CH$_2$, respectively of the stearate anion. The peaks at 1542 cm$^{-1}$ and 1407 cm$^{-1}$ correspond to the asymmetric and symmetric stretching vibrations of the C=O and C-O groups, respectively.
1.2.2.3 Wide Angle X-ray Diffraction (WAXD) Analysis

X-ray diffraction is an important technique popularly used for analyzing samples to provide the information regarding the crystal structure of the material. A randomly oriented powdered or solution sample can be used. The sample diffracts radiation with a wavelength similar in size to the interatomic separations of a few angstroms. From the XRD we can obtain patterns by focusing a beam of x-rays on a sample of crystalline material which is rotated to give a varying angle of incidence (theta) and recording the positions of the diffracted beam with a detector which is rotated through 2θ. The application of XRD is governed by Bragg’s law where \( n\lambda = 2dsin\theta \), \( n \) is an integer.
representing an order of reflection which is 1 in XRD. \( \lambda \) = wavelength of x-ray radiation, (for CuK\( \alpha \) = 1.540562 Å, \( d \) is the distance of the spacing and \( \theta \) is the angular diffraction. Generally, the scanning range for LDH is from 2\( \theta \) 5-70 \( \degree \), however, the starting range could be 2 \( \degree \) which is typical for a large intercalated anion. XRD typical patterns shows diffractions planes indexed in 3R\(_1\).\(^{50}\) For LDH material (Figure 1.9), the basal spacing is conventionally indexed in rhombohedra structure as 003, 006, 006, etc; this values are available from peak list from XRD.\(^{51}\) Thus the lattice parameter \( c \) and \( a \) can be obtained. The value of the parameter \( c \) is obtained from \( c = d_{003}+2d_{006}+3d_{009} \). Similarly, the repeat layer distance, \( d = 1/n(d_{003}+2d_{006}+3d_{009}+...+ nd_{00(3n)}) \). From the non-basal spacing \( d_{110} \) is broad and we can obtain the \( a \) parameter = 2\( d_{110} \).

![XRD pattern](image)

Figure 1.9 XRD pattern of aged 2:1 Zn-Al LDH NO\(_3\).

The tilting angle of the surfactant of a functionalized LDH can be determined for example, using the para-toluene sulfonate LDH (LDH-PTS) (Figure 1.10).
With the interlayer spacing of 1.2 nm and the PTS anion calculated basal spacing of 0.6 nm. Therefore, the PTS anion will be lying perpendicularly to the surface of the hydroxide layers. For other variations of anions, Meyn et al.\textsuperscript{52,53} have studied details regarding orientations of different types.

1.3 Polymer-LDH nanocomposites

Nanocomposites are a new class of composites having nano-scale dispersion, typically in the range 1-100 nm.\textsuperscript{54} In recent years, there has been a tremendous emphasis on the development of polymeric nanocomposites and have drawn great interest from both academic and industry because they exhibit remarkable improvement in properties (at very low clay loading of about 5%) when compared to neat polymer or conventional composites.\textsuperscript{55} Some of the improvements include increased strength and high resistance, high moduli, increase biodegradability and decreased gas permeability and flammability.
Polymer-clay nanocomposites are essentially formed through the union of two materials, the organic and mineral materials. The origin of polymer-clay nanocomposites can be traced to the pioneering work conducted at Toyota central research laboratory and the first practical application of nanocomposites was in the use of a nylon-montmorillonite clay nanocomposite as a timing belt cover on a Toyota Camry automobile.\textsuperscript{56} Due to the nanometer size scale materials obtained by dispersion, nanocomposites display remarkable improved mechanical and thermal properties when compared to the pristine materials. Improvements have been known to include increased strength, moduli, heat resistance, decreases flammability and so on.\textsuperscript{57}

Depending on the degree of separation of the individual clay platelets in the polymer host, three types of clay dispersion are possible when clays are mixed with polymers, and they are immiscible, intercalation or exfoliation.

In immiscible polymer nanocomposites (Figure 1.11), both the clay layers and polymer are not compatible and therefore, the polymer cannot intercalate between the clay layers due to the surface energies which are invariably incompatible for wetting. Therefore, the properties of the materials remains the same or in some cases leads to little enhancement in properties as that of the traditional composites which may have resulted from no intercalation or very negligible interaction, respectively.\textsuperscript{58}

In an intercalated dispersion, the layers swell with some level of polymer chain penetration but the overall stacking of the layered structure is retained (Figure 1.11). In this particular case, the clay layers provide reinforcement for the polymer.\textsuperscript{59}
In an exfoliated dispersion (Figure 1.11), the layers are completely dispersed within the host system. Since the layers are in the nanometer range in thickness, an exfoliated dispersion results in a high aspect ratio reinforced polymer system. Some desirable properties, such as high temperature dimensional stability, increased modulus and decreased permeability, are thus achieved in these systems. A significant impediment to the control of properties is variability in the composition, charge density and iron content of these naturally occurring materials.

Figure 1.11 Schematic of phase separation, intercalation and exfoliation.

1.4 Preparation of Polymer Nanocomposites

Preparation of thermoplastic polymer nanocomposites is done by in-situ polymerization or melt-mixing.
1.4.1 In-situ Polymerization for Polystyrene Nanocomposites

Bulk polymerization is particularly well suited for step polymerization because a high-molecular-weight polymer is not produced until the very last stages of reaction. However, bulk polymerization is difficult to control because of the characteristics of radical chain polymerization. Their highly exothermic nature, the high activation energies involved, and the tendency towards gel effect formation combine to make heat dissipation difficult. Bulk polymerization requires careful temperature control. Furthermore, there is also the need for strong and elaborate stirring equipment since the viscosity of the reaction system increases rapidly at relatively low conversion. The viscosity and exothermic effects make temperature control difficult. Local hot spots may occur, resulting in degradation and discoloration of the polymer product and a broadened molecular weight distribution due to chain transfer to polymer. Bulk polymerization is used in the polymerizations of ethylene, styrene, and methyl methacrylate. The heat dissipation and viscosity problems can be prevented by carrying out the polymerizations to low conversions with separation and recycling of unreacted monomer. An alternative is to carry out polymerization in stages and allow low conversion in a large reactor and then final conversion in thin layers (either on supports or free-falling streams. Some advantages of using bulk polymerization are that we can obtain purest polymeric material needed for most electrical and optical applications. In addition, it is convenient to cast objects to shape and make polymer with increased yield per reactor volume. The disadvantages of using this method include strict control and reaction run slowly and other are the high rate of viscosity and the difficulty to remove the last trace of unreacted
monomer. This is very essential especially if the polymer is used for food based applications.\(^3\)

Solution polymerization involves a monomer and catalyst in the present of solvent. The solvent acts as diluents and aids in the transfer of the heat of polymerization. The viscosity of the reaction mixture is reduced because the solvent allows easy stirring. Thermal control is much easier in solution polymerization compared to bulk polymerization. However, the presence of solvent may present new difficulties. Unless the solvent is chosen with appropriate consideration, chain transfer to solvent can become a problem. Furthermore, the purity of the polymer may be affected if there are difficulties in removal of the solvent. Vinyl acetate, acrylonitrile, and esters of acrylic acid are examples of monomer polymerized in solution. Solution polymerization can overcome many of the disadvantages of the bulk process. Some advantages of using solution polymerization include easy control and heat remover from the process as well as the ability to obtain desired polymer solution.\(^6\)

Emulsion polymerization involves the use of monomers in the presence of emulsions (i.e., colloidal dispersions). The process bears a superficial resemblance to suspension polymerization, but is quite different in mechanism and reaction characteristics. Emulsion polymerization differs from suspension polymerization in the type and smaller size of the particles in which polymerization occurs, in the kind of initiator employed, and in the dependence of polymer molecular weight on reaction parameters. Emulsion polymerization process has some advantages. For example, the physical state of the emulsion (colloidal) system makes it easy to control the process.
Emulsion polymerization process both high molecular weights and high reaction rates. Thermal and viscosity problems are much less significant than in bulk polymerization. The product of an emulsion polymerization, known as latex, can in many instances be used directly without further separations. However, there may be the need for appropriate blending operations. Such applications include paints, coating, finishes, and floor polishes. Apart from the physical difference between the emulsion and other polymerization processes, there is one very significant kinetic difference. However, large increases in molecular weight can be made only by decreasing the polymerization rate by lowering the initiator concentration or the reaction temperature. Generally, emulsion polymerization is a unique process because it can provide the means of increasing the polymer molecular weight without decreasing the polymerization rate.\textsuperscript{3,60}

1.4.2 Melt Blending

This process involves mixing in a co-rotating twin extruder with the disperse phase mixed with the matrix phase.\textsuperscript{61} This advantage of this method is that it does not require solvent or solution. Essentially, therefore, during melt blending, the fillers are mixed with matrix and can result in intercalate or exfoliated nanocomposites. However, material such as organic surfactant can be easily degraded because of the high temperature applied and shear stresses and should be watch carefully. The melt blended materials can then be formed into films by compression molding, spin cast through solutions.
1.4.3 Spin Casting

The method does not result in degradation of the material. Here solvent is used as opposed to the melt blending which does not require solvent.\textsuperscript{62,63} The disadvantage of this is that solvent is used. In a typical spin casting, the material is first dissolved in a solvent and mixed. This is followed by use of a spin caster.

1.4.4 Compression Molding

This is done with heating and applying pressure.\textsuperscript{64} The composite is first palletized as a precursor for the compression molding. Blends of materials are compression molded between two sheets of Teflon using a Carver press to obtain sheets. The Carver press is first pre-heated to the desired temperature and a total of 5 meter tons of pressure is applied at a rate of 0.5 metric tons per minutes.

1.5 Characterization of Polymer Nanocomposites

Dispersion of polymer nanocomposites is determined through a combination of microscopy and X-ray diffraction. Thermal property is determined through calorimetry or thermogravimetry.

1.5.1 X-ray Diffraction Spectroscopy (XRD)

XRD can be used to study the morphological structure of polymer layer nanocomposites. From the micrographs we can observe whether there is phase separation, intercalation or exfoliation. It can be observed that the clay is well dispersed homogenously. Furthermore, in the case of the LDH XRD pattern with polymers, usually the XRD pattern exhibits a sharp (003), (006), (009) diffraction peaks, with its d-spacing.\textsuperscript{65} A no change in the d-spacing of these peaks in the XRD micrographs indicates
phase separation, while a shift to the left of the micrographs leads to an increased d-spacing\textsuperscript{66} indicating an intercalation and finally a complete disappearance of the peaks with no apparent d-spacing indicates exfoliation. The crystallinity of the nanocomposites can be obtained from the Debye-Scherrer relations\textsuperscript{67} and from which the crystallize size can be obtained thus;

\[ D_{hkl} = \frac{0.9\lambda}{\beta_{1/2}\cos\theta} \]

Where \(\lambda\) = the wavelength (1.54 Å), \(\theta\) = the diffraction angle, \(\beta_{1/2}\) = the full width at half-maximum and \(D_{hkl}\) = the crystallize size.

1.5.2 Scanning Electron Spectroscopy (SEM)

The morphological change following the matrix with clay can be studied with SEM. The LDH platelet can be observed for the inorganic type. Thus, we can see the hexagonal platelets of the LDH and consequently estimated the size. However, in the inorganic-organic hybrid a flaky structure\textsuperscript{68} with no apparent pattern or shape is possible and this is indicative of the presence of the organic surfactant.

1.5.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR can also be used to study the morphology of the nanocomposites. In a typical study of LDH/polymer nanocomposites, several characteristics absorption bands are possible. The absorption bands at 3100-2800 cm\(^{-1}\) corresponds to the C-H stretching vibration, the bands at 3500 and 1630 cm\(^{-1}\) indicates the O-H stretching of hydroxyl groups of the LDH and its vibrations. For the carbonate, a strong band at 1365 cm\(^{-1}\) is associated with the stretching vibration of the carbonate anions. There is usually a fingerprint region at 610 and 400-445 cm\(^{-1}\) associated with the M-O stretching modes.
(M = Zn, Mg) in the LDH sheets. The bands with the C=C stretching vibration occurs at 1642 cm\(^{-1}\) while the bands at 1453, 1363 cm\(^{-1}\) indicates the presence of the CH\(_2\) bending vibrations. Bands at 540 cm\(^{-1}\) can be a proof for the presence of the phenyl ring revealing the out of plane deformation of the phenyl ring.

1.5.4 Transmission Electron Spectroscopy (TEM)

TEM is used to study the dispersion of the clay platelets in the polymer matrix. From the TEM micrographs, it can be seen whether or not there is homogenous dispersion of clay in the matrix. Thus we see if the platelets are exfoliated or intercalated in the matrix. The thickness and the lateral sizes of the intercalated or exfoliated LDH layers nanosheets can be estimated.\(^{69}\)

1.5.5 Thermogravimetric Analysis (TGA)

The thermal behavior of the nanocomposite can be studied by TGA. The onset temperature of degradation is measured as the temperature required for 10% degradation.\(^{70}\) Similarly, we can observe the temperature at the maximum rate of change of the curve and the presence of shoulders using the derivative thermo-gravimetry analysis (DTG). From the TGA we can determine the effect of the presence of fillers in the matrix. Weight loss and decomposition as well as decrease or increase in thermal stability is observable. Typically, for LDH/nanocomposites studies, for example, polystyrene LDH nanocomposites, the first weight loss occurring at 120-130 °C indicates the loss of the absorbed water. The region 150-300 °C is due to the loss of hydroxyl layers. The weight loss at 300-450 °C is attributable to the decomposition of the polystyrene chains.
1.5.6 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis is particularly used to measure the transitions in polymer layer nanocomposites that cannot be detected by other techniques. It measures the response of a material to a cyclic deformation. There are three main parameters that can be obtained from DMA. The first one is the storage modulus (E'), this parameter measure the elastic response to deformation, the second parameter, the loss modulus measure the plastic response to deformation and finally, the tan delta (tan δ) measure the transitions involving the mobility leading the glass transition temperature. Thus from the tan δ we can obtain information regarding the glass transition temperature of a material. In response to the E’, a higher value may be attributed to better compatibility and dispersion of the nanocomposites compare to the pure materials. Similarly, the decreasing value of E’ obtained may be due to the softening of the composites compared to pure material.

1.6 Multi-functional Nanocomposites

This can be described as nanomaterials designed and used for several functions or multiple purposes. Polymer materials have proven to be very efficient in the fabrication of several potential applications. Nanometer size scale particles are dispersed in polymer to enhance performance. The highly tunable properties of LDHs make them favorable as a new emerging class for preparation of multifunctional polymer/layered crystal nanocomposite. LDH has been widely used for a number of applications; some of them are in catalyst as LDH derived catalyst materials, catalyst precursors, catalyst support, industry, medicine, anion exchanger or absorbent. Others applications are in
environmental remediation, such as in removal of nitrogen and sulfur oxides, water purification, nuclear waste treatment and so many others. In recent years, there has been intense research on LDH application as flame retardance, storage and delivery of biologically active species. LDH/Polymer nanocomposites have proven their promise as a new class of multifunctional materials. The challenge, therefore, is for us to maximize their potential for multifunctional application.

1.6.1 Flame Retardancy

Flame retardation is essentially a process involving the modification or alteration of the normal degradation or combustion processes of polymers by the addition of certain chemicals. Generally, flame retardant materials have two modes of action which are by dilution as well as reduction of non-combustible gases, i.e. carbon dioxide and water. The water component of the decomposition comes from the loss of interlayer water as well as from the hydroxyl group in the brucites-like layers. These products of thermal degradation generated thus leads to effects which reduce the oxygen concentration at the flame front resulting in flame extinction. Furthermore, water released into the vapor phase during decomposition dilutes the decomposition of any other gaseous materials that are released. This process decreases the concentration of fuel available for combustion and limits the amount of heat that can be fed back to the polymer surface. The resultant effect is a decrease in the mass of burning rate for the polymer. There is a significant treat to human life with the use of polymers at home, industries, public buildings and mass transportation where fire is a treat and the potential for rapid fire spread. The desire, therefore, is for a balance between polymer functionality and risk as a fire hazard. In
many systems, one of our main objectives is to have a reduced ease of ignition and the rate of flame spread.

There is increased interest in intumescent systems, these systems on heating give rise to a swollen multicellular char capable of protecting the underlying material from the action of the flame. Fire protective coatings with intumescent additives in polymeric material are a relatively recent strategy.\(^{72}\) Char acts as a barrier against heat transmission and diffusion of oxygen toward the flame and resultant rate of pyrolysis of the polymer is expected to decrease below flame feeding requirements which leads to flame extinction. During the past decades, halogenated flame retardants have been used for fire precautions with the purpose of protecting human life, health and property. The consumption of halogenated flame retardants has grown worldwide as a result of growth of use of synthetic polymers and the introduction of more rigorous fire safety requirements. Due to the chemical stability of the halogenated flame retardant, these compounds, however, have a tendency to accumulate and spread in the environment. Harmful chemicals are emitted from products in use and have been present in the human body and breast milk in measurable quantities. As a result, worldwide, halogenated flame retardants have been placed on the list of undesirable substances. There is no doubt that the use of flame retardants has an important role in saving lives.\(^{73}\) This issue and more broadly the social advantages of the use of flame retardants are only being studied carefully.

In recent years, there has been an increased research for non-toxic environment friendly flame-retardants. This approach involves the use of filler as flame-retardants in polymer matrix. For example, aluminum hydroxide (ATH), magnesium hydroxide (MH),
etc) are used. ATH and MH have been found to offer enhanced char formation and promote cross-linking as opposed to pyrolytic degradation. ATH has been added in unsaturated polyester resin molding compounds especially in automobiles parts. Nanoparticles fillers such as silicate layer nanocomposites can significantly decreased flammability. However, in spite of several approaches there still remains numerous problems in terms of enhanced properties dispersion at nanometer scale, flammability, etc and because of these there is an increase need for alternative form of flame retardant that can meet the above needs and LDH seems to be potential candidates. There has been report on the use of LDH exchange as well as it use as flame-retardant by Miyata et al. with polymers and obtained improved flammability. Zammarano et al. in a study of epoxy reported synthesis of self-extinguishing LDH/epoxy nanocomposites and observed improved flammability performance with LDH. Qui et al. in a comparative study between LDH and montmorillonite in terms of their thermal degradation activation energy with polyethylene nanocomposites based on LDH obtained lower activation energy with use of LDH.

1.6.2 Drug Delivery

From tailor-made biomaterials synthesized at the nanoscale size-level, we can solve many problems such as delivery efficiency, tailored specificity and controlled release properties. One important and very promising class of drug delivery vehicle that has received more attention in recent years is layered materials. One of the approaches to control drug release is an encapsulation of biologically active substance into neutral nontoxic matrix. In the case of oral administration of a medicine; a matrix based on LDH
may be of special interest. In recent years, research has shown that LDH can be used as
drug carrier and controllable drug delivery system.\cite{80,81} Beneficial effect of layer double
hydroxide on human health has been reviewed by Hoyo.\cite{82} The weak basicity and high
capacity of LDH, for example, MgAl-LDH makes it a candidate as neutralizing agent and
is presumably the active ingredient in magnesium aluminum hydroxide mixtures.
Hydrotalcite has been known\cite{83,84} to have the highest neutralizing capacity among some
antacids.

Intercalation provides a route to obtained biologically active nanohybrid material
that can be \textit{in vitro} and \textit{in vivo}. The release of drugs in drug-intercalated layered materials
is potentially controllable, therefore new nano-biomaterials have a great potential as a
delivery host in the pharmaceutical field. Some layered materials have been studied as the
host in novel drug delivery systems. A review of application of hydrotalcites in medicinal
chemistry has recently been conducted by Costantino and Nocchetti.\cite{85} Danjo et al.\cite{86}
reported the intercalation of the anticancer agent cytarabine and related compounds into
g-titanium phosphate. Suzuki et al.\cite{87} studied intercalation and drug release of synthetic
mica with diclofenac sodium. Ambrogi et al.\cite{88} in their studies of microporous material
obtained from kanemite, a layered polylsilicate, investigated the possibility of
incorporating drugs as well as releasing them from the materials. The interlayer anion
exchangeable capability of LDHs meets the requirement of inorganic matrices for
encapsulating functional biomolecules with negative charge in aqueous media. Choy et
al.\cite{89} intercalated nucleoside phosphates derivatives and DNA into LDH by an ion-
exchange process, and then developed possible applications of bio-nanohybrids as gene
or drug delivery carriers. Similarly, Masarundi et al.\textsuperscript{90} showed that LDH is potential host for a reservoir and delivery of functional oligonucleotides such as genes and RNA for gene therapy, providing both stability and improved protection of the biomaterial from degradation. It has also been reported\textsuperscript{81} that LDHs can be used as agents for the controlled release of a plant growth regulator. Furthermore, Khan et al.\textsuperscript{91} reported the intercalation of the non-steroidal anti-inflammatory (NSAID) drugs. NSAID is a drug used for the relief of symptoms of rheumatoid arthritis and osteoarthritis) such as diclofenac sodium, ibuprofen, naproxen and tolfenamic acid in layered double hydroxides by an ion-exchange process.

In has also been noticed that release for drug molecules from organoLDH-drug revealed 90% release rate of some drugs from LDH interlayer’s in about thirty minutes while maintaining the pH at 4 and 7 in phosphate buffer solution.\textsuperscript{91} In addition, the intercalation and release of ibuprofen has also been investigated.\textsuperscript{92} Fenbufen also an NSAID is also used for the treatment of both rachitis and gout. Its use has some side effect which affects the gastrointestinal tract and the central nervous system and also results in a decreased leucocyte count and an increase in aminotransferase. However, Li et al.\textsuperscript{93} reported the intercalation of fenbufen into LDH using a co-precipitation and in their studies a longer period of gradual release of drug was observed.

1.7 Dissertation Overview

Typical polymer matrices range from amorphous polystyrene, acrylonitrile butadiene styrene, to semi-amorphous polylactic acid and polyethylene. In order to evaluate the potential of LDH to meet multifunctional needs, we use different polymers
and different functionalization. An amorphous polystyrene nanocomposite is used to determine the relationship between the surface treatment of the LDH and the dispersion and property. Table 1.5 depicts a summary of the scope of the dissertation.

For optimized dispersion we utilize in-situ polymerization. Then to establish multifunctional potential we use melt blending. To examine flame retardant potential we utilize an LDH with polyethylene and ABS. This demarcates between the extents of crystallinity for the same functional group on flame retardant potential. Finally the potential for drug delivery by functionalizing LDH with ibuprofen and estimating the performance is examined.

1.8 Conclusions

Table 1.5 Summary of nanocomposites investigated.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Structure</th>
<th>LDH</th>
<th>Processing</th>
<th>Conc. Investigated</th>
<th>Metal–Cation ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>Amorphous</td>
<td>Zn₂Al-LDH-NO₃</td>
<td>Bulk</td>
<td>1, 3, 5, and 7</td>
<td>2:1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn₂Al-LDH-ST</td>
<td>Bulk</td>
<td>1, 3, and 5</td>
<td>2:1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn₂Al-LDH-STH</td>
<td>Bulk</td>
<td>1, 3 and 5</td>
<td>2:1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn₂Al-LDH-STH</td>
<td>Solution</td>
<td>1, 3, 5 and 7</td>
<td>2:1</td>
</tr>
<tr>
<td>ABS</td>
<td>Semi-crystalline</td>
<td>Zn₂Al-LDH-PTS</td>
<td>Melt</td>
<td>10, 30 and 60</td>
<td>2:1</td>
</tr>
<tr>
<td></td>
<td>elastomer</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LDPE</td>
<td>Semi-crystalline</td>
<td>Zn₂Al-LDH-PTS-Ni</td>
<td>Melt</td>
<td>5, 15, 30 and 60</td>
<td>2:1</td>
</tr>
<tr>
<td>PLLA</td>
<td>Semi-crystalline</td>
<td>Zn₂Al-LDH-PTS-Ibu</td>
<td>Solution</td>
<td>1, 3 and 5</td>
<td>2:1</td>
</tr>
<tr>
<td></td>
<td>Bioplastic</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Layer double hydroxide (LDH) continues to offer a wide range of platform that enables various multifunctional chemistry and property in nanocomposites. Information regarding the typical matrices used with LDH, the properties, values of this component and the processing method was reviewed. The synthesis and structure of LDH, chemical composition, characterization techniques, structure and properties was also discussed. Finally, LDH/polymer nanocomposites with proven use as flame retardant and in medical application continues to function as eco-friendly multifunctional nanocomposites. In Table 1.5, the polymer matrices used, the structure, processing and concentration investigated are listed.

1.9 References


32. He, J.; Wei, M.; Li, B.; Kang, Y.; Evans, D. G.; Duan, X. Struct Bond 2006, 119, 89.


64. Isayev, A. I.; Viswanathan, R. Polymer 1995, 36, 1585.


CHAPTER 2
IN-SITU POLYSTYRENE-LDH NANOCOMPOSITES: EFFECTS OF POLYMERIZATION AND LDH DELAMINATION ON NANOCOMPOSITE DISPERSION AND MECHANICAL PERFORMANCE

2.1 Introduction

In recent years, delaminated or exfoliated of layer double hydroxide (LDH), an emerging field, has attracted much attention as a new class of layer nanomaterial because of their excellent practical utility such as in polymer reinforcement,\(^1\) precursor for hollow sphere preparation,\(^2\) quantum dot composites\(^3\) film preparation or emulsion\(^4\) stabilizations and many others.\(^5,6\) Exfoliated nanocomposites are formed when the layer platelets are homogenously dispersed in the polymer matrix resulting in interfacial bonding between the species in contact.\(^7\) The uniform dispersion of clay sheets as well as the huge interfacial area involved between the clay and polymer nanocomposites made delaminated clay/polymer nanocomposites an important utility for many purposes.\(^8\) The nanometer-scale interaction between the clay sheets and polymers, and the tortuous diffusion through such a composite enhance properties such as mechanical strength, hardness, thermal stability, flexibility and durability, and impermeability.\(^9\) Most delaminated layered systems produce colloidal dispersion of negatively charged organo-inorganic nanocomposites which makes the study of layer double hydroxide (LDH) particularly remarkable because new hybrid nanocomposites can be fabricated from the
positively charged nanosheets. However, delamination of LDH is a very difficult process because of the tight bound layers by the high charge density between the layers.\textsuperscript{10}

Polymer layer composites, the type consisting of exfoliated polymer/LDHs nanocomposites have been developed in several polymers.\textsuperscript{11-13} O’Leary et al.\textsuperscript{14} reported the delamination of MgAl-LDH in acrylate monomers with the help of high shear and subsequent polymerization of the acrylate monomers containing the LDH afforded exfoliated polyacrylates/LDH nanocomposites. Adachi-Pagano et al.\textsuperscript{15} first reported the refluxing of LDH dodecyl sulfate in butanol at 120 °C for 16 h and obtained a translucent colloidal solution that shows exfoliation. It has been proposed that the replacement of the interlayer water molecules by the solvent molecules might be driving force for the exfoliation.\textsuperscript{16,17}

Polystyrene (PS) an amorphous polymer is widely used due to its excellent chemical, electrical and mechanical properties for industrial, household and many other purposes. However, its properties can be improved by dispersing nanofillers, for example exfoliated layered material such as the LDH in polystyrene due to the high surface area of the nanosheet thereby making it readily accessible for chemical reactivity.\textsuperscript{15} In a related reaction, Fu and Qutubuddin\textsuperscript{18} reported exfoliated PS-clay nanocomposites via in situ polymerization of styrene and a reactive organoclay. Weimer et al.\textsuperscript{19} anchored a living free radical initiator inside the clay galleries and reported exfoliated PS-clay nanocomposites. Montmorillonite was functionalized with a polymerizable cationic surfactant vinylbenzyl-dimethyldecylammonium chloride. The storage modulus of the nanocomposite was higher depending on the clay loading when compared to pure PS.
Exfoliated PS-clay nanocomposites were also prepared by melt blending of styrene-vinyloxazoline copolymer with organophilic clay by Hoffmann and coworkers.\textsuperscript{20} Furthermore, Qui et al.\textsuperscript{21} have also reported improved thermal stability from results of study involving exfoliation of organo-modified ZnAl-LDH layers with polystyrene to form PS/LDH nanocomposite. Some of the reports mentioned above as well as others have described the restacking of LDH solvated monolayers by evaporating the solvent or even altering the polarity of the medium.\textsuperscript{22-24}

Recently, in a related study, delamination of LDH has been reported by Ding and Qu.\textsuperscript{25} involving the use of organo-inorganic LDH hybrid with the of N-lauroyl-glutamate surfactants in an emulsion in-situ polymerization of styrene. To our knowledge, no report of the in-situ bulk polymerization of styrene with the use of isolated delaminated LDH stearate has been reported. Therefore, this study presents new experimental results that reveal the exfoliation of LDHs/PS nanocomposite with disordered LDH layers successfully synthesized by a two stage process with an in situ polymerization, which consists of styrene and organically modified LDH. A comparative study involving the use of undelaminated LDH and as well as the nitrate LDH from which the stearate LDH was derived from by functionalization were carried out. The LDH layers were individually and homogenously dispersed in PS matrix. A systematic study on the effects of LDH loading on mechanical and thermal properties of the nanocomposites has been made. The extent of exfoliation and dispersion of the LDHs within the PS matrix was evaluated using XRD and TEM. The thermal stability of all the different types of the nanocomposites was also studied by DSC and TGA technique. These nanocomposites
were also subjected to DMA analysis to examine the viscoelastic behavior of the nanomaterials.

2.2 Experimental

2.2.1 LDH Preparation and Delamination

2.499 g Zn(NO$_3$)$_2$.6H$_2$O (8.40 mmol, 98%, Sigma-Aldrich) and 1.047 g Al(NO$_3$)$_3$.9H$_2$O (2.79 mmol, 98.0 - 102.0 %, Aefar Aesar) were dissolved in 50 mL deionized water. To this 0.88 mL 50% NaOH solution (16.80 mmol, reagent grade, Alfa Aesar) was added under nitrogen gas with stirring. The mixture was aged overnight with stirring at a nominal external oil bath temperature of 95 -110 °C for 24 hours. The mixture was cooled and the precipitate was then centrifuged, and washed twice with deionized water. To this LDH precipitate, an exchange reaction was performed by adding a solution of stearic acid prepared by dispersing 0.794 g stearic acid (2.79 mmol, 95% Aldrich) in 50 mL deionized water neutralized with 0.10 mL 50% NaOH solution. The mixture was stirred for 1 hour after which time the precipitate was centrifuged, and washed several times with deionized water. The as-collected precipitate was dried in vacuum over molecular sieves, and is referred to as as-prepared ZnAl-LDH-stearate and designated as LDH-ST and the stearate as ST.$^{26}$

Two thirds of the as-prepared LDH-ST was aged in 50 mL n-hexadecane (C$_{16}$H$_{34}$, 98%, Avocado; used as supplied) in an oil bath at 120 °C with vigorous stirring overnight. After cooling down and stopping the stirring, the delaminated LDH fell to the bottom of the flask and was separated from excess C$_{16}$H$_{34}$ by centrifugation, followed by a single washing with n-hexane (98.5%, EM; used as supplied). The delaminated LDH
was collected as a white powder after drying over molecular sieves in an evacuated desiccator overnight, and is referred to as as-exfoliated ZnAl-LDH-stearate hexadecane and designated as LDH-STH.

2.2.2 Synthesis of LDH-NO$_3$/PS Nanocomposites from Bulk Polymerization

LDH-NO$_3$/PS was prepared by bulk polymerization method. Styrene (99%, Fisher Scientific) with 10-15 ppm $p$-tert-butylcatechol stabilizer was used as supplied. Benzoyl peroxide (0.2% wt) initiator and LDH-NO$_3$ (1-5% wt) were added to this liquid styrene. The mixture was stirred at room temperature until the LDH-NO$_3$ appeared to the eye to be fully dispersed, and then heated to cause polymerization. This was carried out at 70 °C for 6 hours, then 90 °C for 6 hours and finally at 110 °C for another 6 hours. In order to achieve uniform incorporation of LDH-NO$_3$ into the polystyrene matrix, stirring was continued until prevented by the growing viscosity. The as-prepared sample is denoted as LDH-NO$_3$/PS nanocomposite. LDH-free PS nanocomposites was prepared by a similar procedure. LDH-NO$_3$/PS nanocomposite and PS disks weighing 10 g were then pressed in a mold at 180 °C under 40 MPa for further characterization. The 1wt% Zn-Al LDH-NO$_3$/PS (1/99), 3wt% Zn-Al LDH-NO$_3$/PS (3/97), 5wt% Zn-Al LDH-NO$_3$/PS (5/95) and 7wt% Zn-Al LDH-NO$_3$/PS (7/93) are referred to as 1LDH-NO$_3$/PS, 3LDH-NO$_3$/PS, 5LDH-NO$_3$/PS and 7LDH-NO$_3$/PS, respectively.

2.2.3 Synthesis of LDH-ST/PS Nanocomposites from Bulk Polymerization

LDH-ST/PS was prepared by bulk polymerization method. Styrene (99%, Fisher Scientific) with 10-15 ppm $p$-tert-butylcatechol stabilizer was used as supplied. Benzoyl peroxide (0.2% wt) initiator and LDH-ST (1-5% wt) were added to this liquid styrene.
The mixture was stirred at room temperature until the LDH appeared to the eye to be fully dispersed, and then heated to cause polymerization. This was carried out at 45 °C for 24 hours, then 65 °C for 48 hours. In order to achieve uniform incorporation of LDH into the polystyrene matrix, stirring was continued until prevented by the growing viscosity. The as-prepared sample is denoted as LDH-ST/PS nanocomposite. LDH-free PS nanocomposites was prepared by a similar procedure. LDH-ST/PS nanocomposite and PS disks weighing 10 g were then pressed in a mold at 180 °C under 40 MPa for further characterization. The 1wt% Zn-AL LDH-ST/PS (1/99), 3wt% Zn-AL LDH-ST/PS (3/97) and 5wt% Zn-AL LDH-ST/PS (5/95) are referred to as 1LDH-ST/PS, 3LDH-ST/PS and 5LDH-ST/PS.

2.2.4 Synthesis of LDH-STH/PS Nanocomposites from Solution Polymerization

LDH-STH/PS was prepared by the solution polymerization method. Styrene (99%, Fisher Scientific) with 10-15 ppm p-tert-butylcatechol stabilizer was used as supplied. Benzoyl peroxide (0.2% wt) initiator and delaminated LDH (1-5% wt) were added to this liquid styrene and 50 mL toluene. The mixture was stirred at room temperature until the delaminated LDH appeared to the eye to be fully dispersed, and then heated to cause polymerization. This was carried out by heating the mixture at 80 °C for about 24 hours. In order to achieve uniform incorporation of LDH into the polystyrene matrix, stirring was continued until prevented by the growing viscosity. The as-prepared sample is denoted as LDH/PS nanocomposite. LDH-free PS nanocomposites was prepared by a similar procedure. LDH/PS nanocomposite and PS disks weighing 10 g were then pressed in a mold at 180 °C under 40 MPa for further characterization. The
1wt% Zn-AL LDH-STH/PS (1/99), 3wt% Zn-AL LDH-STH/PS (3/97) and 5wt% Zn-AL LDH-STH/PS (5/95) are referred to as 1LDH-STH/PS, 3LDH-STH/PS and 5LDH-STH/PS, respectively.

2.2.5 Synthesis of LDH-STH/PS Nanocomposites from Bulk Polymerization

LDH-STH/PS was prepared by bulk polymerization method. Styrene (99%, Fisher Scientific) with 10-15 ppm p-tert-butylcatechol stabilizer was used as supplied. Benzoyl peroxide (0.2% wt) initiator and delaminated LDH (1-5% wt) were added to this liquid styrene. The mixture was stirred at room temperature until the delaminated LDH appeared to the eye to be fully dispersed, and then heated to cause polymerization. This was carried out at 70 °C for 6 hours, then 90 °C for 6 hours and finally at 110 °C for another 6 hours. In order to achieve uniform incorporation of LDH into the polystyrene matrix, stirring was continued until prevented by the growing viscosity. The as-prepared sample is denoted as LDH/PS nanocomposite. LDH-free PS nanocomposites was prepared by a similar procedure. LDH/PS nanocomposite and PS disks weighing 10 g were then pressed in a mold at 170 °C under 40 MPa for further characterization. The 1wt% Zn-AL LDH-STH/PS (1/99), 3wt% Zn-AL LDH-STH/PS (3/97) and 5wt% Zn-AL LDH-STH/PS (5/95) nanocomposites are referred to as 1LDH-STH/PS, 3LDH-STH/PS and 5LDH-STH/PS.
2.3 Characterization

2.3.1 LDH Characterization

2.3.1.1 Metals and C, H, N Analysis of LDHs

The metals analysis was conducted by atomic absorption spectroscopy (AAS) using a Perkin-Elmer Analyst 300, with standards and element lamps supplied by Perkin-Elmer. The LDH samples were completely dissolved in a 5% HNO$_3$ solution at 50 °C overnight. The C, H, N analysis was performed by EAI-Elemental Analysis, Inc.

2.3.1.2 Fourier Transform Infrared (FTIR) Analysis

The FTIR spectra were obtained as 1-2% sample pellets in 200 mg KBr (FTIR grade, Alfa Aesar), using a Perkin-Elmer Spectrum B, against 200 mg KBr reference as the background source. Each spectrum was collected from 4000 – 400 cm$^{-1}$ with a total forty scans at a resolution of 4 cm$^{-1}$.

2.3.1.3 Wide Angle X-ray Diffraction (WAXD) Analysis

The powder XRD patterns were obtained using a Rigaku model D/Max AQ5 Ultima III X-Ray Diffractometer (generated at 44mA and 40 kV). Each sample was scanned from 2 - 70° (2θ), with a step size of 0.05° and a dwell time of 1.34 seconds, using CuKα radiation ($\lambda$ =1.540562Å).

2.3.1.4 Transmission Electron Microscopy (TEM) Analysis

TEM was used to complement WAXD results on LDH sample. Bright field TEM images were recorded on Philips EM 420 equipment at an accelerating voltage of 120 kV. Prior to the analysis, LDH samples were first dissolved in alcohol and solution was transferred onto a 200-mesh copper grid.
2.3.2 PS/LDH Nanocomposites

The Nanocomposites were characterized by Fourier transform infrared spectroscopy (FT-IR), powder x-ray diffraction (XRD), differential scanning calorimetry (DSC) and dynamic mechanic analysis (DMA).

2.3.2.1 Dispersion

2.3.2.1.1 Wide Angle X-ray Diffraction (WAXD) Analysis

The XRD measurements were conducted on the nanocomposites using a Rigaku model D/Max AQ5 Ultima III X-Ray Diffractometer (generated at 44mA and 40 kV). Each sample was scanned from 2 - 70° (2θ), with a step size of 0.05° and a dwell time of 1.34 seconds, using CuKα radiation (λ =1.540562Å).

2.3.2.1.2 Transmission Electron Microscopy (TEM) Analysis

Bright field TEM images AQ5 were recorded on Philips EM 420 equipment at an accelerating voltage of 120 kV. Before the analysis, samples of the PS/LDH nanocomposites were sandwiched and glued between two sheets of epoxy resin. Samples of the polymer nanocomposites were then cut into slices of a nominal thickness of 90 nm with a diamond knife on an RMC MT AQ7 6000 ultra microtome at room temperature. The sections were transferred from water at room temperature onto a 200-mesh copper grid. All samples TEM except LDH-STH/PS nanocomposites from solution polymerization were carried with TEM images recorded on a Philips EM 400T electron microscope operating at a voltage of 100 kV. All images were taken in bright field mode with a Soft Imaging System CCD camera (Cantega 2K). A Leica Ultracut UCT microtome was used to cut thin sections (thickness less than 100 nm) of the polymer
samples. Measurements of the layer platelets regarding the diameters, length and thickness of the Layer double hydroxide were carried out with Image J version 1.24.

2.3.2.2 Thermal analysis

2.3.2.2.1 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) was measured using Perkin-Elmer DSC6 apparatus. The system was calibrated using elemental indium. The sample was run from 10 - 200 °C at the heating rate of 5 °C/min and then cooled to 10 °C at a cooling rate of 5 °C/min.

2.3.2.2.2 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was performed using a TA instruments TGAQ500/Q50. Each sample (10-12 mg) was pyrolyzed under N₂ in a platinum sample pan from 30 to 600 °C at a heating rate of 20 °C/min.

2.3.2.3 Mechanical properties

2.3.2.3.1 Dynamic Mechanic Analysis (DMA)

Dynamic mechanic analysis (DMA) experiments were performed using RSA III (Rheometric solids analyzer, Rheometric scientific inc., Piscataway, NJ, USA) in compression mode. Deformation was applied in the 3 point bending mode. The mean sample dimensions were 5 mm × 25 mm with a mean thickness of 140 µm. The temperature range varied from 30 to 150 °C. The frequency was set at 1 Hz and the heating rate was 3 °C/min.
2.4 Results and Discussion

2.4.1 X-ray Diffraction Spectroscopy (XRD) and Elemental Analysis

Figure 2.1 shows the LDH-NO$_3$, conventionally indexed in 3R$_1$ as (003), (006), (009) etc. The XRD pattern of LDH-NO$_3$ precursor (Figure 2.1) shows an interlayer spacing of 0.89 nm at a 2Theta of 9.84°. The detailed list of d spacing is given in (Table 2.1). The d$_{006}$, d$_{009}$, d$_{0012}$ and the other reflections can also be seen clearly in the pattern and this indicates superior crystallinity of the material. The LDH-ST (Figure 2.1 and Table 2.1) shows the well crystalline with sharp basal XRD pattern conventionally indexed in 3R$_1$ as (003), (006), (009) etc. The average interlayer spacing of 3.16 nm, calculated from powder x-ray diffraction data with a formula of \( (d_{003} + 2d_{006} + ... + nd_{00(3n)})/n \), is in good agreement with reported values for LDH-ST with an anion-monolayer (strictly speaking, interlacing) structure that is schematically shown in Figure 2.3A. The peaks at ca. 21° and 23°, corresponding to a spacing of 0.4 to 0.5 nm, could be assigned to the scattering by the hydrocarbon chains due to their regular arrangement in the interlayer (Figure 2.1). The crystallites size can be calculated using the Debye-Scherrer equation,

\[
D_{hkl} = \frac{0.9\lambda}{\beta_{1/2} \cos\theta}
\]

Where \( \lambda \) is the X-ray wavelength = 1.54 Å, \( \theta \) the diffraction angle, \( \beta_{1/2} \) the width at half-maximum intensity.
Figure 2.1 XRD patterns of LDH-NO$_3$, LDH-ST and LDH-STH.

Table 2.1 XRD data of LDH-NO$_3$ and LDH-ST.

<table>
<thead>
<tr>
<th></th>
<th>LDH-ST</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$hkl^e$</td>
<td>(003)</td>
<td>(006)</td>
<td>(009)</td>
<td>(012)</td>
</tr>
<tr>
<td>20 ($^\circ$)$^a$</td>
<td>2.76</td>
<td>5.40</td>
<td>8.65</td>
<td>11.68</td>
<td>12.59</td>
</tr>
<tr>
<td>$d$ spacing (nm)$^b$</td>
<td>3.16</td>
<td>1.63</td>
<td>1.02</td>
<td>0.76</td>
<td>0.62</td>
</tr>
<tr>
<td>FWHM$^c$</td>
<td>0.59</td>
<td>0.49</td>
<td>0.41</td>
<td>0.39</td>
<td>0.12</td>
</tr>
<tr>
<td>XS(nm)$^d$</td>
<td>14.08</td>
<td>16.96</td>
<td>20.31</td>
<td>21.40</td>
<td>69.62</td>
</tr>
<tr>
<td></td>
<td>LDH-NO$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(20)$^a$</td>
<td>9.89</td>
<td>19.7</td>
<td>29.9</td>
<td>34.3</td>
<td>37.7</td>
</tr>
<tr>
<td>$d$ spacing (nm)$^b$</td>
<td>0.89</td>
<td>0.45</td>
<td>0.30</td>
<td>0.26</td>
<td>0.24</td>
</tr>
<tr>
<td>FWHM$^c$</td>
<td>0.49</td>
<td>0.50</td>
<td>0.53</td>
<td>0.75</td>
<td>0.71</td>
</tr>
<tr>
<td>XS(nm)$^d$</td>
<td>17.01</td>
<td>16.85</td>
<td>16.21</td>
<td>11.58</td>
<td>12.35</td>
</tr>
</tbody>
</table>

$^a$2-Theta degree, $^b$Interlayer spacing, $^c$Full width half maximum, $^d$Crystallite size, $^e$Reflection planes.

In order to establish the composition in LDHs, CHN and elemental analysis were conducted on the LDHs samples. The elemental analysis results are given in Table 2.2. The metal ratio of Zn/Al in the as-prepared and as-exfoliated LDH samples is 1.99 and
1.94, respectively, matched well with the theoretical ratio of 2.00. Considering the C and H weight percent, the as-prepared LDH-ST can be approximately expressed in composition as $\text{Zn}_2\text{Al(OH)}_6(\text{stea}r\text{ate})_{1.1}.2\text{H}_2\text{O}$ as this formula gives the elemental contents and C/Al ratio close to the observed values.

Table 2.2 Comparison of observed and estimated element contents (weight percent) in the as-prepared and as-exfoliated LDH-STH.

<table>
<thead>
<tr>
<th>LDH sample</th>
<th>Zn%</th>
<th>Al%</th>
<th>C%</th>
<th>H%</th>
<th>Zn/Al</th>
<th>C/Al</th>
<th>Residue %</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-prepared ZnAl-stearate-LDH</td>
<td>20.2</td>
<td>4.19</td>
<td>42.4</td>
<td>8.43</td>
<td>1.99</td>
<td>22.7</td>
<td>28.0</td>
</tr>
<tr>
<td>$\text{Zn}_2\text{Al(OH)}<em>6(\text{stea}r\text{ate})</em>{1.1}.2\text{H}_2\text{O}$</td>
<td>22.6</td>
<td>4.66</td>
<td>41.0</td>
<td>8.37</td>
<td>2.00</td>
<td>19.8</td>
<td>38.1</td>
</tr>
<tr>
<td>As-exfoliated ZnAl-stearate-LDH</td>
<td>13.4</td>
<td>2.85</td>
<td>52.6</td>
<td>8.91</td>
<td>1.94</td>
<td>41.5</td>
<td>21.0</td>
</tr>
<tr>
<td>$\text{Zn}_2\text{Al(OH)}<em>6(\text{stea}r\text{ate})</em>{1.1}(\text{hexadecane})$</td>
<td>17.0</td>
<td>3.51</td>
<td>55.8</td>
<td>10.2</td>
<td>2.00</td>
<td>35.8</td>
<td>27.8</td>
</tr>
</tbody>
</table>

Figure 2.2 depicts the XRD of PS, LDH-NO$_3$ and its nanocomposites with styrene monomer from bulk polymerization. Note that the broad scattering around 20° is due to the PS matrix. From the figure there are no sign of the presence of the exfoliation because of the presence of a peak occurring at 2 Θ indicating the (003) of the LDH-NO$_3$. In addition, the position of the peak did not shift when compared to that of the LDH. That is, there is no change in $d$ spacing, which therefore indicated that intercalation did not exist, (Table 2.3) but an immiscibility leading to the phase separation. The presence of the phase separation may be due to hydrophobic interaction that exist between the polystyrene and the LDH and therefore result in polarized induction between the two phases. In Table 2.3, the crystallize size appears to increase with increase in the LDH.

Table 2.3 $d$ spacing and crystallite size of LDH NO$_3$ and it nanocomposites with PS.
<table>
<thead>
<tr>
<th>Sample</th>
<th>$Hkl$</th>
<th>$2\Theta$ ($^\circ$)</th>
<th>$H%$</th>
<th>d (nm)</th>
<th>FWHM</th>
<th>XS(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDH-NO$_3$</td>
<td>(003)</td>
<td>9.849</td>
<td>100</td>
<td>0.8972</td>
<td>0.648</td>
<td>12.86</td>
</tr>
<tr>
<td>1LDH-NO$_3$/PS</td>
<td>(003)</td>
<td>9.803</td>
<td>100</td>
<td>0.9015</td>
<td>0.744</td>
<td>11.20</td>
</tr>
<tr>
<td>3LDH-NO$_3$/PS</td>
<td>(003)</td>
<td>9.907</td>
<td>100</td>
<td>0.8921</td>
<td>0.569</td>
<td>14.65</td>
</tr>
<tr>
<td>5LDH-NO$_3$/PS</td>
<td>(003)</td>
<td>9.896</td>
<td>100</td>
<td>0.8930</td>
<td>0.471</td>
<td>17.69</td>
</tr>
<tr>
<td>7LDH-NO$_3$/PS</td>
<td>(003)</td>
<td>9.802</td>
<td>100</td>
<td>0.9015</td>
<td>0.470</td>
<td>17.71</td>
</tr>
</tbody>
</table>

*2-Theta degree, brelative intensity %, cInterlayer spacing, dFull-width half maximum, eCrystallite size.*

<table>
<thead>
<tr>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>003</td>
<td>006</td>
<td>009</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 2.2 XRD pattern of pure PS, LDH-NO$_3$ and its nanocomposites with PS from bulk polymerization.

concentration which indicate a possible dispersion different from phase separation. However, the general concept of phase separation is not conclusive yet until TEM is used for confirmation.
Figure 2.3 Schematic of the delamination processes from (A) monolayer LDH-ST, to (B) bilayer LDH-STH, and to (C) delaminated sheet in LDH/PS nanocomposite.

To obtain LDH-STH, the LDH-ST was subjected to thermal treatment in hexadecane and undergoes some reaction, as demonstrated by sharp changes in the x-ray diffraction patterns shown in Figure 2.1. In Figure 2.3 the $3R_1$ layer structure of as prepared LDH-ST is transformed into another poly type (possibly $3R_2$, although such different poly types should still show the 110 or 110/113 reflections), with a
characteristic series of peaks at ~ 4.1, 6.2, 8.2, 10.3, 12.4, and 14.5 °. Such a new layer structure has an interlayer spacing of 4.3 nm, presumably assigned to the so-called bilayer structure as shown in Figure 2.3B. The interlayer spacing suggests that the tilt angle of the hydrocarbon chains to the hydroxide layer is less than 55 ° which is the normal angle in monolayer and bilayer organo-LDH with a straight chain. The formation of such a bilayer structure could be attributed to the weak electrostatic and hydrophobic interactions between two sheets, which can be readily overcome for exfoliation when dispersed in hexadecane and styrene solution, as presented shortly. Note that there are few peaks in 20h24 °, indicating that the regular arrangement of the hydrocarbon chains is preserved.

Table 2.4 XRD data of LDH-ST and its nanocomposites with PS from bulk polymerization.

<table>
<thead>
<tr>
<th>Sample</th>
<th>hkl</th>
<th>2θ °a</th>
<th>H%b</th>
<th>d (nm)c</th>
<th>FWHMd</th>
<th>XS(nm)e</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDH-ST</td>
<td>(003)</td>
<td>2.796</td>
<td>100</td>
<td>3.157</td>
<td>0.745</td>
<td>11.1</td>
</tr>
<tr>
<td></td>
<td>(006)</td>
<td>5.646</td>
<td>50.9</td>
<td>1.564</td>
<td>0.498</td>
<td>16.7</td>
</tr>
<tr>
<td>1LDH-ST/PS</td>
<td>(003)</td>
<td>4.767</td>
<td>5.9</td>
<td>1.852</td>
<td>0.420</td>
<td>19.8</td>
</tr>
<tr>
<td></td>
<td>(006)</td>
<td>2.323</td>
<td>100</td>
<td>3.800</td>
<td>0.367</td>
<td>22.6</td>
</tr>
<tr>
<td>3LDH-ST/PS</td>
<td>(003)</td>
<td>4.769</td>
<td>5.5</td>
<td>1.851</td>
<td>0.502</td>
<td>16.6</td>
</tr>
<tr>
<td></td>
<td>(006)</td>
<td>2.249</td>
<td>91.4</td>
<td>3.924</td>
<td>0.509</td>
<td>16.3</td>
</tr>
<tr>
<td>5LDH-ST/PS</td>
<td>(003)</td>
<td>4.746</td>
<td>7.5</td>
<td>1.860</td>
<td>0.534</td>
<td>15.5</td>
</tr>
</tbody>
</table>

a2-Theta degree, brelative intensity %, cInterlayer spacing, dFull-width half maximum, eCrystallite size.

Figures 2.4 and 2.5 (low angle) shows the XRD patterns of the LDH-ST/PS nanocomposites from bulk polymerization. Results indicated that some intercalations with styrene monomer (Table 2.4).
As observed in Table 2.4, the $d$ spacing moves slightly to the left indicating intercalation especially with the peak associated with interlayer distance, the (003). Though this peak is not quite visible in the 1LDH-ST/PS nanocomposite, but is present in the 3 and 5LDH-ST/PS. In addition, (006) are also seen with a small shift in the 2 $\theta$. The crystallize size increases for all the nanocomposites showing the nucleating effect of this LDH. Note that the broad scattering at 20 $^\circ$ with a d-spacing of 0.46 nm is due to the PS matrix and also few peaks in 20-24 $^\circ$, indicated that the regular arrangement of the hydrocarbon chains is preserved.

![Figure 2.4 XRD patterns of LDH-ST/PS nanocomposites from bulk polymerization.](image)

Figure 2.4 XRD patterns of LDH-ST/PS nanocomposites from bulk polymerization.
Figure 2.5 Low angle XRD patterns of LDH-ST/PS nanocomposites from bulk polymerization.

Figure 2.6 XRD patterns of the LDH-STH/PS nanocomposites from bulk polymerization.
Similarly, samples of LDH-STH with styrene were polymerized by bulk polymerization. Figure 2.6 and 2.7 (low angle), shows the XRD patterns of the LDH-STH/PS nanocomposites from bulk polymerization. Results indicated that the LDH-STH peaks can be observed to be present in 1, 3 and 5 and 7LDH-STH/PS samples. This means that some of the LDH-STH was exfoliated while some of the LDH-STH still remaining.

Figure 2.7 Low angle XRD patterns of LDH-STH/PS and its nanocomposites from bulk polymerization.

Further studies of the Figures 2.6 indicate that the LDH-STH sample also contain additional peaks from 2θ (30 ° to 70 °) that can be indexed to a hexagonal wurtzite structure with cell constants of $a = 0.324$ nm and $c = 0.519$ which are consistent with the
standard values for ZnO (Zincite) with space group $P6_3mc$, JCPDF#36-1451. As expected, the ZnO peaks and their intensities are in agreement with those from these results. This confirmed the presence of ZnO in our LDH-STH sample. Thus, there exist a two phase phenomenon occurring in the sample, that is, the ZnO phase and the exfoliated LDH phase. These ZnO peaks are also present in our LDH-STH/PS nanocomposites, though because of the relative small concentration of LDH to the polymer, they are not quite visible, but if enlarge, we can see some peaks indicative of the presence of ZnO in the LDH/PS nanocomposites (Figure 2.8).

Figure 2.8 High angle XRD patterns of LDH-STH and its nanocomposites with PS from bulk polymerization

These polymer results are consistent with that obtained by Chae and Kim. In their studies of ZnO with PS in solution polymerization obtained nanocomposites in which the ZnO has no effect on the XRD pattern of the nanocomposites. They reported
that the incorporation of the ZnO nanoparticles produce no new peaks or cause any change in the shift of peaks and therefore suggested a two phase structures. Furthermore, Ding and Qu\textsuperscript{25} had similar results from XRD data in their studies of emulsion polystyrene with exfoliated LDH, but did not explain what the peaks were. They noticed the presence of new peaks occurring in their nanocomposites in XRD results with asterisks but did not provide information or details on what the asterisks were. Now from this results, and since I have similar results, it can be explained what the new peaks were. Therefore, the new peaks that were present in their polymer results are in fact, ZnO peaks (Figure 2.8 and Table 2.5). The calculated average lattice parameter $a$ and $c$ for the ZnO in LDH-STH were $a = 0.3248$ nm and $c = 0.5206$ nm consistent with calculated value of pure ZnO ($a = 0.3249$ nm and $c = 0.5206$ nm).

![Figure 2.9 Comparing ZnO and LDH-STH sample.](image-url)
Figure 2.9 shows the XRD of the ZnO sample (obtained from Fisher Scientific) and LDH-STH sample. The XRD of the pure ZnO is compared with the ZnO in LDH-STH sample. Thus, conclusion is reached after confirmation of my results with XRD, TEM, Uv-vis as well as literature data.

Table 2.5 Comparing XRD data of pure ZnO to LDH-STH.

<table>
<thead>
<tr>
<th>Sample</th>
<th>hkl</th>
<th>2Ө (º)</th>
<th>d (nm)</th>
<th>FWHM</th>
<th>XS(nm)</th>
<th>a</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>(100)</td>
<td>31.755</td>
<td>0.281</td>
<td>0.217</td>
<td>39.79</td>
<td>0.3250</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(002)</td>
<td>34.408</td>
<td>0.260</td>
<td>0.224</td>
<td>38.81</td>
<td></td>
<td>0.5206</td>
</tr>
<tr>
<td></td>
<td>(101)</td>
<td>36.251</td>
<td>0.247</td>
<td>0.226</td>
<td>38.67</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(102)</td>
<td>47.550</td>
<td>0.191</td>
<td>0.251</td>
<td>36.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(110)</td>
<td>56.601</td>
<td>0.162</td>
<td>0.266</td>
<td>35.45</td>
<td>0.3248</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(103)</td>
<td>62.855</td>
<td>0.147</td>
<td>0.257</td>
<td>37.87</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(112)</td>
<td>67.954</td>
<td>0.137</td>
<td>0.265</td>
<td>37.79</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(201)</td>
<td>69.099</td>
<td>0.135</td>
<td>0.268</td>
<td>37.62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LDH-STH</td>
<td>(100)</td>
<td>31.752</td>
<td>0.281</td>
<td>0.368</td>
<td>23.46</td>
<td>0.3250</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(002)</td>
<td>34.408</td>
<td>0.260</td>
<td>0.395</td>
<td>22.00</td>
<td></td>
<td>0.5206</td>
</tr>
<tr>
<td></td>
<td>(101)</td>
<td>36.253</td>
<td>0.247</td>
<td>0.389</td>
<td>22.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(102)</td>
<td>47.550</td>
<td>0.191</td>
<td>0.390</td>
<td>23.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(110)</td>
<td>56.644</td>
<td>0.162</td>
<td>0.397</td>
<td>23.76</td>
<td>0.3246</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(103)</td>
<td>62.856</td>
<td>0.147</td>
<td>0.433</td>
<td>22.47</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(112)</td>
<td>67.951</td>
<td>0.137</td>
<td>0.360</td>
<td>27.81</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(201)</td>
<td>69.081</td>
<td>0.135</td>
<td>0.383</td>
<td>26.32</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table notes:
- a: Reflection planes,
- b: 2-Theta degree,
- c: Interlayer spacing,
- d: Full width half maximum,
- e: Crystallite size,
- f: ZnO nanoparticles in LDH-STH sample, a and c are lattice parameters in nanometers.

Following the same procedure but samples of LDH-STH with styrene were polymerized by solution polymerization using toluene. See the schematic for the solution polymerization process (Figure 2.10).
Figure 2.10 Schematic of the delamination processes under in situ solution polymerization.

Figure 2.11 shows the XRD patterns of the LDH-STH/PS nanocomposites very similar to that from bulk polymerization. Results indicated that the (003) peaks completely disappears in 1, 3 and 5LDH-STH/PS samples. Note that the broad scattering at 20° with a d-spacing of 0.46 nm is due to the PS matrix and also few peaks in 20-24°, indicated that the regular arrangement of the hydrocarbon chains.
2.4.2 Transmission Electron Spectroscopy, (TEM)

TEM can be used for the determination of the degree of exfoliation or intercalation in clay particles, and thus produces the most verifiable form of information confirming the results of XRD. (Figures 2.12, 2.13, 2.14, 2.15) shows the TEM results of slices of the resultant LDH-NO$_3$/PS, that is, the 1, 3, 5, and 7LDH-NO$_3$/PS, respectively. As shown in these Figures, there are regions of LDH layers as well as polymers observed for all the nanocomposites composition. This therefore means that the type of dispersion evident in the nanocomposite is phase separation as suggested by XRD results and now confirmed by TEM. Figure 2.16 shows the TEM of a pure 1%ZnO with PS (ZnO was commercially obtained from Aldrich) used as control for comparison in this study.
Figure 2.12 TEM image of 1LDH-NO$_3$/PS nanocomposites from bulk polymerization.

Figure 2.13 TEM image of 3LDH-NO$_3$/PS nanocomposites from bulk polymerization.
Figure 2.14 TEM image of 5LDH-NO₃/PS nanocomposites from bulk polymerization.

Figure 2.15 TEM image of 7LDH-NO₃/PS nanocomposites from bulk polymerization.
The amount per weight percent, dispersion of the LDH particles, and the separation of the layers all contribute to the XRD patterns showing no Bragg reflections between 2° and 5° (2θ). Ultimately, for the determination of the degree of exfoliation of clay particles. Therefore, to confirm the microstructure of the LDH-ST and LDH-STH obtained by XRD, the TEM image of the LDH-ST and LDH-STH were conducted. Figures 2.17 and 2.18 shows the TEM of LDH-ST and LDH-STH, respectively. For the undelaminated LDH (LDH-ST), the layers are clearly visible having a thickness of about 1.5 – 2.9 nm and lateral size of 50 – 100 nm. The exfoliated LDH (LDH-STH) has single exfoliated nanosheets well dispersed along with the presence of hexagonal ZnO structure. The measured repeat distance between similar stripes of undelaminated LDH-ST is 2.67-2.96 nm, in good agreement with the interlayer spacing (3.157 nm) given by XRD and
Figure 2.17 TEM image of LDH-ST.

Figure 2.18 TEM image of LDH-STH.
Figure 2.19 TEM image 1LDH-ST and its nanocomposites with PS from bulk polymerization.

Figure 2.20 TEM image 3LDH-ST and its nanocomposites with PS from bulk polymerization.
the thickness and lateral size ranges from 0.5 – 2.1 and 40 – 60 nm, respectively. The size of this ZnO in the LDH-STH sample ranges from 7 – 25 nm. In the case of the TEM of LDH-ST/PS nanocomposites, Figures 2.19, 2.20 and 2.21, the TEM results of 1, 3, 5LDH-ST/PS. As shown in these Figures, the LDH shows massive intercalation of the layer platelets which are clearly visible in the polymeric matrix. These intercalates seem to have form aggregation in some areas with thickness and length of the lateral size ranging from 1 – 2.3 nm and 50 – 200 nm, respectively.

Furthermore, for the LDH-STH/PS nanocomposites from solution polymerization, the TEM images of all the nanocomposites indicated exfoliation with the layer platelets
well dispersed showing that there were good dispersion. Figures 2.22, 2.23 and 2.24 showed the TEM images of the 1, 3 and 5LDH-STH/PS nanocomposites from solution polymerization. Clearly, good dispersion is noticed, along with a larger degree of exfoliation. The good dispersion of delaminated LDH sheets into polystyrene matrixes is attributed to hydrophobic interactions between polystyrene and delaminated LDH sheets. The perpendicular alignment of the clay layers, with respect to the sliced sample section, is clearly visible, with the length of the dispersed nanosheet layers to be 40 - 200 nm and thickness of 0.5 – 1.5 nm. Even though there are local areas of high clay layer population, the hydrophobic stearate and hexadecane molecules did have an effect on pulling the layers apart.

Figure 2.22 TEM image of 1LDH-STH/PS from solution polymerization.
Figure 2.23 TEM image of 3LDH-STH/PS from solution polymerization.

Figure 2.24 TEM image of 5LDH-STH/PS from solution polymerization.
Similarly, the TEM images of the 1, 3, 5 and 7LDH-STH/PS nanocomposites made from bulk polymerization process are shown in Figures 2.25, 2.26, 2.27 and 2.28. For the particles, good dispersion is noticed, along with a larger degree of exfoliation with presence of some exfoliated LDH-STH. The thickness and lateral size of the exfoliated nanosheets are 0.5 – 1.5 and 10 - 35 nm, respectively. Although there are local areas of high clay layer population, the hydrophobic stearate and hexadecane molecules did have an effect on pulling the layers apart. The TEM results are similar to that of Ding and Qu.\(^{25}\) In their studies, it was reported that the dispersed exfoliated LDH sheets in PS were parallel to the grid, hence their TEM results. However, it can be explained that the results they had were as a result of the presence of ZnO in the exfoliated polymer nanocomposites. The ZnO particles observed in the TEM images have a rod-like morphology.\(^{29}\) This result is consistent with that obtained by Seo et al.\(^{30}\) in their investigation of the particle size and morphology of ZnO, MgO and NiO nanoparticles. Similarly, Britto et al.\(^{31}\) in a study with layered double hydroxide (LDH) carbonate and nitrate observed crystalline oxide mixture comprising ZnO and zinc aluminate spinel ZnAl\(_2\)O\(_4\) resulting from the solution decomposition at a low temperature. It can be seen that the particles have a nanometer-scale morphology. The average particle sizes in diameter range from 6.05 – 40 nm. Figure 2.16 shows the TEM of a pure 1%ZnO with PS (ZnO was commercially obtained from Aldrich) used as control for comparison in this study. The morphology is similar to those in the nanocomposites. The diameter of the nanocomposites is between 9.5 – 36.7 nm which is consistent with values obtained in the
Figure 2.25 TEM image of 1LDH-STH/PS nanocomposite from bulk polymerization.

Figure 2.26 TEM image of 3LDH-STH/PS nanocomposite from bulk polymerization.
Figure 2.27 TEM image of 5LDH-STH/PS nanocomposite from bulk polymerization.

Figure 2.28 TEM images of 7LDH-STH/PS nanocomposite from bulk polymerization.
PS studies with LDH. This ZnO is now confirmed with XRD, TEM, UV and literature data.

2.4.3 Ultraviolet (UV) Spectra Analysis

The UV-vis absorption spectra of PS and PS/LDH-STH nanocomposites are shown in Figure 2.29. The absorption peak can be seen at 365 nm for all the nanocomposites, thus the 1, 3, 5 and 7LDH-STH/PS all contains ZnO particles. Also shown is the wavelength of the pure ZnO particles which is consistent with the values for the LDH-STH and all the nanocomposites. Furthermore, the LDH-ST and pure polystyrene did not show any absorption at that wavelength which indicated the absence of ZnO in the samples.

Figure 2.29 Uv-vis spectra of pure PS, ZnO, LDH-ST, LDH-STH, 1, 3, 5, and 7LDH-STH/PS nanocomposites, (pure ZnO was purchased from Fisher Scientific ACS).
2.4.4 Fourier Transform Spectroscopy (FTIR)

FTIR measurements were carried out to evaluate the interface affinity between PS and LDHs. Figure 2.30 shows the FTIR-ATR spectra of PS and PS/LDH-NO$_3$ nanocomposites.

![FTIR spectra of LDH-NO$_3$ and its nanocomposites with pure PS from bulk polymerization.](image)

The spectra of the nanocomposites clearly exhibit the characteristic absorption peaks corresponding to only polymeric groups. There is the presence of the characteristic peak at 400 - 425 cm$^{-1}$ due to the layer M-O stretching vibrations (M= Zn). This peak is diagnostic of well-organized 2:1 Zn:Al LDH. The stretching peak at around 3486 cm$^{-1}$, is
attributed to layer OH group and interlayer water molecules. The characteristic vibration bands of aromatic C-C arising from the styrene units are observed at 1605, 1497, and 1455 cm$^{-1}$. Also important is the nitrate vibration peak occurring at the 1380 cm$^{-1}$. The peaks at 2928 and 2854 cm$^{-1}$ are assigned to the asymmetric and symmetric stretching vibrations corresponding to the C–H stretching vibration of the CH$_2$ and CH groups on the main PS chain, respectively. The absorption bands ranging from 3078 - 3028 cm$^{-1}$ are assigned to aromatic C–H stretching on the polystyrene side chains.

In addition, the bands at 756 and 697 cm$^{-1}$ indicated that a monosubstituted ring was present. Therefore, from the results, it is observable that there is no shift or sharpening of absorption band is detected in all the composites. This indicated that there was no chemical linkage or interaction between PS and LDH-NO$_3$ nanoparticles in the resulting composites.

While in the case of the LDH-NO$_3$, LDH-ST and LDH-STH FTIR (Figure 2.31) there is the characteristics peak at 1383 cm$^{-1}$ indicative of the presence of nitrate, this peak is not present in the LDH-ST showing that most of the nitrate has been functionalized by the stearate. The LDH-ST due to the formation of stearate anion by functionalization of nitrate now have absorption peak at 1542 cm$^{-1}$ confirming the formation of the LDH-ST. All other absorption characteristics of LDH with respect to the nitrate and the stearate LDH analog are present. As for the LDH-STH, it can be observed that the integrity of the individual hydroxide layers was unaffected by delamination, as shown by the presence of the characteristic peaks at 724 and 425 cm$^{-1}$ in all cases which are ambiguously due to the layer M-O stretching vibrations. The peak at 425 cm$^{-1}$, in
particular, is diagnostic for well-organized 2:1 Zn: Al LDH. It is not unexpected that the vibrations due to C=O (1540-1561 and 1451 cm\(^{-1}\)) and C-O (1004-1005 cm\(^{-1}\)) stretching modes, remain almost unchanged. Not surprisingly, the intensity of the OH stretching peak at around 3459 cm\(^{-1}\), attributed to layer OH group and interlayer water molecules, becomes weaker after hexadecane intercalation, showing that some or all interlayer water is removed during the aging at 120 °C in n-hexadecane.

![Figure 2.31 FTIR of LDH-NO\(_3\), LDH-ST and LDH-STH.](image)

From bulk polymerization of the LDH-ST with styrene, the FTIR conducted on the polymeric product shows the characteristics peaks of LDH-ST and polystyrene (Figure 2.32). The presence of C=O group and the OH group are also very important in
stearate LDH at 1599 cm\(^{-1}\) and 3489 cm\(^{-1}\), respectively. Finally, there is the characteristic peaks occurring at 425 and 415 cm\(^{-1}\) in all the nanocomposites can be assigned to the metal-oxide stretching vibrations of the LDH for the brucite-like component. It is not unexpected that the vibrations at 1540-1561 and 1453 cm\(^{-1}\) are due to C=O while stretching modes around 1004-1005 cm\(^{-1}\) correspond to C-O and

Figure 2.32 FTIR of pure PS and its nanocomposites with LDH-ST from bulk polymerization.

FTIR was also conducted on the solution polymerized polymer using the LDH-STH and styrene monomer. There is the presence of the characteristic peaks at 724, 425 and 415 cm\(^{-1}\) in all the cases (Figure 2.33) which are ambiguously due to the layer M-O stretching vibrations.
Figure 2.33 FTIR of LDH-STH and its nanocomposites with PS from solution polymerization.

The stretched vibrations at 1540-1561 and 1451 cm\(^{-1}\) are due to C=O while stretching modes around 1004-1005 cm\(^{-1}\) correspond to C-O and these remain almost unchanged in all the nanocomposites as well. The OH stretching peak appears at around 3470 cm\(^{-1}\), attributed to the layer OH group. Similarly, the characteristic vibration bands of aromatic C-C arising from the styrene units can be observed at 1605, 1497, and 1455 cm\(^{-1}\). The peaks at 2941 and 2910 cm\(^{-1}\) are assigned to the asymmetric and symmetric stretching vibrations corresponding to the C–H stretching vibration of the CH\(_2\) and CH
groups on the main PS chain, respectively. The absorption bands ranging from 3078 - 3002 cm\(^{-1}\) are assigned to aromatic C–H stretching on the polystyrene side chains. In addition, the bands at 755 and 697 cm\(^{-1}\) indicated that a monosubstituted ring was present. Therefore, from the results, it is observable that there was no shift or sharpening of absorption band is detected in all the composites.

Table 2.2 also shows that the as-exfoliated LDH-STH has a much higher C content (52.6% vs. 42.4% in the as-prepared LDH sample). It can be said that intercalation of hexadecane has taken place between the stearate hydrocarbon chains taking up the space vacated by the stearate chains from the adjacent layer that had been present before hexadecane intercalation. This postulation is supported by the IR spectra. LDH-STH in Figure 2.33 shows broadening of the C-H stretching vibration peaks after intercalation, with slight shifts to higher frequency, and an increase in the relative intensity of the peak at 2954 cm\(^{-1}\) which is only due to the C-H asymmetric vibration in CH\(_3\). This interpretation is also supported by the difference spectrum (normalized using the 425 cm\(^{-1}\) peak, supporting information) which shows as its only significant feature bands at 2931, 2846, 1458 and 724 cm\(^{-1}\), attributable to the C-H stretching, bending and rocking vibrations of intercalated C\(_{16}\)H\(_{34}\). Therefore, the inclusion of hexadecane is confirmed by the elemental analysis results. As shown in Table 2.2, the chemical composition of as-exfoliated LDH sample could be approximately written as Zn\(_2\)Al(OH)\(_6\)(stearate)\(_{1,1}\)(hexadecane) although this formula leads to a bit higher weight percentage for these 4 elements.
Moreover, the FTIR of PS and LDH-STH/PS nanocomposites (1, 3, 5 and 7LDH-STH/PS) from bulk polymerization are shown in Figure 2.34. As in the solution polymerized, there is the presence of the characteristic peaks at 724, 425 and 415 cm\(^{-1}\) in all the nanocomposites corresponding to the Zn-O stretching vibrations. The stretching vibrations at 1540-1561 and 1451 cm\(^{-1}\) are due to C=O while that at around 1004-1005 cm\(^{-1}\) correspond to C-O and they appears in all the nanocomposites.

![FTIR of pure PS and its nanocomposites with LDH-STH from bulk polymerization.](image)

The small broad band occurring at around 3470 cm\(^{-1}\), can be attributed to layer OH group. The characteristic vibration bands of aromatic C-C arising from the styrene
units are observed at 1605, 1497, and 1455 cm$^{-1}$. The peaks at 2941 and 2910 cm$^{-1}$ are assigned to the asymmetric and symmetric stretching vibrations corresponding to the C–H stretching vibration of the CH$_2$ and CH groups on the main PS chain, respectively. The absorption bands ranging from 3078 - 3002 cm$^{-1}$ are assigned to aromatic C–H stretching on the polystyrene side chains and finally, the bands at 755 and 697 cm$^{-1}$ indicated the phenyl ring which comes from PS.

2.4.5 Differential Scanning Calorimeter Analysis (DSC)

Differential scanning calorimeter analysis was performed in the neat PS and the LDH-ST nanocomposites in order to evaluate the changes in the glass transition temperature ($T_g$), with increasing LDH content.

![DSC thermograms](image)

Figure 2.35 DSC thermograms of pure PS and its LDH-NO$_3$/PS nanocomposites from bulk polymerization.
Figure 2.35 shows the DSC results of the neat PS and the LDH-NO₃/PS nanocomposites. As in Figure 2.43, the effect of LDH-NO₃ on thermal transitions is illustrated. The $T_g$ of the nanocomposites shifted to lower temperature with increase in the clay content (Table 2.6).

Table 2.6 DSC of pure PS and LDH-NO₃/PS nanocomposites from bulk polymerization.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ (°C)</th>
<th>ΔCp(J/g °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PS</td>
<td>96.5</td>
<td>0.396</td>
</tr>
<tr>
<td>1LDH-NO₃/PS</td>
<td>78.5</td>
<td>0.399</td>
</tr>
<tr>
<td>3LDH-NO₃/PS</td>
<td>59.3</td>
<td>0.441</td>
</tr>
<tr>
<td>5LDH-NO₃/PS</td>
<td>51.1</td>
<td>0.400</td>
</tr>
<tr>
<td>7LDH-NO₃/PS</td>
<td>30.5</td>
<td>0.344</td>
</tr>
</tbody>
</table>

An increase in $T_g$ results usually from intercalated or exfoliated nanocomposite where chemical bonding, weak as in hydrogen bond or strong as in covalent bond may be existing between the filler and polymer chain. In our results, the $d$ spacing remains unchanged, a consequence that may be interpreted by the hydrophilic/hydrophobic interaction between the surface active LDH-NO₃ and styrene monomer. The effect experienced in our nanocomposites may be the results of plasticization. In the case, the LDH-NO₃ is acting as a plasticizer leading to the increase in the mobility of the styrene chain segments which ultimately results in the decrease in the $T_g$ of the polystyrene. Styrene, due to its immiscibility between itself and LDH-NO₃ formed the morphology as observed for the nanocomposites.

In a comparative study, Figure 2.36, present the results of the effect of undelaminated LDH-ST on thermal transitions of PS. The $T_g$ of the nanocomposites shifted to higher temperature for all the samples except the 5LDH-ST/PS. This is in direct
contrast with result obtained with LDH-NO$_3$/PS nanocomposites. $T_g$ is largely related to the molecular mobility of polymer chains also affected by molecular packing, chain rigidity and linearity. However, the increases in our glass transition values can be attributed to higher interactions between the polymer chains and the layered ST surfaces. Nanometer sizes of ST layers and good dispersion of these platelets restrict the segmental motions of polymer chains at the interface leading to increase in $T_g$ values. The flexible phenyl pendant group lowered the frictional interaction between the polymer chains thereby reducing the $T_g$.

![Graph](image.png)

**Figure 2.36** DSC of pure PS and its nanocomposites with LDH-ST from bulk polymerization.

**Figure 2.37**, illustrate the effect of LDH-ST on thermal transitions of PS using nanocomposites samples from solution polymerization. The $T_g$ of the nanocomposites shifted to lower temperature before it begins to increase with increase in the clay content:
(Table 2.7) $T_g$ values were 71.6, 72.6, and 78.3 °C at the content of 1, 3 and 5LDH-STH/PS, respectively. The $T_g$ value of the PS matrix is due to entrapped solvent. Similar result was recorded by Nair et al.\textsuperscript{32} and they attributed their results to the presence of some residual solvent entrapped during the mixing cycle of the composite. $T_g$ is largely related to the molecular mobility of polymer chains also affected by molecular packing, chain rigidity and linearity. However, the increases in our glass transition values can be attributed to higher interactions between the polymer chains and the layered ST surfaces. Nanometer sizes of ST layers and good dispersion of these platelets restrict the segmental motions of polymer chains at the interface leading to increase in $T_g$ values. The flexible phenyl pendant group lowered the frictional interaction between the polymer chains thereby reducing the $T_g$. The solvent acting as a plasticizer and as concentration of the

![Figure 2.37 DSC thermograms of pure PS and its nanocomposites from solution polymerization.](image-url)
LDH increases the plasticizer arranges itself with the PS phenyl group resulting in dipole interaction and thus reduce the mobility of the polymer thereby leading to increase in $T_g$ in the results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ (°C)</th>
<th>$\Delta C_p$ (J/g °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>67.2</td>
<td>0.0564</td>
</tr>
<tr>
<td>1LDH-STH</td>
<td>71.6</td>
<td>0.0167</td>
</tr>
<tr>
<td>3LDH-STH</td>
<td>72.7</td>
<td>0.0239</td>
</tr>
<tr>
<td>5LDH-STH</td>
<td>78.3</td>
<td>0.0341</td>
</tr>
</tbody>
</table>

Figure 2.38 DSC thermograms of pure PS and its nanocomposites with LDH-STH from bulk polymerization.

In contrast to the LDH-STH/PS nanocomposites obtained by solution polymerization, and as in Figure 2.37, the effect of LDH-STH on thermal transitions of PS for the LDH-STH/PS nanocomposites by bulk polymerization is presented here also.
(Figure 2.38). The $T_g$ of the nanocomposites shifted to lower temperature before it begins to increase with increase in the clay content: $T_g$ values were 96.5, 67.8, etc, (Table 2.8).

Table 2.8 DSC of pure PS and LDH-STH/PS nanocomposites from bulk polymerization.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ (°C)</th>
<th>Peak2 (°C)</th>
<th>$\Delta$Cp (J/g °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PS</td>
<td>96.5</td>
<td>-</td>
<td>0.396</td>
</tr>
<tr>
<td>1LDH-STH/PS</td>
<td>67.8</td>
<td>-</td>
<td>0.355</td>
</tr>
<tr>
<td>3LDH-STH/PS</td>
<td>75.7</td>
<td>-</td>
<td>0.293</td>
</tr>
<tr>
<td>5LDH-STH/PS</td>
<td>59.6</td>
<td>106.1</td>
<td>0.289</td>
</tr>
<tr>
<td>7LDH-STH/PS</td>
<td>62.3</td>
<td>105.1</td>
<td>0.265</td>
</tr>
</tbody>
</table>

The lower $T_g$ value of the PS matrix is due to entrapped solvent, the hexadecane which is acting as a plasticizer. In all the cases with the addition of the LDH-STH, there was a decrease in $T_g$, the effect was more in the case of 5% and then begins to increase again in the case of 7%. In addition, additional peak is seen for the 5 and 7% at ca 110 °C indicating the formation of secondary $T_g$ probably due to the effect of the presence of ZnO. Generally, on a molecular level, plasticizer induces the weakening of intermolecular interactions and cause increase in the space among molecules. Therefore, physical and mechanical properties of the polymer are altered with the addition of the plasticizer, operating by embedding itself between the chains of polymers and space it apart leading to increased free volume, and thus significantly lowering the glass $T_g$. Several attempts have been made to explain plasticization with application of the gel, the lubricity, and the free volume theories. The gel theories suggest that changes in the mechanical properties are related to the formation of gel. The lubricity theory proposes that the plasticizer improves the movement of the macromolecules over each other. Fox and Flory first introduced the concept of free volume. The free volume is a measure of
the internal space or hole available in polymer for the movement of polymer chains across. The increase of the free volume is the basis of a mechanistic theory of plasticization. The free volume becomes increased by the use of plasticizer. Anderson et al. have used the free volume model to explain the effects of plasticization as well as the anti-plasticization in polymeric materials. In the last case of the anti-plasticization, inclusion of small molecules into a polymer improves the rigidity of the composites. In a related study, Queiroz et al, present results of free volume variations due to the plasticization. It was also observed that anti-plasticization exist in samples with increased $T_g$ values related to free volume concentration which decreased with plasticizer content. They rationalized their results by applying the hole-filling mechanism with additional interactions between plasticizer and polymer. In our studies, the results that we had are indication of plasticizing and anti-plasticizing effects in these materials. The plasticization can be attributed to the increasing free volume and lubrication provided as the hexadecane water swell up around the polystyrene and cause a disruption in polystyrene–polystyrene hydrogen bonding. Similarly, anti-plasticization, due to a decrease in fractional free volume at the chain ends can be attributed to the small increase in $T_g$ for some of the values. The smaller holes are initially filled by hexadecane chain ends whose action then restricts the mobility of the chain ends and thus results in higher moduli and $T_g$.

2.4.6 Dynamic Mechanical Analysis (DMA)

Dynamic mechanic analysis is used to determine the viscoelastic property of a material. Figure 2.39 shows the storage modulus, loss modulus and tan delta for the
LDH-NO₃/PS nanocomposites. Results indicated from the figure that the storage modulus increases as the LDH content increases and then decreased. The $E''$ prime for the LDH-NO₃/PS shifted to lower temperature confirming the DSC results obtained in the $T_g$ decreasing with the increase in the LDH contents, compared to the pure PS. These results show the dispersive nature of the LDH material that result in the interaction between the LDH layers and the PS chains. Samakande et al.⁴⁶ obtained similar results with polymer-

Figure 2.39 Storage modulus ($E'$) of pure PS and nanocomposites with LDH-NO₃ from bulk polymerization.

clay nanocomposites studies. In the case of the LDH-NO₃/PS, the $T_g$ decreases linearly as the concentration decreases. This may be attributable to the plasticizing effect of the LDH resulting from binding to one side of the PS chains thereby pushing the chains apart in an intercalated and exfoliated structure and secondary valence bonds become disrupted and

95
the mobility of the chains segment of the plasticizer increases significantly and the PS is plasticized resulting in decrease in the elastic modulus and nanocomposites soft.

As seen in Figure 2.40, the loss modulus curves for the composites shifted to the lower temperature region, indicating a lower $T_g$ value for the composite, compared to the pure PS. The $E''$ for the LDH-NO$_3$/PS showed a confirmation of the effect of the LDH on PS, and in this case, a decreased in $E''$ occur with increase in LDH content while the

Figure 2.40 Loss modulus ($E''$) of pure PS and its nanocomposites from bulk polymerization.

7LDH $E''$ lies between the 3 and 5LDH. This shifting is attributable to the increased mobility of the PS matrix resulting from the polymer–LDH interaction.

The tan delta (loss factor) is essentially a measure of dissipation energy and is the ratio of storage modulus to the loss modulus. Figure 2.41 shows the tan delta ($\delta$) of the
Figure 2.41 Tan delta (δ) of pure PS and its nanocomposites with LDH-NO₃ from bulk polymerization.

pure PS and its composites. There is a shift to lower temperature in the tan delta peaks of the PS nanocomposites compared to the neat sample of PS. Tan delta (δ) for the LDH-PS as well as the LDH-NO₃/PS with bulk polymerization showing two temperature transitions corresponding to the β and α relaxation peaks, respectively. The figure reveals a decreasing effect of the LDH on the PS matrix. The low temperature loss peak is attributable to the rotation of the segments of the backbone chain. As observed in the Figure 2.43, the tan delta (δ) decreases as the LDH content increases. An α relaxation temperature which corresponds to the $T_g$ can be attributed to the concept of free volume. The molecular mobility and therefore the relaxation time around the $T_g$ depend on the free volume. In addition to the normal expansion process, the free volume expansion results in a larger expansion of the PS. This provides sufficient room for molecular
motion rotation or translation to occur. The large increase in the dissipation factor in $\alpha$ relaxation temperature $T_g$ can be due to this increase in chain segment mobility.

Similar studies of the storage modulus, loss modulus and tan delta of the LDH-ST/PS nanocomposites were also undertaken. Figure 2.42 shows the results of these studies and from the figure, and in contrast to the LDH-NO$_3$/PS nanocomposites the storage modulus increases as the LDH content increases in all the composition when compared to the pure polystyrene.

![Figure 2.42 Storage modulus ($E'$) of pure PS and its nanocomposites with LDH-ST bulk polymerization.](image)

The tan delta ($\delta$) (loss factor) is essentially a measure of dissipation energy and is the ratio of storage modulus to the loss modulus. In Figure 2.43, the tan delta of the pure PS and its nanocomposites with the LDH-ST, the tan delta for the 1 and 3LDH-ST/PS nanocomposites shifted to higher temperature compared to the neat sample of PS. In addition, the $T_g$ of the nanocomposites appears higher than that of the neat PS except
5LDH-ST/PS nanocomposites with a slight increase with the LDH content. These results are also in agreement with similar studies conducted by Tyan et al.\textsuperscript{37}

![Graph](image)

Figure 2.43 Tan delta (δ) of pure PS and its nanocomposites with LDH-ST from bulk polymerization.

Application of the same studies on an exfoliated LDH/PS nanocomposites, the LDH-STH/PS nanocomposite from solution polymerization revealed a similar trend. Figure 2.44 shows the temperature curves of the storage modulus indicating the effect of LDH loading and degree of exfoliation on the thermo-mechanical properties of the ZnAl-LDH/PS nanocomposites. As observed from the figure, the storage modulus increases as the LDH content increases. The 5LDH-STH/PS has higher modulus than the 3LDH-STH/PS, and this in turn higher than that of the 1LDH-STH/PS, compared to the pure PS. These results show the dispersive nature of the LDH material that result in the interaction between the LDH layers and the PS chains.
Figure 2.44 Storage modulus (E’) of pure PS and its nanocomposites from solution polymerization.

Furthermore, in Figure 2.45, the loss modulus curves for the composites shifted to the high temperature region, indicating a higher $T_g$ value for the composite, compared to the pure PS. This is attributable to the decreased mobility of the PS matrix resulting from the polymer–LDH interaction. The tan delta ($\delta$) (loss factor) is essentially a measure of dissipation energy and is the ratio of storage modulus to the loss modulus. Figure 2.46 shows the tan delta of the pure PS and its composites. There is a shift to higher temperature in the tan delta peaks of the PS nanocomposites compared to the neat sample.
Figure 2.45 Loss modulus ($E''$) of pure PS and its nanocomposites from solution polymerization.

Figure 2.46 Tan delta ($\delta$) of pure PS and its nanocomposites from solution polymerization.
Table 2.9 Thermo-mechanical properties of pure PS and its nanocomposites from solution polymerization.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T_g (°C) (tan δ)</th>
<th>E’ (GPa) at 30 °C</th>
<th>E’(GPa) at 40 °C</th>
<th>E’ (GPa) at 60 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>71.7</td>
<td>1.31</td>
<td>1.28</td>
<td>1.20</td>
</tr>
<tr>
<td>1LDH-STH/PS</td>
<td>79.2</td>
<td>1.44</td>
<td>1.52</td>
<td>1.49</td>
</tr>
<tr>
<td>3LDH-STH/PS</td>
<td>85.5</td>
<td>1.58</td>
<td>1.57</td>
<td>1.71</td>
</tr>
<tr>
<td>5LDH-STH/PS</td>
<td>87.1</td>
<td>1.69</td>
<td>1.69</td>
<td>1.77</td>
</tr>
</tbody>
</table>

Figure 2.47 Storage modulus (E’) of pure PS and its nanocomposites with LDH-STH/PS from bulk polymerization.

of PS. A similar observation was reported by Samakande et al.\textsuperscript{36} and they attributed their results to the restricted PS chain mobility which results from the LDH/PS interaction. In Figure 2.46 and Table 2.9, the T_g of the nanocomposites is higher than that of the neat PS and there is a slight increase with the LDH content.
Comparing the results above with the nanocomposites obtained in the case of LDH-STH and styrene with bulk polymerization shows the following results. Figure (2.47, Table 2.10) shows the storage modulus of 1, 3, 5 and 7LDH-STH/PS nanocomposites from bulk polymerization. Furthermore, the nanocomposites with 1LDH-STH/PS has the highest $E'$, followed by 5 and 3LDH-STH/PS. The 7LDH-STH/PS occurs between 3 and 5LDH-STH. This result indicate that the maximum $E'$ can be obtained with only 1LDH and any additional amount of fillers result in the lowering of the $E'$. This is quite different from that of LDH-STH/PS made from solution polymerization as well as the LDH-ST/PS illustrating the effect of solvent.

Figure 2.48 Loss modulus ($E''$) of pure PS and its nanocomposites from bulk polymerization.

Moreover, in Figure 2.48, the loss modulus, $E''$ for the LDH-STH/PS, shows a
confirmation of the effect of the LDH-STH on PS, and in this case, a decreased in $E''$ occurred with increase in LDH-STH content while the 7LDH-STH $E''$ lies between the 3 and 5LDH-STH.

The tan delta ($\delta$) for the LDH-STH/PS (Figures 2.49 and Table 2.10) from bulk polymerization shows two temperature transitions corresponding to the $\beta$ and $\alpha$ relaxation peaks, respectively. The figure reveals a decreasing effect of the LDH-STH on the PS matrix. The low temperature loss peak is attributable to the rotation of the segments of the backbone chain. The tan delta for the LDH-STH/PS show a decreasing trend with the increase in LDH-STH but the 7LDH-STH lies in between the 3 and 5LDH-STH. The $\alpha$ relaxation temperature which corresponds to the $T_g$ can be attributed to the concept of free volume.

Figure 2.49 Tan delta ($\delta$) of pure PS and its nanocomposites from bulk polymerization.
The molecular mobility and therefore the relaxation time around the $T_g$ depend on the free volume. In addition to the normal expansion process, the free volume expansion results in a larger expansion of the PS. This provides sufficient room for molecular motion rotation or translation to occur. The large increase in the dissipation factor in $\alpha$ relaxation temperature $T_g$ can be due to this increase in chain segment mobility.

Table 2.10 Thermo-mechanical properties of pure PS and its nanocomposites with LDH-STH from bulk polymerization.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ (°C)</th>
<th>(tan $\delta$)</th>
<th>$E'$ (GPa) at 30 °C</th>
<th>$E'$ (GPa) at 40 °C</th>
<th>$E'$ (GPa) at 60 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>96.1</td>
<td>107.5</td>
<td>1.16±0.30</td>
<td>1.18±0.30</td>
<td>1.13±0.25</td>
</tr>
<tr>
<td>1LDH-STH/PS</td>
<td>67.6</td>
<td>90.6</td>
<td>2.82±0.01</td>
<td>2.85±0.01</td>
<td>2.21±0.18</td>
</tr>
<tr>
<td>3LDH-STH/PS</td>
<td>73.1</td>
<td>93.3</td>
<td>2.08±0.72</td>
<td>2.18±0.69</td>
<td>2.14±0.27</td>
</tr>
<tr>
<td>5LDH-STH/PS</td>
<td>66.7</td>
<td>70.7</td>
<td>2.66±0.07</td>
<td>2.72±0.10</td>
<td>0.49±0.19</td>
</tr>
<tr>
<td>7LDH-STH/PS</td>
<td>65.4</td>
<td>87.0</td>
<td>2.24±0.15</td>
<td>2.27±0.10</td>
<td>1.35±0.20</td>
</tr>
</tbody>
</table>

2.4.7 Thermo-gravimetric Analysis (TGA)

Figure 2.50 TGA of pure PS, LDH-NO$_3$ and its nanocomposites with PS from bulk polymerization.
TGA was used to determine the thermal stability of all the LDH: LDH-NO₃, LDH-ST, LDH-STH, the pure PS and its nanocomposites with the LDHs. In TGA, the thermal analysis technique essentially involves a measure of the change in weight of a sample as a function of temperature or time. TGA was used to determine the thermal stability of PS as well as the impact of LDH-NO₃ nano-crystals on PS matrix. The thermal decomposition of layered double hydroxides typically involves dehydration, dehydroxylation, and decomposition leading to the removal of anions. Evidently, the decomposition onsets of LDH-NO₃/PS nanocomposites shifted to higher temperatures compared to that of pure PS. As shown in Figure 2.50, the TGA of LDH-NO₃ appears to have three degradation steps at 71.4, 187.2 and 243.4 °C, which are attributed to the absorbed water, the OH groups and the nitrate anions, respectively.

Figure 2.51 DTG of pure PS, LDH-NO₃ and its nanocomposites with PS from bulk polymerization.
PS have one degradation step at 389.2 °C which is attributed to the PS chain. In the case of LDH-NO₃/PS nanocomposites, it can be seen that the first degradation step for 1, 3, 5 and 7LDH-NO₃/PS began at 195.2, 171.1, 159.8, and 159.8 °C corresponding to dehydroxylation of the layers while the second degradation pathway corresponds to the decomposition of the nitrate anions which begins from 416.8, 413.6, 411.9 and 410.3 °C. Therefore, evidently, the thermal stability of PS was improved in all the compositions of the LDH. The greatest stability was achieved with 1LDH-NO₃ indicating the optimum nanocomposites concentration composition. There is however a decrease in the thermal stability as the concentration is increased and this decreased was linear for all the compositions used.

As seen in the TGA and DTG (Figure 2.51), the temperature at maximum degradation rate increases largely from 430.0 °C for pure PS to 442.4, 439.3, 439.3 and 439.3 °C, for 1, 3, 5 and 7LDH-NO₃/PS nanocomposites, respectively. Therefore, the presence of clay still plays an important role in enhancing the thermal stabilities of PS, by hindering the out-diffusion of the volatile decomposition products. The introduction of LDH into PS results in a higher residue, seemingly leading to a higher thermal stability. This could be attributable to the catalytic activity of the mixed oxides to the formation of carbonaceous char during the decomposition.
Figure 2.52 TGA and DTG of LDH-ST.

Figure 2.52 and 2.53 shows the TGA and DTG of LDH-ST and LDH-STH, respectively. The first weight loss (ca 6.2%) occurs between 100 and 155 °C, arising from the dehydration of the physically adsorbed and/or crystalline water in the interlayer.

The second weight loss (ca 12%) takes place at temperature range of 150–300 °C, due to the dehydroxylation of the LDH hydroxide layers. The third weight loss (ca 55%) due to the thermal decomposition of the stearic chains takes place in the region between 320–510 °C, with ca 27% residue left at 750 °C. In the case of as-exfoliated LDH-STH (Figure 2.53), a total weight loss (ca 13%) between 30–300 °C, corresponds to possible dehydration and dehydroxylation stages. Also seen in the TGA is a major decomposition in the region between 350 and 450 °C, with a weight loss of about 62%, which can be assigned to the combustion of the hydrocarbon chains from both ST and hexadecane.
Figure 2.53 TGA and DTG of LDH-STH.

The final residue, i.e., the mixed oxide at 750 °C only 21%, which is much smaller than the estimated residue (27.8%, Table 2.2). The less residue (28%) is also noted for the as-prepared LDH sample (vs. the estimated 38.1%, Table 2.2). The over-weight loss could be presumably attributed to ZnO evaporation since the combustion of hydrocarbon chains in air can release a large amount of heat and cause a higher temperature in some local regions that could evaporate ZnO just formed.

Figure 2.54 presents the thermal decomposition of pure PS and with undelaminated LDH-ST nanocomposites 1, 3 and 5LDH-ST/PS, respectively, obtained via bulk polymerization. The onset temperature of decomposition is higher for the 3 and 5LDH-ST/PS nanocomposites compositions compared to the neat PS. The hydroxylation
step for the nanocomposites which begins at ca. 171 °C continues to ca. 300 °C and then followed by the decomposition of the surfactant which starts at ca. 392 °C for both the 3 and 5LDH-ST/PS while in the case of 1LDH-ST/PS it is at ca. 388 °C much lower than the pure, 3 and 5LDH-ST/PS nanocomposites. From the figure, it can be observed that the highest temperature of decomposition being the 5 which is followed by the 3LDH-ST/PS nanocomposites. At 50% weight loss for the nanocomposites, the thermal decomposition temperatures for pure PS as well as 1, 3 and 5LDH-ST/PS nanocomposites were determined as 426.9, 416.4, 430.2 and 435.1 °C, respectively. Thus, the LDH-ST enhances thermal stability of PS in all the nanocomposites. These results indicated the advantage of using LDH in polymers wherein the LDH increases the charring process of the polymer matrix thereby resulting in the hindering effect of the
LDH layers for the diffusion of oxygen and volatile products throughout the nanocomposites materials during the thermal decomposition of the nano materials. Similar result was reported by Ding and Qu\textsuperscript{38} in their synthesis and characterization of polystyrene/layered double hydroxide via emulsion and suspension polymerization. In their report, the nanocomposites with low filler content exhibited low thermal stability because the amount of LDH was not sufficient to cause any significant improvement of the thermal stability. Similarly, in this case, the nanocomposites with 1LDH-ST/PS had lower thermal stability. However, when the LDH content was increased by 3 and 5LDH-ST, the amount of the filler was then sufficient to increase the thermal stability of the PS. These results indicated that the 5LDH-ST/PS nanocomposite had the highest thermal decomposition temperature. The thermal stability of the pure PS and LDH-STH/PS nanocomposites whose polymerization was performed via solution process was determined. The thermal decomposition of layered double hydroxides typically involves dehydration, dehydroxylation, and decomposition leading to the removal of anions. Figure 2.55 shows the thermal decomposition of pure PS and nanocomposites 1, 3 and 5LDH-STH/PS.

The onset temperature of degradation for all the nanocomposites is generally lower than for the pure PS (Figure 2.55). As can be seen, the thermal stability of PS is lowered by the LDH, but somewhat the same at around 40% weight loss where the curves for all the nanocomposites joined together with the pure PS. Since solvent is involved here, the solvent may have contributed to sort of stabilize the catalytic process during the decomposition leading to no appreciable temperature than that of the pure PS. The most
Figure 2.55 TGA of pure PS and the LDH-STH/PS nanocomposites from solution polymerization.

Thermally stable in all the nanocomposites is the 3LDH-STH/PS indicating the optimum temperature for this type of nanocomposite than those from LDH-ST/PS. An additional amount of LDH results in decrease thermal stability.

In Figure 2.56 the thermal decomposition results of pure PS and 1, 3, 5 and 7LDH-STH/PS nanocomposites are shown, respectively, obtained through bulk polymerization process. In contrast to the thermal behavior of LDH-STH/PS nanocomposites from solution polymerization, the onset temperature of degradation, measured as the temperature for 10% degradation is higher for all the nanocomposites than for the pure PS. As can be seen in all the nanocomposites, there is a significant increase in thermal stability as the thermal stability of PS is increased by the LDH.
Figure 2.56 TGA of pure PS and LDH-STH/PS nanocomposites from bulk polymerization.

Clearly, the decomposition onsets of 1, 3, 5, and 7LDH-STH/PS nanocomposites shifted to higher temperatures at 406.7, 418.6, 415.4 and 418.6 °C compared to that of pure PS at 389.2 °C. Similar behavior was observed by Matusinovic et al.\textsuperscript{39} In their studies, improved thermal behavior stability was obtained with use of exfoliated LDH layers in the nanocomposites.

A low filler level resulted in significant improvement in thermal stability. Use of exfoliated LDH above 5% LDH content decreases the thermal stability in the nanocomposites. As shown in TGA and DTG (Figure 2.57), pure PS appears to have one degradation pathway at 389.2 °C, which can be attributed to the degradation of the polystyrene hydrocarbons. In the case of LDH-STH/PS nanocomposites, it can be seen that the first degradation step for 1, 3, 5 and 7LDH-STH/PS began at 116.2 °C and end at
Figure 2.57 DTG of PS and LDH-STH/PS nanocomposites from bulk polymerization. 201.5 °C largely corresponding to dehydroxylation of the layers while the second degradation pathway corresponds to the decomposition of the hexadecane hydrocarbons which begins from 190.3 °C and end at 320 °C.

Therefore, it is apparent that the presence of clay stabilizes both steps of degradations for the nanocomposites though further increase in clay concentration from 5 to 7 % does not seem to affect decomposition temperature much. As seen in the TGA and DTG, the temperature at maximum degradation rate increases largely from 430.0 °C for pure PS to 437.7, 441.7, 439.7 and 442.2 °C, respectively for 1, 3, 5 and 7LDH-STH/PS nanocomposites, respectively. Although clay is known to be concentrated on the exterior surfaces of PS particles, it seems that the presence of clay still plays an important role in enhancing the thermal stabilities of PS, by hindering the out-diffusion of the volatile decomposition products. The introduction of LDH into PS results in a higher residue,
seemingly leading to a higher thermal stability. This could be attributable to the catalytic activity of the mixed oxides to the formation of carbonaceous char during the decomposition.

2.5 Conclusions

This study concludes the synthesis and characterization of segment of the LDH research with LDH-nitrate (LDH-NO₃), LDH-stearate (LDH-ST) and LDH-stearate hexadecane (LDH-STH) for use with styrene monomer in situ polymerization. XRD results indicated that the incorporation of LDH-NO₃ nanoparticles with styrene monomer produces neither a new peak nor a peak shift with respect to LDH-NO₃ indicating immiscibility. TEM results showed regions of LDH regions with no nanofillers confirming the results. Furthermore, LDH-NO₃ was functionalized with stearate anion to afford LDH-ST and subsequently obtained exfoliated LDH-STH after treatment with hexadecane. Both the LDHs were used with PS to afford LDH-ST/PS and LDH-STH/PS intercalated and exfoliated nanocomposites, respectively. In the case of the LDH-ST that was used for studies with PS, some intercalated nanosheets in addition to the individual exfoliated sheets were observed in the TEM nanocomposites for all the samples. Similarly, for the LDH-STH/PS from bulk polymerization, the XRD patterns of the LDH-STH/PS nanocomposite show no sign of the presence of the pristine LDH phase. The good dispersion of delaminated LDH nanosheets into PS matrix can be attributed to the hydrophobic interactions between polystyrene and delaminated LDH sheets. The presence of the delaminated LDH-STH/PS was confirmed by TEM. In addition to exfoliated nanoparticles, evidence for the presence of ZnO nanoparticles present in the
polymer obtained by bulk polymerization were obtained by XRD, UV-vis and TEM, and thus confirmed the presence of zinc oxide in LDH-STH and in nanocomposites made from it with PS.

DSC results indicated that LDH-NO$_3$ acted as a plasticizer decreasing the PS $T_g$ and nanoparticles moduli were lowered in softening of the nanoparticles as the concentration of the nanofiller was increased with PS. It can be observed that this is a case of success of application of nanofiller, LDH-NO$_3$ in softening nanomaterials that produces linear results leading to the production of desired products in an in situ bulk polymerization reaction with styrene monomer. The $T_g$ of the PS was lowered by about 20% with the use of LDH-NO$_3$ as observed in the $1\text{LDH-NO}_3/\text{PS}$ nanocomposites and this decrease appears to be linear. Similar decrease was observed for the LDH-STH/PS nanocomposites with about 40% compared to the pristine PS obtained from bulk polymerization. In the case of the LDH-ST/PS and LDH-STH/PS nanocomposites from bulk and solution polymerization, respectively, increased $T_g$ was observed in all the nanocomposites. About 10% increase in $T_g$ was observed for the LDH-ST/PS nanocomposites while the effect of solvent in the solution polymerization produces a moderate increase in the $T_g$ in the LDH-STH/PS nanocomposites. Plasticizing and anti-plasticizing effects has been invoked to explain some of the changes experienced in $T_g$ for some of the values.

Results from TGA indicated that the nanofiller thermally enhanced the PS and therefore, could be utilized for such other purposes. TGA results showed that both the
LDH-ST/PS and LDH-STH/PS nanocomposites thermal stability were improved and this advantage can be utilized when the polymer-clay mixture must be processed at relatively high temperatures. DMA studies on the nanocomposites indicated that the LDH nanoparticles improved mechanical properties exhibiting higher storage modulus than the neat PS for all the nanocomposites from bulk and solution polymerization. Table 2.11 depicts a summary of the work in this chapter and relates the method of polymerization, concentration of the LDH used, characterization and the various nanocomposites synthesized.

Finally, as for exfoliated LDH/PS nanocomposites, they differ significantly from others that undergo restacking. In these studies, no appreciable restacking of the delaminated hydroxide layers was observed. Therefore, the success of these results can be attributed to the use of a suitable solvent-anion combination, and with the large distance between the negative charge of the head groups of the surfactant molecules attached to one layer, and the positive charge of the adjacent layer. Although this study was
concentrated on the LDH/PS, this technique could be widely applied to many other polymers.

2.6 References


CHAPTER 3

ABS-LDH NANOCOMPOSITES: FLAME RETARDANCY, MECHANICAL AND
LOW TEMPERATURE PERFORMANCE

3.1 Introduction

In recent years, much attention has been paid to polymer clay nanocomposites because of their improved properties at very low loading levels (3-5 %) compared with conventional filler composites. Various researches have showed that polymer clay nanocomposites (PCN) provides improved mechanical properties, gas barrier properties, solvent resistance and decreased flammability, compared to the neat polymer. PCN are usually divided into three general types: intercalated, exfoliated and conventional. In an intercalated dispersion, the layers swell with some level of polymer chain penetration but the overall stacking of the layered structure is retained. In an exfoliated dispersion, the layers are completely dispersed within the host system. Since the layers are in the nanometer range in thickness, an exfoliated dispersion results in a high aspect ratio reinforced polymer system. Some desirable properties, such as high temperature dimensional stability, increased modulus and decreased permeability, are thus achieved in these systems. In the conventional case, the clay is neither intercalated nor exfoliated, but acts as filler.

Recent research has raised concerns about persistence and toxicity of the flame retardants. Some flame retardants are ubiquitous in the environment. Due to the chemical stability of the halogenated flame retardant, these compounds, however, have a tendency
to accumulate and spread in the environment. Rapidly increasing levels have been measured in sediments, marine animals and humans indicating a significant potential for damage to ecological and human health. They are also emitted from products in use and have been present in the human body and breast milk in measurable quantities. As a result, and worldwide, halogenated flame retardants have been placed on the list of undesirable substances and there has been considerable interest in halogen free flame retardants and metal hydroxides such as aluminum hydroxide and magnesium hydroxide which are already in commercial use. A significant impediment to the control of properties is variability in the composition, charge density and iron content of these naturally occurring materials. Synthetic clays such as anion exchanged layer double hydroxides (LDH) are therefore of increasing interest.

LDH\textsuperscript{7-9} are a group of anion-exchanging materials containing metal hydroxide layers similar to those of brucite, Mg(OH)\textsubscript{2}, in which, typically, up to one third of the divalent cations (e.g. Mg, Ni, Co, Zn) have been replaced by a trivalent cation (e.g. Al, Fe(III)). The resulting positive charge is balanced by exchangeable anions in the interlayer space, which generally also contain water hydrogen-bonded to the anions and/or hydroxide groups. Synthesis of LDH is generally accomplished by coprecipitation on addition of base to a solution containing the metal cations and a suitable anion, or by exchange of interlayer anion in an existing LDH, care being taken to exclude carbon dioxide because LDH has a high selectivity for carbonate.

Acrylonitrile-butadiene-styrene (ABS) is an engineering thermoplastic material widely used because of its excellent chemical, electrical and mechanical properties, fine
surface appearance and good processing characteristics.\textsuperscript{10} Some of its uses include in automotive body parts, dash boards, electronic enclosures for business machines and consumer products; sporting goods; manufacturing fixtures; handles and enclosures for power tools; prototypes and end-use parts in other industries such as aerospace, medical, toys and industrial goods.

However, one drawback of this polymer is its inherent flammability, which is typical of most styrene based polymers.\textsuperscript{11} Only few reports about ABS/clay nanocomposites have been reported. For example, Lee et al. reported the synthesis of ABS/montmorillonite nanocomposites by emulsion polymerization.\textsuperscript{12} Hu et al. reported the preparation and thermal properties of ABS/montmorillonite nanocomposites.\textsuperscript{13-15} Yeh et al.\textsuperscript{16} studied the effect of montmorillonite on the thermal stability, mechanical strength and surface wettability of ABS/clay nanocomposites. Other authors\textsuperscript{17-19} have studied the thermal degradation behavior and flammability of SAN/clay nanocomposites. Recently, Patiñó-Soto et al.\textsuperscript{20} reported the effect of acrylonitrile content on the thermal stability and morphology of ABS/clay nanocomposites. ABS polymers consist of two phases, a continuous phase of styrene-acrylonitrile (SAN) copolymer, and a dispersed phase of grafted polybutadiene particles. Each of these phases possesses unique characteristics to the ABS polymer. SAN exhibits the combined properties of the ease of processability of polystyrene and the rigidity and chemical resistance of acrylonitrile, while butadiene gives high impact strength properties of the ABS/polymer composites. It is imperative to note that the acrylonitrile components is the most polar of the three components of ABS,
and its substance can result in polar interactions with any modified clay in the nanocomposite.

Three approaches have been taken for the formation of nanocomposites: melt-blending, solution-mixing, and in situ polymerization. In the case of melt-blending, the polymer is mixed with the clay with a blender while in solution the clay is dispersed in the polymer. In the case of in situ polymerization, the clay is dispersed in the monomer followed by polymerization reaction.\textsuperscript{21} Much of the work performed to date has been either by the melt-blending or by the solution-mixing process.

It is well known that acrylonitrile butadiene styrene is highly inflammable, but to our knowledge, the use of LDH as a flame retardant has never been reported. Therefore, the objective of this work is to investigate the morphology, thermal stability and flame retardance property of synergism organoclay system LDH on ABS. ABS/LDH composites were prepared by melt-blending. Thermogravimetry (TGA) and UL-94 were used to study the thermal stability and fire retardance property, respectively, of the composites and x-ray diffraction (XRD) studies and TEM analysis were used to analyze the microstructure.

3.2 Experimental

3.2.1 Materials

Zinc nitrate hexahydrate (Zn(NO$_3$)$_2$.$6\text{H}_2\text{O}$, 98\%, reagent grade), para-toluene sulfonic acid (pTSA, 98.5\%, ACS reagent grade) and aluminum nonahydrate (Al(NO$_3$)$_3$.$9\text{H}_2\text{O}$, 98 \%, ACS reagent grade) were obtained from Sigma-Aldrich. Sodium
hydroxide (50% NaOH, reagent grade) solution was obtained from Aefar Aesar. Acrylonitrile butadiene styrene (ABS) was obtained from Polimeri Sinkral as pellets.

3.2.2 Preparation of the LDH-Nitrate

2.499 g Zn (NO\(_3\))\(_2\).6H\(_2\)O (8.40 mmol) and 1.047 g Al(NO\(_3\))\(_3\).9H\(_2\)O (2.79 mmol) were dissolved in 50 mL deionized water. 0.88 mL 50% NaOH solution (16.80 mmol) was added under nitrogen gas with stirring. The mixture was aged overnight with stirring at a nominal external oil bath temperature of 95 - 110 °C for 24 hours. The mixture was cooled and the precipitate was then centrifuged, and washed twice with deionized water to afford the ZnAl-LDH-NO\(_3\) precipitate.

3.2.3 Preparation of LDH-PTS

To this LDH precipitate, an exchange reaction was performed by adding a solution of p-toluene sulfonate prepared by dispersing equivalent amount of para-toluene sulfonic acid (pTSA) in 50 mL deionized water neutralized with 0.10 mL 50% NaOH solution. The mixture was stirred for 1 hour after which time the precipitate was centrifuged, and washed several times with deionized water. The as-collected precipitate was dried in vacuum over molecular sieves, and is referred to as-prepared ZnAl-LDH-PTS.

3.2.4 Preparation of the ABS/LDH Composites

Both the LDH-PTS and ABS were dried before processing in an oven at 70 °C for 4 hours. The dried LDH-PTS were blended with ABS in the concentration of 10, 30 and 60 wt% in Brabender with a speed of 80 rpm at 230 °C for 5 min. The mixtures were palletized and compression molded between two sheets of Teflon using a Carver press.
into bars for UL-94 testing. The Carver press was pre-heated to 230°C and a total of 5 metric tons of pressure was applied at a rate of 0.5 metric tons per minute. The dimensions of the bars used were 130 mm x 14 mm x 4 mm. We used designation 10LDH for 10wt% LDH-PTS ABS (10/90), 30LDH and 60LDH for 30wt% LDH ABS (30/70) and 60wt% LDH ABS (60/40), respectively.

3.3 Characterization

3.3.1 LDH Characterization

3.3.1.1 Metals and C, H, N Analysis of LDH

The metals analysis was conducted by atomic absorption spectroscopy (AAS) using a Perkin-Elmer Analyst 300, with standards and element lamps supplied by Perkin-Elmer. The LDH samples were completely dissolved in a 5% HNO$_3$ solution at 50 °C overnight. The C, H, N analysis was performed by EA Elemental Analysis, Inc.

3.3.1.2 Fourier Transform Infrared (FTIR) Analysis

FTIR measurements on pure LDH samples was performed in attenuated total reflectance (ATR) mode under atmospheric conditions in the spectral range of 400 to 4000 cm$^{-1}$ for a total of 64 scans each.

3.3.1.3 Wide Angle X-ray Diffraction (WAXD) Analysis

The powder XRD patterns were obtained using a Rigaku model D/Max AQ5 Ultima III X-Ray Diffractometer (generated at 44mA and 40 kV). Each sample was scanned from 2 - 70° (2θ), with a step size of 0.05° and a dwell time of 1.34 seconds, using CuK$\alpha$ radiation ($\lambda$ =1.540562Å).
3.3.1.4 Scanning Electron Microscopy (SEM)

SEM image was obtained using the SEM Quanta 200 and samples were platinum plated before SEM examination.

3.3.2 ABS/LDH Nanocomposites

The neat ABS and blended materials were characterized by Fourier transform infrared spectroscopy-attenuated total reflection- (FTIR-ATR), x-ray diffraction (XRD), dynamic mechanic analysis (DMA), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM).

3.3.2.1 Dispersion

3.3.2.1.1 Wide Angle X-ray Diffraction (WAXD) Analysis

The XRD patterns were obtained using a Rigaku Ultima III X-Ray Diffractometer no internal or external standards. Each pattern was scanned from 2 - 50° (2θ), with a step size of 0.05° and a dwell time of 1.34 second, using CuKα radiation (λ =1.540 Å).

3.3.2.1.2 Transmission Electron Microscopy (TEM) Analysis

Samples for electron microscopy were sectioned using a Reichert-Jung Ultracut E cryogenic ultramicrotome to a thickness of about 50–70 nm with the knife at room temperature for SAN samples, and at K45 8C for the ABS samples. Knife speed was 0.5 mm/s. The sections were imaged using a JEOL 2010 F electron microscope operating at 120 kV. The ABS samples were photographed in stained form in order to provide optimized information about the location of the clay platelets. The stained sections were exposed on the grids to OsO₄ vapor for 24 h. All specimens were prepared such that the reported images represent views along the flow direction (FD). Image analysis was
performed on digitally captured images using 100–200 particles from over four different sites in TEM mode.

3.3.2.2 Interaction

A Nicolet Nexus 6700 FTIR-ATR was used to study changes in chemical species and bonding. FTIR measurements on films for neat ABS and their blends were performed in attenuated total reflectance (ATR) mode under atmospheric conditions in the spectral range of 400 to 4000 cm$^{-1}$ for a total of 64 scans each.

3.3.2.3 Thermal Analysis

3.3.2.3.1 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) was measured using a Perkin-Elmer DSC6 apparatus. The system was calibrated using elemental indium. The sample was run from 30 to 200 °C at the heating rate of 10 °C/min and at a cooling rate of 5 °C/min.

3.3.2.3.2 Thermogravimetric Analysis (TGA)

TGA were performed using a Perkin-Elmer TGA6. Each 20 – 25 mg sample was pyrolyzed under nitrogen gas in a ceramic sample pan from 30 to 600 °C, at a heating rate of 10°C/min.

3.1.1.1 Flammability Test

UL-94 HB flame testing was performed on 5 samples according to ASTM D 635-98 standard of an average dimension of 130 mm x 14 mm x 4 mm. The time and extent of burning and the linear burn rate is obtained suspended horizontally above a cotton patch. The material is subjected to two 30 s flame exposures within a chamber which is free from the effects of external air currents. After the first 30 s exposure, the flame is
removed, and the time for the sample to self-extinguish is recorded. Cotton ignition is noted if polymer dripping ensues; dripping is permissible if no cotton ignites. Then the second ignition is performed on the same sample, and the self-extinguishing time and dripping characteristics recorded.

3.4 Results & Discussion

3.4.1 Elemental and XRD Analysis of LDH-PTS

In order to establish the composition in LDHs, CHN and elemental analysis were conducted on the LDHs samples. The elemental analysis results are given in Table 3.1.

Table 3.1 Comparison of observed and estimated elemental content for LDH sample.

<table>
<thead>
<tr>
<th>LDH Sample</th>
<th>%Zn</th>
<th>%Al</th>
<th>C%</th>
<th>H%</th>
<th>S%</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-prepared Zn₂Al(OH)₆(C₇H₈SO₃)·2H₂O</td>
<td>26.8</td>
<td>5.6</td>
<td>17.3</td>
<td>3.5</td>
<td>6.6</td>
</tr>
<tr>
<td>Zn₂.10Al(OH)₀.₇(C₇H₈SO₃)₀.₈(CO₃)₀.₁₆·₅H₂O</td>
<td>26.9</td>
<td>5.6</td>
<td>17.3</td>
<td>3.9</td>
<td>6.6</td>
</tr>
</tbody>
</table>

Figure 3.1 XRD of LDH-NO₃ and LDH-PTS.
Table 3.2 XRD data for LDH-NO$_3$ and LDH-PTS.

<table>
<thead>
<tr>
<th>Sample-</th>
<th>ZnAl LDH-NO$_3$</th>
<th>hkl$^c$</th>
<th>(003)</th>
<th>(006)</th>
<th>(009)</th>
<th>(012)</th>
<th>(015)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(20)$^a$</td>
<td></td>
<td></td>
<td>9.89</td>
<td>19.7</td>
<td>29.9</td>
<td>34.3</td>
<td>37.7</td>
</tr>
<tr>
<td>$d$ spacing (nm)$^b$</td>
<td></td>
<td></td>
<td>0.89</td>
<td>0.45</td>
<td>0.30</td>
<td>0.26</td>
<td>0.24</td>
</tr>
<tr>
<td>FWHM$^c$</td>
<td></td>
<td></td>
<td>0.49</td>
<td>0.50</td>
<td>0.53</td>
<td>0.75</td>
<td>0.71</td>
</tr>
<tr>
<td>XS(nm)$^d$</td>
<td></td>
<td></td>
<td>17.01</td>
<td>16.85</td>
<td>16.21</td>
<td>11.58</td>
<td>12.35</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ZnAl LDH-PTS</th>
<th></th>
<th>(003)</th>
<th>(006)</th>
<th>(009)</th>
<th>(012)</th>
<th>(015)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(20)$^a$</td>
<td></td>
<td>5.05</td>
<td>10.20</td>
<td>15.35</td>
<td>20.59</td>
<td>25.80</td>
</tr>
<tr>
<td>$d$ spacing (nm)$^b$</td>
<td></td>
<td>1.759</td>
<td>0.860</td>
<td>0.576</td>
<td>0.344</td>
<td>0.268</td>
</tr>
<tr>
<td>FWHM$^c$</td>
<td></td>
<td>0.633</td>
<td>0.447</td>
<td>0.407</td>
<td>0.409</td>
<td>0.407</td>
</tr>
<tr>
<td>XS(nm)$^d$</td>
<td></td>
<td>13.13</td>
<td>18.65</td>
<td>20.58</td>
<td>20.63</td>
<td>20.93</td>
</tr>
</tbody>
</table>

$^a$2-Theta degree, $^b$Interlayer spacing, $^c$Full width half maximum, $^d$Crystallite size, $^e$Reflection planes.

The metal ratio of Zn/Al in the as-received LDH samples is 2.1 matched well with the theoretical ratio of 2.00. Considering the C and H weight percent, the as-prepared LDH-PTS can be approximately expressed in composition as Zn$_{2.10}$Al$_6$OH$_6$(C$_7$H$_8$SO$_3$)$_{0.80}$(CO$_3$)$_{0.16}$·5H$_2$O closed to observed values (Table 3.1). From Figure 3.1, illustrating the XRD patterns of the LDH-PTS along with LDH-NO$_3$, it can be seen that the diffractions peaks especially the (003) associated to the interlayer distance moves to lower angles as a result of the replacement of the nitrate ions with the p-toluene sulfonate ions (PTS) with increase in the interlayer distance of the LDH from 0.89 to 1.76 nm (Table 3.2). This indicated the intercalation of the PTS anions in the LDH and the thickness of the LDH layer is evaluated to be 0.48 nm. Figure 3.2 depicts the orientation of the PTS anion in the interlayer of the LDH. It can be observed that the PTS is vertical in the interlayer that is intercalated perpendicularly to the brucite in a way of interlocking bilayer arrangement.
3.4.2 X-ray Diffraction Spectroscopy

Figure 3.3 shows the XRD patterns of the ABS and the blends. The X-ray diffractograms of the LDH shows characteristics peaks of hydrotalcite-like materials. Peaks were conventionally indexed\(^2\) in 3R as (003), (006), (009), and so on. The corresponding intergallery spacing from (003) corresponds to 17.325 Å with diffraction peak at \(2 \theta = 5.097^\circ\) (Table 3.3). The lattice parameter \(a\) and \(c\) can be calculated for the LDH-PTS. \(a\) and \(c\) is calculated as below:

\[
c = d_{003} + 2d_{006} + 3d_{009}
\]

\[
= 1.759 + 2(0.860) + 3(0.576) = 5.207 \text{ nm}
\]
The parameter $a$ can be estimated from the relation

$$a = 2 \, (d_{110}) = 2 \, (0.151) = 0.302 \, \text{nm}$$

The crystallites size can be calculated using the Debye-Scherrer equation,

$$D_{hkl} = \frac{0.9 \lambda}{\beta_{1/2} \cos \theta}$$

where $\lambda$ is the x-ray wavelength (1.54 Å), $\theta$ is the diffraction angle, $\beta_{1/2}$ is the width at half-maximum intensity.

![XRD patterns of LDH, ABS and composites.](image)

Figure 3.3 XRD patterns of LDH, ABS and composites.

It can be seen that in all LDH/ABS composites with different clay contents, the diffraction peak shifts to lower angles, indicating an increase in intergallery spacing.
Studies have shown that an increase in the intergallery spacing results in a new diffraction pattern corresponding to the increased spacing of the clay galleries which is related to the intercalation of the polymer through the clay galleries. Moreover, the degree of intercalation in the composite material could be determined by the sharpness and intensity change that arises with the corresponding reflection peaks. It can be observed that the samples with 10LDH showed a slightly noticeable peak at $2\theta = 4.751^\circ$, with an intergallery spacing of around 18.581 Å, but for the sample with 30 and 60LDH, the intensity of the diffraction peak remains almost the same even with an increase in the LDH content in the composites. This indicates the possibility of intercalation as well as exfoliated of clay dispersed in the ABS matrix. This could be evident from additional peaks that are seen on the XRD patterns. Similar results were obtained by Patiño-Soto et.al.\textsuperscript{20} Their result presents a level of morphology with a higher degree of disordered structures as well as intercalated/exfoliated clay layers.

Table 3.3 Some representative XRD data of LDH and LDH/ABS composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>hkl</th>
<th>$2\Theta$ ($^\circ$)\textsuperscript{a}</th>
<th>Height\textsuperscript{b}</th>
<th>d(nm)\textsuperscript{c}</th>
<th>XS(nm)\textsuperscript{d}</th>
<th>FWHM\textsuperscript{e}</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDH</td>
<td>(003)</td>
<td>5.09</td>
<td>10419</td>
<td>1.732</td>
<td>54.69</td>
<td>0.152</td>
</tr>
<tr>
<td>10LDH</td>
<td>(003)</td>
<td>4.75</td>
<td>674</td>
<td>1.858</td>
<td>28.27</td>
<td>0.294</td>
</tr>
<tr>
<td>30LDH</td>
<td>(003)</td>
<td>4.78</td>
<td>3460</td>
<td>1.843</td>
<td>18.55</td>
<td>0.448</td>
</tr>
<tr>
<td>60LDH</td>
<td>(003)</td>
<td>4.79</td>
<td>4693</td>
<td>1.843</td>
<td>17.06</td>
<td>0.487</td>
</tr>
</tbody>
</table>

\textsuperscript{a}2-Theta degree, \textsuperscript{b}peak height %, \textsuperscript{c}Interlayer spacing, \textsuperscript{d}Crystallite size, \textsuperscript{e}Full width half maximum.

Furthermore, XRD results as seen in Figures 3.3 indicate that the LDH-PTS/PS nanocomposites samples (10, 30 and 60LDH) also contains additional peaks from $2\theta$ (30° to 70°) that can be indexed to a hexagonal wurtzite structure with cell constants of $a =$
0.324 nm and \( c = 0.519 \) which are consistent with the standard values for ZnO with space group \( P6_{3}mc \), JCPDF#36-1451.\(^{23}\) As expected, the ZnO peaks and their intensities are in agreement with those from these results. This confirmed the presence of ZnO in our LDH-PTS /PS nanocomposite. These polymer results are consistent with that obtained by Chae and Kim.\(^{24}\) In their studies of ZnO with PS in solution polymerization obtained nanocomposites in which the ZnO has no effect on the XRD pattern of the nanocomposites. They reported that the incorporation of the ZnO nanoparticles produce no new peaks or cause any change in the shift of peaks and therefore suggested a two phase structures.

3.4.3 Fourier Transform Spectroscopy

![FT-ATR spectra for LDH, ABS and composites.](image)

Figure 3.4 FT-ATR spectra for LDH, ABS and composites.
FTIR-ATR spectra have been commonly used to characterize polymer and its nanocomposites. The FT-ATR reflection absorption spectra of ABS and its nanocomposites are presented in Figure 3.3. The absorption bands at 2842 - 3025 cm\(^{-1}\) are due to the C-H-stretching vibration in ABS. These bands are represented in all the composites, but due to the relative concentration of the ABS in the composite, this group is less evident in the absorption bands of the composites. We see a broad absorption band indicating the presence of OH groups in the LDH at 3436 cm\(^{-1}\), which also appeared on the composite, the effect is much more enhanced for the 60LDH composite. The group is broader for the composites with more LDH concentration. The band occurring at the 1033 cm\(^{-1}\) is characteristic of C-O stretch in the ABS, but the LDH also have bands at this region. However, in the composite, as expected the intensity is enhanced especially in the 60LDH. This probably indicates the presence of inherent interaction between the ABS and the LDH groups. In the spectra, there is the presence of characteristics vibration bands of ABS absorbing at the 760 and 700 cm\(^{-1}\) (aromatic), and 557 cm\(^{-1}\). Also present for LDH is the 445 cm\(^{-1}\) for the Zn-O. Moreover, the stretch at 1622 cm\(^{-1}\) is indicative of the presence of ABS carbonyl group and that of LDH surfactant. As the concentration of the LDH increases, as in the case of the 60LDH, the intensity increases. These results suggest possible an H-bonding interaction between the carbonyl group of the ABS and the OH–stretching vibration of the LDH.

3.4.4 Differential Scanning Calorimetry

Figure 3.5 shows the results of differential scanning calorimeter analysis (DSC) performed in the pure ABS and the LDH composites in order to evaluate the changes in
the glass transition temperature ($T_g$), with increasing LDH content. As in Figure 3.5 and Table 3.4, the effect of LDH on thermal transitions is illustrated. The thermogravimetric temperature ($T_g$) of the composites shifted to higher temperatures with the increase of the clay content. As seen in the graphs (Figure 3.5), there is a corresponding increase in $T_g$ with an increase in clay content. $T_g$ is largely related to the molecular mobility of polymer chains which is also affected by molecular packing, chain rigidity and linearity. Chen et al.\textsuperscript{26} found similar results in their study of the polymer/clay composites. In addition, Yeh et al.\textsuperscript{16} studied the effect of organoclay on the thermal stability, mechanical

![Figure 3.5 DSC curves for LDH, ABS and composites.](image)

136
Table 3.4 DSC data for pure ABS and composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$</th>
<th>$\Delta C_p$ (J/g °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure ABS</td>
<td>104.6</td>
<td>0.589</td>
</tr>
<tr>
<td>10LDH</td>
<td>105.6</td>
<td>0.280</td>
</tr>
<tr>
<td>30LDH</td>
<td>109.9</td>
<td>0.369</td>
</tr>
<tr>
<td>60LDH</td>
<td>117.7</td>
<td>0.312</td>
</tr>
</tbody>
</table>

strength, and surface wettability of injection-molded ABS/Clay nanocomposite materials prepared by melt intercalation reported similar result. They found that the incorporation of organoclay resulted in an increase in the $T_g$ compared to pure ABS. They attributed their result to confinement of the intercalated polymer chains within the organoclay galleries that prevent the segmental motions of the polymer chains. Therefore, these increases in our glass transition values can be attributed to increase interactions between the polymer chains and the layered surfactant surfaces.

3.4.5 Dynamic Mechanical Analysis

The temperature dependence of the storage modulus ($E'$), loss modulus ($E''$) and $\tan \delta$ of pure ABS and ABS/LDH composites is shown in Figure 3.6 (A, B, C), respectively. Storage modulus represents the ratio of the in-phase stress to the applied strain, which is further related to the energy stored per cycle of deformation. Storage modulus determines the dynamic rigidity of a material, which originates from the elastic response of the material. The values of $E'$ of ABS and the composites at -100 °C, -80 °C, 0 °C and 100 °C are summarized in Table 3.5. It is clear from Figure 3.5(A) and Table 3.5
that $E'$ of the material increases in the presence of LDH, and also as LDH content increases $E'$ of the composites improves. The $E'$ values of the ABS/LDH composites containing 10, 30 and 60wt% LDH increase by 65, 22 and 11%, respectively, when compared with those of neat ABS at -100 °C. Besides, the $E'$ values decrease for both the pure ABS and the composites with increasing temperature due to the softening of the ABS matrix. The $E'$ shows that there are two transitions exhibiting some phase separation in the copolymers. It can be observed that the modulus change significantly over a narrow range of temperature. Between these two transitions, a plateau region of lesser change of modulus with temperature is observed. The ABS contains hard and the soft blocks (or segments) corresponding to the butadiene elastomer and styrene, respectively. Similar behavior is observed in the pure ABS and all the composites.

Figure 3.6(B) shows the $E''$ of the ABS and composites. Two transitions are seen exhibiting the butadiene phase at subabient and styrene phase ambient temperature. Both the pure and the composites follow regular trends. For the butadiene and styrene, the pure ABS damping is lower than all follow by 10LDH in the styrene phase while the 60LDH has the highest peak. This is reversed in the butadiene region. This effect can be attributable to the restriction of the molecular chain which is more in the case of the increase in LDH content affecting the thermogravimetric temperatures ($T_g$). This seems to be more prevalent in styrene segment because of the ABS pendant (phenyl ring) and as for the butadiene segment; increase of the LDH causes damping. As shown in Figure 3.6(C), the height of the tan $\delta$ peak for both the butadiene and styrene segment decreases with the presence of LDH. One possible explanation of this phenomenon is that the neat
ABS shows a sharp and intense peak because there is no restriction to the chain motion, while the presence of LDH hinders the chain mobility, leading to the reduction of sharpness and height of the tan δ peak. The restriction leads to changes in the $T_g$ of the composites. Furthermore, the damping in the transition region measures the imperfections in the elasticity, and much of the energy used to deform a material during dynamic testing is dissipated directly as heat. Hence, the molecular mobility of the composites decreases and the mechanical loss to overcome intermolecular chain friction is reduced with the addition of the LDHs. It is also considered that the reduction in tan delta also denotes an improvement in the hysteresis of the system and a reduction in the internal friction.
Figure 3.6 Storage modulus (A), loss modulus (B) and tan delta (C) of pure ABS and composites.
Table 3.5 Storage modulus (E’) of pure ABS and its composites with LDH

<table>
<thead>
<tr>
<th>Sample</th>
<th>E’(GPa) 100 °C</th>
<th>E’(GPa) 80 °C</th>
<th>E’(GPa) 0 °C</th>
<th>E’(GPa) 100 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS</td>
<td>1.11 ± 0.01</td>
<td>0.93 ± 0.11</td>
<td>0.75 ± 0.07</td>
<td>0.80 ± 0.14</td>
</tr>
<tr>
<td>10LDH</td>
<td>1.84 ± 0.50</td>
<td>1.63 ± 0.52</td>
<td>1.22 ± 0.42</td>
<td>1.12 ± 0.35</td>
</tr>
<tr>
<td>30LDH</td>
<td>2.26 ± 0.05</td>
<td>2.03 ± 0.03</td>
<td>1.57 ± 0.01</td>
<td>1.40 ± 0.04</td>
</tr>
<tr>
<td>60LDH</td>
<td>2.52 ± 0.11</td>
<td>2.41 ± 0.08</td>
<td>1.92 ± 0.01</td>
<td>1.72 ± 0.15</td>
</tr>
</tbody>
</table>

3.4.6 Thermogravimetry Spectrometry

Figure 3.7 shows the thermal stability of the LDH and its nanocomposites. From the results, the thermal stability is affected by the inclusion of LDH particles, the effect resulting in the lowering of the stability. This effect appears to increase with the increase in LDH content. The ABS shows an onset temperature of at 340 °C. This is consistent with Suzuki et.al. investigated the flammability of styrenic polymer clay nanocomposites based on a methyl methacrylate oligomerically-modified clay. In their
studies, degradation begins at 340 °C resulting in the formation of butadiene monomer. This is followed by degradation of acrylonitrile and styrene at 400 and 420 °C, respectively. Similarly, for the composites, degradation essentially begins in the butadiene region of the polymer then proceeds to the Styrene acrylonitrile portion. The amount of residue that is produced is directly related to the butadiene content of the sample. In the case of the 60LDH, about 50% of the residues were left after thermal studies.

3.4.7 Flame Retardancy (UL-94)

The fire properties of these LDH/ABS composites were measured by UL-94\textsuperscript{31,32} and Figure 3.8 shows digital photos of burning characteristics of the sample during flame testing for (a) ABS, (b) 10LDH, (c) 30LDH and (d) 60LDH composites and the results are reported in Table 3.6.

The data shows that the composites have better flammability properties than virgin ABS. The time for these materials to ignition remains the same, but all other properties show enhanced fire behavior with increased LDH concentration. Using the virgin ABS, 100% of the sample was consumed after an average of some times (Figure 3.9a). The 10LDH sample though has a better flame retarding property, but burnt completely producing char that maintained its bar form (Figure 3.9b), but the 30LDH bars were put out after some time (Figure 3.9c). The flame retarding of 60LDH (Figure 3.9d) showed remarkable success with flame extenuation even after second ignition is performed on the same sample.
The flammability behavior for Pure ABS samples showed high dripping, the
dripped material would fall on the mesh and reignite and burn for a longer time. Pure
ABS is highly flammable and showed a lot of dripping and large amounts of smoke was
produced on flame testing (Figure 3.9a).

Figure 3.8 Digital photographs of burning characteristics of the sample during flame
testing for (a) ABS, (b) 10LDH, (c) 30LDH and (d) 60LDH composites.
Figure 3.9 Char from flame testing for (a) ABS, (b) 10LDH, (c) 30LDH and (d) 60LDH composites.

Table 3.6 UL-94 data for pure ABS and LDH composites.

<table>
<thead>
<tr>
<th>Pure Sample</th>
<th>ABS</th>
<th>l(mm)</th>
<th>w(mm)</th>
<th>t(mm)</th>
<th>Time (sec)</th>
<th>L(Burn Length, mm/min)</th>
<th>V(linear burn rate, mm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>130</td>
<td>14.05</td>
<td>5.25</td>
<td>622.9</td>
<td>80</td>
<td>7.70</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>130</td>
<td>14.03</td>
<td>5.23</td>
<td>817.8</td>
<td>80</td>
<td>5.86</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>129</td>
<td>14.18</td>
<td>5.32</td>
<td>550.5</td>
<td>80</td>
<td>8.71</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>130</td>
<td>14.07</td>
<td>5.36</td>
<td>550.7</td>
<td>80</td>
<td>8.71</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>130</td>
<td>13.95</td>
<td>5.32</td>
<td>570.5</td>
<td>80</td>
<td>8.41</td>
</tr>
</tbody>
</table>
The char produced formed a very sticky mass which was stuck to the mesh and had to be burnt off prior the next test. The 10LDH samples showed reduction in dripping,

<table>
<thead>
<tr>
<th>10LDH Sample</th>
<th>l(mm)</th>
<th>w(mm)</th>
<th>t(mm)</th>
<th>Time (sec)</th>
<th>L(Burn Length, mm/min)</th>
<th>V(linear burn rate, mm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>131</td>
<td>14.12</td>
<td>4.92</td>
<td>476.9</td>
<td>80</td>
<td>10.06</td>
</tr>
<tr>
<td>2</td>
<td>131</td>
<td>14.20</td>
<td>5.01</td>
<td>520.8</td>
<td>80</td>
<td>9.21</td>
</tr>
<tr>
<td>3</td>
<td>131</td>
<td>14.08</td>
<td>4.99</td>
<td>665.5</td>
<td>80</td>
<td>7.21</td>
</tr>
<tr>
<td>4</td>
<td>131</td>
<td>14.24</td>
<td>5.00</td>
<td>480.7</td>
<td>80</td>
<td>9.98</td>
</tr>
<tr>
<td>5</td>
<td>131</td>
<td>14.06</td>
<td>4.94</td>
<td>492.1</td>
<td>80</td>
<td>9.75</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>30LDH Sample</th>
<th>l(mm)</th>
<th>w(mm)</th>
<th>t(mm)</th>
<th>Time (sec)</th>
<th>L(Burn Length, mm/min)</th>
<th>V(linear burn rate, mm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>131</td>
<td>14.20</td>
<td>4.89</td>
<td>414.3</td>
<td>80</td>
<td>11.58</td>
</tr>
<tr>
<td>2</td>
<td>131</td>
<td>14.11</td>
<td>4.94</td>
<td>387.5</td>
<td>80</td>
<td>12.38</td>
</tr>
<tr>
<td>3</td>
<td>131</td>
<td>14.00</td>
<td>4.90</td>
<td>390.1</td>
<td>80</td>
<td>12.30</td>
</tr>
<tr>
<td>4</td>
<td>131</td>
<td>14.13</td>
<td>4.66</td>
<td>361.3</td>
<td>80</td>
<td>13.28</td>
</tr>
<tr>
<td>5</td>
<td>131</td>
<td>14.16</td>
<td>4.74</td>
<td>376.3</td>
<td>80</td>
<td>12.75</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>60LDH Sample</th>
<th>l(mm)</th>
<th>w(mm)</th>
<th>t(mm)</th>
<th>Time (sec)</th>
<th>L(Burn Length, mm/min)</th>
<th>V(linear burn rate, mm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>131</td>
<td>14.12</td>
<td>4.93</td>
<td>406.3</td>
<td>80</td>
<td>9.59</td>
</tr>
<tr>
<td>2</td>
<td>131</td>
<td>14.08</td>
<td>4.94</td>
<td>170.0</td>
<td>80</td>
<td>3.52</td>
</tr>
<tr>
<td>3</td>
<td>131</td>
<td>14.14</td>
<td>4.84</td>
<td>614.1</td>
<td>80</td>
<td>7.81</td>
</tr>
<tr>
<td>4</td>
<td>131</td>
<td>14.18</td>
<td>4.96</td>
<td>511.2</td>
<td>80</td>
<td>8.56</td>
</tr>
<tr>
<td>5</td>
<td>131</td>
<td>14.14</td>
<td>4.67</td>
<td>698.5</td>
<td>80</td>
<td>6.87</td>
</tr>
</tbody>
</table>
and slight reduction in smoke. The char produced after the test stuck to the mesh and had to be burnt prior to another test (Figure 3.9b). Similarly, 30LDH samples showed smoke suppression. Dripping reduced significantly and the char was not sticky or viscous in nature and could easily be scraped off from the mesh. The char was hard which clung together (Figure 3.9c). Most samples of 60LDH passed the UL-94 HB test (Figure 3.9d). Self extinguishing nature was observed with highest smoke suppression as compared to pure ABS, 10 and 30LDH. It also showed very less dripping. Also, to be noted was that

![Dependence of Linear Burn rate on LDH Concentration](image)

Figure 3.10 Burning rate of ABS and LDH/ABS composites.

the smoke suppression was observed from the exhaust fumes and also the interior of the flame chamber. The test time for pure ABS and 10LDH samples could be noticed only after the exhaust was switched on. There were lots of depositions of flying char particles
around the surrounding area. The entire chamber was filled with smoke and even the test time could not be seen and had to be cleaned. This was not the case in 30 and 60LDH samples. Figure 3.10 shows the burning rate of ABS and LDH/ABS composites, it can be observed that the burning rate decreased with the 60LDH content. These results suggest that an ABS with a higher LDH content can produce an ABS/clay composite with greater flame resistance.

3.4.8 Scanning Electron Microscopy

![Figure 3.11 SEM of LDH-PTS.](image)

Figure 3.11 shows the result of scanning electron microscopy of the LDH-PTS material. The LDH-PTS material appears to be constituted of non-uniform, round edged, hexagonal plate-like particles. The presence of organic molecules in the interlamellar
space has produced a change of the superficial interaction between particles that influences aggregation between particles. It is known that hydrotalcite-like structures give hexagonal plates that display some edge-rounding upon intercalation.

3.4.9 Transmission Electron Microscopy

The morphological structure of the intercalated-exfoliated LDH/ABS composites was further studied by the TEM analysis. Figure 3.12 depicts the TEM of the 10, 30 and 60 LDH/ABS composites. It can be seen that the LDH layers with the PTS surfactant (the dark part) are homogenously dispersed in the ABS matrix. It is observed that the TEM micrographs indicated the presence of exfoliated LDH platelets with thickness of ca 1.6 – 2.7 nm. The arrow on the images points to region of the individual exfoliated layers for the composites (A, C and E). This confirms the results obtained from XRD diffraction above. ABS generally contains materials 20-30% acrylonitrile in the styrene-acrylonitrile (SAN) copolymer. The acrylonitrile is known to contribute both toughness and higher $T_g$ to the plastic. Haiyun et al.\textsuperscript{33} in their ABS/organo montmorillonite composites studies obtained grey continuous region that corresponds to SAN phase and the spherical rubber particles that appear as islands. An excellent way to study the morphology of ABS involves staining with OsO$_4$ and examining the features with TEM. Typical results are shown in Figures 3.12 (A-F) which shows typical morphology for spherical cellular particles with relatively large uniform domains of polystyrene occluded inside (B, D and
Figure 3.12 TEM morphology of OsO4 stained LDH/ABS composites (10, 30 and 60 LDH/ABS) corresponding to A and B, C and D, and E and F, respectively. Note rubber phases with different spherical sizes in (B, D and F images).
The rubber domains with different sizes spread from 38 – 500 nm in diameter. The block copolymer rubber domains are between 985 – 2000 nm in size, with the PS occlusions being much smaller. The dark spots in (A, C and E) are the ZnO nanoparticles. The size of the ZnO in the LDH-PTS/ABS sample ranges from 17 – 50 nm.

3.5 Conclusions

Non-halogenated layered double hydroxide (LDH) compounds have been successfully synthesized and characterized. Melt blending with ABS produces intercalated-exfoliated LDH/ABS composites. XRD and TEM analysis showed that the LDH was well dispersed as well as some level of intercalation and exfoliation present in it. DSC showed that the dispersed clay improves the thermo-gravimetric temperature of ABS. UL-94 flame test showed that the LDH was effective as an unprecedented fire retardant. The morphology evaluated by SEM indicates good dispersion and adhesion between LDH and ABS and TEM indicates most of the LDH exfoliated with formation of SAN occluded in the phases. Generally, composites may fulfill the requirements for a high-performance additive-type flame retardant system, i.e., one that reduces flammability while improving the other performance properties of the final formulated product. Therefore, LDH-PTS can be utilized as a flame retardant additive or in combination with other flame retardant additives. Indeed, this approach can be utilized to successfully improve both the flammability and the mechanical properties of many polymer systems.

3.6 References


CHAPTER 4

POLYETHYLENE-LDH NANOCOMPOSITES: FLAME RETARDANCY
AND MECHANICAL PERFORMANCE

4.1 Introduction

Over the years there has been a great concern worldwide for fire safety which has resulted in an increase focused on developing fire retarding materials for various applications. For example, linear density polyethylene (LDPE), a combustible material, but has excellent mechanical properties, low-temperature resistance, insulation properties, and chemical corrosion resistance is widely used as a commodity thermoplastic polymer. However, the drawback of LDPE is that it catches fire easily and burns with dripping. Therefore, it cannot meet all the required properties for specific purpose. A wide range of flame retardants materials has been used for LDPE to reduce its flammability. For several years, halogenated flame retardant materials were used to produce flame retardant polymeric materials, however, during a fire, materials containing halogen produce corrosive and toxic gases as well as dense smoke that make escape difficult. Recent research has raised concerns about persistence and toxicity of the flame retardants. Some flame retardants are ubiquitous in the environment. Rapidly increasing levels have been measured in sediments, marine animals and humans indicating a significant potential for damage to ecological and human health. Therefore, there is also an increasing demand from the market for eco-friendly halogen-free flame retardants, such as aluminum.
hydroxide and magnesium hydroxide which are already in commercial use. These materials reduce the flammability of the plastic by virtue of their endothermic decomposition which absorbs heat from the substrate and accompanying evolution of water vapor which dilutes the oxygen in the surroundings. In addition to improving resistance to ignition, a second key property of flame retardants is the ability to suppress smoke production if a fire does occur.

In general, intumescent flame retardants and bromine containing flame retardants are effective flame retardants for polyolefins. Compounds such as ammonium polyphosphate (APP) acts as synergists in the polyolefin matrix. This additive system forms char and barrier layer on the surface of the ignited plastic thus preventing burning. The unfavorable characteristics of such a system are low compatibility, poor appearance and susceptibility to melt dripping. Metal hydroxides work on the mechanism of endothermic decomposition, the process is accompanied by a foaming process. The inert gas which is released by the metal oxide helps in diluting the flammable gaseous degradation process. The ignition of the material is prevented by cooling, insulating and diluting phenomena. Haurie et al.\textsuperscript{2} reported a synthetic hydromagnesite material from an industrial by-product and used as a flame retardant with the combination of aluminum hydroxide. Furthermore, the development of systems based on nanostructure hybrid organic-inorganic materials is a topic of increased research in recent years. In this context, much attention has been focused on the systems in which layered materials (layered silicates and layered double hydroxides) are dispersed at a nanometric level in a polymeric matrix, which exhibit specific properties, not attainable from only one of the
two single components. However, the most studied systems are those based on clay or layered silicates, due to easily available clay starting materials and well-understood intercalation and exfoliation chemistry. Recently, studies have been focused on layered double hydroxides (LDHs) which represent a different class of nanofillers for polymers.

LDH’s is a new emerging class of the most favorable layered crystals for preparation of multifunctional polymer/layered crystal nanocomposites. In contrast to clay minerals with negatively charged layers, LDHs are host-guest materials consisting of positively charged metal oxide or hydroxides sheets with intercalated anions and water molecules. LDH are anionic clays of the general formula $[M^{(II)}_{1-x}M^{(III)}_x(OH)_2]^{x^+}[A^{m-}]_{x/m} \cdot 2H_2O$ where $M^{(II)}$ is a divalent metal ion (like Mg$^{2+}$, Zn$^{2+}$, etc.), $M^{(III)}$ is a trivalent metal ion (like Al$^{3+}$, Cr$^{3+}$, etc.) and $A^-$ is an anion (like CO$_3^{2-}$, Cl$^-$, NO$_3^-$, etc.).

![Figure 4.1 Typical structure of LDH](image)

The basic layer structure of LDHs is based on that of brucite [Mg(OH)$_2$] which is of the CdI$_2$ type, typically associated with small polarizing cations and polarizable anions. It consists of magnesium ions surrounded octahedrally by hydroxide ions. These
octahedral units form infinite layers by edge-sharing, with the hydroxide ions sitting perpendicular to a plane of the layers. The layers then stack on top of one another to form the three-dimensional structure. Conventionally synthesized LDHs are strongly hydrophilic materials, either amorphous or microcrystalline with hexagonal habit, and the dominant faces developed parallel to the metal hydroxide layers. Adjacent layers are tightly bound to each other. Properties of LDH are as follows: Highly surface active, uniform size and shape synthetic nanofillers. Functionalization can be tailored to release water and carbon dioxide and chemistry can be also tailored to enhance char formation. One of the advantages of LDHs among layered materials is the great number of possible compositions and metal-anion combinations that can be synthesized.

LDH compared to Montmorillonite layered silicates have high charge density dependent on the metal ratio. A lowers divalent: trivalent ratio, the higher the charge density; more trivalent the metal, more positive charge. They can be synthesized by control of particle size distribution. Recent studies have shown that LDH has better flame retarding properties than either ATH or MH and the layered structure play a key role in this respect. Previous studies have been focused on the montmorillonite-type of layered silicate compounds, whereas the LDH systems have been much less studied because of the strong interlayer electrostatic interactions, small gallery space, and hydrophilic property of LDH and endothermic decomposition.

Polyethylene is an easily combustible material and to achieve flame retardancy a number of routes are commercially available. For example, addition of fillers to polyethylene matrix to form composites is a route to achieve fire resistance. Li et al.
have studied the flame retardancy of LDPE and wood fiber composites, both easily flammable materials. Samples were prepared by mixing LDPE, wood-fiber, maleated polyethylene and other additives. Ammonium polyphosphate is used as a flame retardant and Pentaerithritol (PER), a low molecular weight polyalcohol was chosen as a char forming agent as it can be easily dispersed into the interface wood fiber and maleated polyethylene. In general, intumescent flame retardants and bromine containing flame retardants are effective flame retardants for polyolefins.

The most recent research in the field of flame retardancy of polyethylene using LDH, functionalized with organic materials has been carried out by Costa et al. However, despite current research endeavor, polyethylene continues to burn easily and till date not much has been accomplished as a way of success in order to slow down the rate of combustion in a variety of additives that has been added to it. Therefore, the objective of this work focuses on the preparation of a new non-halogen synergism organo LDH hybrid materials and its effect on polyethylene. In addition, an examination of the thermal and mechanical properties of this nanocomposite was made. Nanocomposites of LDPE and LDH were prepared by melt bending in an extruder. The nanocomposites were characterized by x-ray diffraction spectroscopy (XRD), scanning electron microscopy (SEM), thermo-gravimetric analysis (TGA) and transmission electron spectroscopy (TEM). The morphological features of the LDH particles after melt compounding show a decrease in particle size and agglomeration of particles. TGA results revealed increasing onset decomposition temperature and the darkening of the color of the residue indicated the presence of some carbonaceous materials. Fire retardancy test by UL-94 with both the
vertical and horizontal were conducted. All the samples failed the vertical burn test, but useful information regarding the dripping behavior was obtained. The LDPE/LDH nanocomposites pass the UL-94 HB rating. The linear burn rate steadily decreased with an increase in percentage of LDH. The LDH materials facilitate formation of carbonaceous char during combustion making them more effective flame retardants than metal hydroxides. As the LDH concentration increases, the melt viscosity also increases.

4.2 Experimental

4.2.1 Materials

The LDPE was purchased from CP Chem in the form of pellets of grade Marlex and Marflex™. Magnesium nitrate hexahydrate (Mg(NO$_3$)$_2$.6H$_2$O, 98%, reagent grade), para-toluene sulfonic acid (pTSA, 98.5%, ACS reagent grade), Aluminum monohydrate (Al(NO$_3$)$_3$.9H$_2$O, 98%, ACS reagent grade) and Nickel chloride hexahydrate NiCl$_2$.6H$_2$O (ReagentPlus) were obtained from Sigma-Aldrich. Sodium hydroxide (50% NaOH, reagent grade) solution was obtained from Aefar Aesar.

4.2.2 Synthesis of Mg$_2$NiAl(OH)$_6$C$_7$H$_8$SO$_3$.2H$_2$O

139.4 g Mg(NO$_3$)$_2$.6H$_2$O (0.18 mol, 99%, ACS reagent, Sigma-Aldrich) was added to 68.0 g Al(NO$_3$)$_3$.9H$_2$O (0.18 mol, 98%, ACS reagent, Sigma-Aldrich) in a three necked flask. Into these mixtures were added about 1,813 ml of deionized water and a stirrer. The solution under N$_2$ was warmed up to 40 °C, and at this temperature 56.8 ml 50% NaOH (0.18 mol, Sigma-Aldrich) was added to the mixture. This solution was allowed to age for 24 hours, followed by cooling and centrifuging and washed two more times. The wet LDH NO$_3$ in a flask was first flushed with N$_2$ and then solution containing
68.9 g \( \text{C}_7\text{H}_8\text{O}_3\text{S.H}_2\text{O} \) (0.36 mol, 98.5%, ACS reagent, Sigma-Aldrich) in 750 ml deionized water and 18.9 ml 50% NaOH (0.36 mol, Sigma-Aldrich) was added to it under \( \text{N}_2 \). The solution was stirred for about 1 hr followed by centrifuging, washing two more times. To the wet LDH \( \text{C}_7\text{H}_8\text{SO}_3 \) in a flask was added a solution containing 43.1 g of \( \text{NiCl}_2\cdot6\text{H}_2\text{O} \) (0.18 mol, ReagentPlus, Sigma-Aldrich) in 750 ml of deionized water. The solution was stirred for about one hour, followed by centrifuging, washed two more times and the sample was dried over vacuum at 70\(^\circ\)C. Table 4.1 shows comparison of observed and estimated elemental content weight % in as-prepared and Mg to Al in the LDH sample.

4.2.3 Preparation of LDH/LDPE Nanocomposites

The LDH was further dried at 80°C for 30 minutes to reduce moisture. A batch processor, C. W. Brabender, was used for melt mixing LDPE and the desired weight percent LDH. The Brabender was preheated to a temperature of 160°C and various mixtures with 5, 15, 30 and 60% by weight of LDH were prepared from the melt at a speed of 80 rpm for 5 minutes at a temperature of 160°C. The composite so obtained was pelletized as a precursor to the compression molding. The different blends were compression molded between two sheets of Teflon using a Carver press to obtain sheets. The Carver press was preheated to 160°C and a total of 5 metric tons of pressure was applied at a rate of 0.5 metric tons per minute. Dimensions of sample used, for the length = 128 mm, width = 13.4 mm and thickness = 4.65 mm.
4.3 Characterization

4.3.1 LDH Characterization Techniques:

4.3.1.1 Metals and C, H, N Analysis of LDH

The metals analysis was conducted using a Perkin-Elmer Analyst 300, with Perkin-Elmer supplied standards and element lamps. The LDH samples were dissolved in a 5% HNO$_3$ solution. The C, H, N, S analysis was performed by Elf Analytical Services, Inc.

4.3.1.2 Fourier Transform Infrared (FTIR) Analysis

To ensure that the nitrate anions were successfully exchanged by PTS anions, FTIR measurements of LDH NO$_3^-$, LDH PTS samples were performed using a Nicolet Nexus 6700 FT-IR spectrometer (Nicolet, USA) having a resolution of 4 cm$^{-1}$, a scan range of 4000 to 400 cm$^{-1}$. A total of 64 scans per sample were performed.

4.3.1.3 Wide Angle X-ray Diffraction (WAXD) Analysis

The XRD patterns were obtained using a Rigaku Ultima III X-Ray Diffractometer no internal or external standards. Each pattern was scanned from 2$\theta$ = 2 - 70$^\circ$ (2$\theta$), with a step size of 0.05$^\circ$ and a dwell time of 1.34 second, using CuK$\alpha$ radiation ($\lambda$ =1.540 Å).

4.3.2 LDPE/LDH Nanocomposites

4.3.2.1 Dispersion

4.3.2.1.1 Wide Angle X-ray Diffraction (WAXD) Analysis

X-ray diffraction technique was used to study the dispersion of clay in an LDPE matrix. X-ray diffraction patterns were collected at a scanning rate of 0.5°/min from 2$\theta$ =
2° to 2Θ = 70° with CuKα radiation (λ = 1.54Å) on a Rigaku Miniflex X-ray
diffractometer with a variable slit width Å on a Rigaku Miniflex.

4.3.2.1.2 Optical Microscopy

Optical microscopy was conducted using a Nikon optical microscope. The lens
magnification was 10X. The pictures were taken using a Nikon camera. The samples
were prepared by cutting the specimen with a sharp razor blade and freeze polished using
liquid nitrogen.

4.3.2.1.3 Scanning Electron Microscopy (SEM)

The fractured surface of the LDPE and LDH/LDPE nanocomposites obtained after
tensile testing were used for SEM imaging to study the distribution of clay platelets in the
polyethylene matrix on Nova 200 Dual Beam FIB / FESEM. The fractured surfaces were
sputter coated with gold to reveal the microstructure. The morphology of LDH and the
char structure of LDPE and LDPE/LDH nanocomposites were studied by ESEM –FEI
Quanta. The imaging was done in the low vacuum mode at a chamber pressure of 0.23
Torr and a voltage of 15 kV at a spot size of 5.

4.3.2.2 Thermal Analysis

4.3.2.2.1 Differential Scanning Calorimetry (DSC)

DSC data was obtained on a Perkin-Elmer DSC 7 instrument. The system was
calibrated using elemental indium. About 5-10 mg of sample was used for each run. A
first heating scan was from 30°C to 200°C at the heating rate of 10 °C/min. It was held at
200 °C for one minute and cooled from 200 °C to 30°C at a cooling rate of 10°C/min. The
second scan was a repetition of the first heating and cooling cycle.
4.3.2.2 Thermo-gravimetric Analysis (TGA)

TGA measurements were carried out with a TGA 6 Perkin-Elmer analyzer under a nitrogen atmosphere. Around 10 mg of sample was used. The measurements were performed from 30-800 °C.

4.3.2.3 Mechanical Properties

Mechanical properties of the films were measured by means of material test system (MTS). Tensile measurements for the samples are of the dimensions specified in ASTM D638.

4.3.2.4 Flammability Test

UL-94 HB Flame testing was on 5 samples according to ASTM D 635-98 standard. The time and extent of burning and the linear burn rate was obtained.

4.4 Results and Discussion

4.4.1 Elemental and X-Ray Diffraction Analysis

The results from elemental analysis showed that the Zn : Al content in the LDH samples were in agreement with the as-prepared LDH, though with few amount of carbonate in the sample (Table 4.1).

<table>
<thead>
<tr>
<th>LDH Sample</th>
<th>%Mg</th>
<th>%Al</th>
<th>%Ni</th>
<th>C%</th>
<th>H%</th>
<th>S%</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-prepared Mg$_2$NiAl(OH)$_6$(C$_7$H$_8$SO$<em>3$)$</em>{0.7}$(CO$<em>3$)$</em>{0.15}$.5H$_2$O</td>
<td>12.5</td>
<td>6.6</td>
<td>4.6</td>
<td>15.6</td>
<td>4.5</td>
<td>5.2</td>
</tr>
<tr>
<td>Mg$<em>2$Ni$</em>{0.3}$Al(OH)$_{6.8}$</td>
<td>12.6</td>
<td>6.7</td>
<td>4.4</td>
<td>15.0</td>
<td>4.8</td>
<td>5.6</td>
</tr>
</tbody>
</table>
Table 4.2 XRD patterns of LDH showing the characteristics of the different reflectance peaks.

<table>
<thead>
<tr>
<th></th>
<th>MgNiAl-LDH-PTS</th>
<th>MgAl-LDH-NO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2θ)°</td>
<td>(003) 5.047 (006) 10.344 (009) 20.645</td>
<td>(003) 9.85 (006) 19.80 (009) 34.40</td>
</tr>
<tr>
<td>d spacing(nm)</td>
<td>1.749 0.854 0.429</td>
<td>0.897 0.447 0.260</td>
</tr>
<tr>
<td>FWHM</td>
<td>0.858 0.604 0.635</td>
<td>0.732 0.693 0.532</td>
</tr>
<tr>
<td>XS(nm)</td>
<td>9.68 13.80 13.41</td>
<td>11.38 12.16 16.34</td>
</tr>
</tbody>
</table>

°2-Theta degree, Full-width half maximum, Crystallite size.

Figure 4.2 XRD of LDH-NO₃ and LDH-PTS-Ni.

From Figure 4.2, illustrating the XRD patterns of the LDH-PTS/Ni along with LDH-NO₃, it can be seen that the diffractions peaks especially the (003) associated to the interlayer distance moves to lower angles as a result of the replacement of the nitrate ions with the p-toluene sulfonate ions (PTS) with increase in the interlayer distance of the LDH from
0.89 to 1.75 nm (Table 4.2). This indicated the intercalation of the PTS anions in the LDH and the thickness of the LDH layer is evaluated to be 0.48 nm. The orientation of the PTSNi will be similar to that of the anions in chapter 3 with PTS anions lying perpendicular to the brucite layer. The uptake amount of nickel is very small and the ratio of Zn to Al in the Ni doped materials is also 2:1. XRD and elemental analysis shows that there is no significant difference between the LDH PTS with and LDH PTSNi. This indicates that the nickel presents in the sample cannot be present in the interlayer area and also cannot be in the LDH sheets. Therefore, nickel will be adsorbed onto the surface of the LDH layer.

Figures 4.3 and (Table 4.3) shows the XRD patterns of LDH and LDH/LDPE. The (110) peak of PE is observed at a reflectance angle of 21.3° and the d-spacing is 0.41 nm while the (200) peak is observed at a reflectance angle of 23.5° and the d-spacing at 3.7 nm. The predominant peak of LDH is at (003) peak at a reflectance angle of 4.5° and d-spacing 1.78 nm and the FWHM is found to be 1.31. The crystallites size can be calculated using the Debye-Scherrer equation,

\[ D_{hkl} = \frac{0.9 \lambda}{\beta_{1/2} \cos \theta} \]

where \( \lambda \) is the X-ray wavelength, \( \theta \) the diffraction angle, \( \beta_{1/2} \) the width at half-maximum intensity.
Figure 4.3 XRD patterns of LDPE and LDH nanocomposites.

Table 4.3 XRD patterns of LDH and the nanocomposites: effect of LDH addition on the (110) peak.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$2\theta$ (°)$^a$</th>
<th>d (nm)$^b$</th>
<th>FWHM$^c$</th>
<th>XS (nm)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE</td>
<td>21.3</td>
<td>0.41</td>
<td>0.86</td>
<td>9.82</td>
</tr>
<tr>
<td>5LDH</td>
<td>21.4</td>
<td>0.41</td>
<td>0.70</td>
<td>12.07</td>
</tr>
<tr>
<td>15LDH</td>
<td>21.4</td>
<td>0.41</td>
<td>0.67</td>
<td>12.61</td>
</tr>
<tr>
<td>30LDH</td>
<td>21.4</td>
<td>0.41</td>
<td>0.89</td>
<td>9.49</td>
</tr>
<tr>
<td>60LDH</td>
<td>21.4</td>
<td>0.41</td>
<td>0.68</td>
<td>12.42</td>
</tr>
</tbody>
</table>

$^a$2-Theta degree, $^b$Interlayer spacing, $^c$Full width half maximum, $^d$Crystallite size, $^e$Reflection planes.

In the nanocomposites, the effect of LDH on LDPE was studied in the LDPE contributive peaks. XRD data indicates the intercalation of LDPE with LDH. It can be observed that the layered structure of the LDH was retained in the nanocomposites.
indicating intercalation. The addition of the nanoclays increases the crystallinity of the LDPE matrix.

4.4.2 Differential Scanning Calorimetry

Figure 4.4 DSC heating and cooling scan of LDPE and composites.
Table 4.4 Detailed information obtained from DSC thermal analysis of LDPE and its composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_m$ (°C)$^a$</th>
<th>$T_c$ (°C)$^b$</th>
<th>$\Delta H_m$ (J/g)$^c$</th>
<th>$\Delta H_c$ (J/g)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE</td>
<td>98.87</td>
<td>98.8</td>
<td>44.2</td>
<td>44.2</td>
</tr>
<tr>
<td>5LDH</td>
<td>115.0</td>
<td>101.8</td>
<td>76.3</td>
<td>89.1</td>
</tr>
<tr>
<td>10LDH</td>
<td>114.7</td>
<td>113.0</td>
<td>36.9</td>
<td>48.2</td>
</tr>
<tr>
<td>30LDH</td>
<td>114.9</td>
<td>103.0</td>
<td>38.9</td>
<td>54.9</td>
</tr>
<tr>
<td>60LDH</td>
<td>114.2</td>
<td>103.9</td>
<td>60.6</td>
<td>35.4</td>
</tr>
</tbody>
</table>

$^a$Melting temperature, $^b$Crystallization temperature, $^c$Melting enthalpy, $^d$Crystallization enthalpy.

Figure 4.4 shows the DSC chromatograms of pure LDPE and its composites with LDH. DSC results indicate an increase in melting point in the heating scan with the addition of LDH. These results indicated a favorable interaction existing between the LDH surfactant and LDPE chains, the latter segmental motion being restricted by the formal leading to improved thermal properties experienced (Table 4.4). The LDH incorporates crystallinity to the PE matrix. The peak shift is a maximum at 5% LDH, and not much change is observed with the increase in weight percentage of LDH. This implies that 5% is the threshold. A slight transition region is observed at around 50° C which is typical of LDPE. A peak shift is also observed in the cooling scan with the addition of LDH in the LDPE matrix. The temperature of transition is a maximum at 60% LDH, there is no significant difference in the temperature of transition with the increase in weight percentage of LDH. The value of $\Delta H$ decreases with an increase in LDH. Nucleation is observed with the shifting of the curve towards higher temperatures an increase in the start of crystallization, attributing to the short chained structure of LDPE.
Figure 4.5 Optical images of the microstructures of (a, b, c and d) for 5, 15, 30 and 60% LDH, respectively, in LDPE matrix showing the formation of LDH agglomerates in PE matrix.

4.4.3 Optical Microscopy

As observed from the optical microscopy images (Figures 4.5), agglomerates were found in all concentrations of LDH/LDPE matrix. The agglomeration tends to increase with an increase in the LDH content and uniform dispersion was observed in the case of nanocomposites. The optical microscope images indicated increased particle size and a decrease in the number of particles indicated the formation of agglomerates in the nanocomposites. Also observed is the maximum particle size which increases with the increase in weight percentage of the nanoclays.
4.4.4 Thermo-gravimetric Analysis

Figure 4.6 TGA curves of pure LDPE and blends with LDH.

Figure 4.6 shows the TGA curves of 5, 15, 30 and 60 % LDH blends. As in the figure, the TGA curve of pure LDH exhibits a single weight loss zone below 200°C and is centered at 131°C and multiple weight loss zones from 200 to 800 °C. The multiple weight loss zones are centered at 381 and 496°C. The first weight loss zone is attributed to evaporation of water present in LDH. The layered structure of LDH collapses at the second weight loss zone indicating the loss of the hydroxyl layers of the LDH and at the third weight loss zone, the degradation of PTS takes place. The thermal stability of the blends increases with increasing LDH content at 50% weight loss. It has been observed in TGA results that as the percentage of nanoclays increases, the weight loss percentage also
decreases thus indicating improvement of char formation with increased LDH concentration. Weight loss onsets, however, decrease with increased concentration as seen in Table 4.5.

Table 4.5 TGA data for LDPE and LDH nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Onset, °C</th>
<th>Endset, °C</th>
<th>Temp. of Max. Weight Loss, °C</th>
<th>Weight Loss, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE</td>
<td>456.61</td>
<td>487.54</td>
<td>480.16</td>
<td>99.91</td>
</tr>
<tr>
<td>LDH</td>
<td>358.08</td>
<td>544.32</td>
<td>506.75</td>
<td>36.30</td>
</tr>
<tr>
<td>5LDH</td>
<td>456.89</td>
<td>489.68</td>
<td>478.76</td>
<td>97.87</td>
</tr>
<tr>
<td>15LDH</td>
<td>456.73</td>
<td>489.55</td>
<td>477.56</td>
<td>88.75</td>
</tr>
<tr>
<td>30LDH</td>
<td>451.09</td>
<td>487.19</td>
<td>475.16</td>
<td>77.05</td>
</tr>
<tr>
<td>60LDH</td>
<td>355.43</td>
<td>477.36</td>
<td>477.36</td>
<td>57.92</td>
</tr>
</tbody>
</table>

4.4.5 Flame Retardancy Testing

Flame retardancy (FR) and the melt dripping of polyethylene has been a limiting factor in application of polyethylene. The flame retardancy of polymers can be improved by incorporating flame retardant chemicals in two ways: first as additives, second as reactives. Additives are compounds, which are mechanically mixed with polymers. On the other hand, reactives are chemically bound as an integral part of polymer structures.\textsuperscript{23,24} Layered double hydroxides are an emerging class of flame retardants. They have demonstrated excellent performance as flame retarding agents by incorporating self extinguishing properties in various polymers.\textsuperscript{25-27}
Figure 4.7 Char formation during HB 94 flame testing.
The flame retardant layer double hydroxide synthesized in our laboratory is used here in LDPE and Figure 4.7 and 4.8 shows digital photograph obtained during flame testing as well as results of flame retardant test results, respectively, for and LDH/LDPE nanocomposites. The pure LDPE samples burnt completely and left a slight residue on the mesh which had to be burned off to repeat the test for other samples. There was no charring with the addition of LDH, the samples burnt till the clamp and the formation of char was increased. The density of the chars increased with the percentage of LDH. The char of the LDH nanocomposites produced a hardened and viscous mass. The 60% by weight specimen extinguished before the flame front reached the reference mark thus passing the 94 HB test (Figure 4.8). It was observed that with an increase in the weight
percentage of LDH, there was a decrease in the linear burn rate indicating longer time for flame propagation. The effect appears to be more in the case of LDH indicating that the LDH effectively showed down the rate of burning of LDPE providing time for the fire Marshall to extinguish the flame. Furthermore, the morphology of the char thus becomes an important study. It has also been observed that with the increase in percentage of LDH, the smoke evolved decreased considerably; this was observed by the exhaust fumes. Typically, additive system forms char and also barrier layer on the surface of the ignited plastic thus preventing burning. The unfavorable characteristics of such a system are low compatibility, poor appearance and susceptibility to melt dripping. Anna et al have come up with a novel idea of introducing a special type of elastomer in the system. The structure of elastomer helps in increasing the melt viscosity and the flame retardancy is improved by formation of ceramic barrier surface layer created during the combustion process.  

4.4.6 Morphological Analysis of Char

The study of char structure and morphology is important to understand the mechanism of flame retardance. The combustion appearance, the structure of the residual char and the polymers ability to affect combustion reveal the characteristics of both the polymer and the flame retarding material. A char can prevent combustible gases from feeding the flame and also separate oxygen from the burning material. During burning, there is a possibility of formation of instantaneous char which can extinguish the flame or there can be a presence of carbonaceous char which can be formed and destroyed several times during burning. Therefore, the residue is considered to be the final char.
Figure 4.9 depicts the char morphology of the LDH material. With an increase in the weight percent of clay, there is an increase in the char formation in both cases. PE and LDH nanocomposite shows small, equally sized particles which are well distributed and also nanocomposites showed agglomerates and chunks of particles. This morphology can
be due to formation of cross links between the LDH and PE and also to the collapse of the hydroxide layers and formation of larger sized particles, thus explaining the barrier formation mechanism. Slow volatilization of fuel polymer and 60 LDH nanocomposites reveals a dense char structure acting as a protective barrier which aided in the flame extinction.

4.4.7 Scanning Electron Microscopy

Figure 4.10 SEM of (a, b, c and d) for 5, 15, 30 and 60% LDH, respectively, in LDPE matrix showing the formation of LDH agglomerates in PE matrix.
Figure 4.10 shows SEM images of LDH/LDPE nanocomposites. The SEM images showed the distribution of the clay platelets in the polymer matrix. A few particles of LDH can be observed evenly distributed in the matrix as agglomerates which are distributed all over the matrix. As weight percentage of clay increases, the formation of agglomerates and their size also increases. As can be observed from the images of 60 wt% LDH, Figure 4.13 shows the formation of large lumps of LDH in the LDPE matrix. This microstructure supports the barrier formation mechanism of flame retardance, wherein, the agglomerates help in retarding the fire from propagating by forming a protective outer layer. Moreover, the morphology of the nanocomposites are supported by the optical microscopy images.

4.4.8 Mechanical Properties

![FR data of PE and LDH nanocomposites](image)

Figure 4.11 Dependence of linear burn rate on weight % of LDH nanocomposites.
Figure 4.12 Young modulus and strain at break.

(a) Young modulus

(b) Strain at break
Figures 4.11, 4.12 and Table 4.6 shows the mechanical properties of LDH with the polymer. As in the figure, the modulus of LDPE/LDH nanocomposites increases with the addition of 5 weights of percent of both clays. Further increase in the clay content resulted in a decrease in the modulus. This result shows the dispersive nature of LDH material that result in the interaction between the LDH and the polymer chains affecting the polymer matrix. The LDH/LDPE nanocomposites, showed a steady increase in the modulus value with 30 % and then a sharp decrease with the addition of 60 % clay. Studies have shown that clay was effective in enhancing thermal stability and mechanical properties of polymers.\textsuperscript{30,31} and as well as enhancing flame retardancy properties.\textsuperscript{32}

Table 4.6 Mechanical properties.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Young’s Modulus (MPa)</th>
<th>Strain at break</th>
<th>Elongation at break (N/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>538.4 ± 5.98</td>
<td>95.1 ± 3.60</td>
<td>32.4 ± 4.56</td>
</tr>
<tr>
<td>5 LDH</td>
<td>564.8 ± 2.98</td>
<td>25.8 ± 3.81</td>
<td>15.1 ± 2.33</td>
</tr>
<tr>
<td>15 LDH</td>
<td>567.6 ± 2.76</td>
<td>14.4 ± 2.56</td>
<td>9.4 ± 3.14</td>
</tr>
<tr>
<td>30 LDH</td>
<td>494.9 ± 1.02</td>
<td>11.5 ± 1.69</td>
<td>5.6 ± 1.34</td>
</tr>
<tr>
<td>60 LDH</td>
<td>449.1 ± 1.10</td>
<td>1.7 ± 0.09</td>
<td>0.8 ± 0.02</td>
</tr>
</tbody>
</table>

In the case of LDPE/ LDH nanocomposites, as for the strain, the LDPE/ LDH nanocomposites shows an increase in the percentage of LDH resulted in a decrease in the strain at break values. A steep decrease at 5% LDH loading was observed and not a significant change thereafter. In the case of LDPE/LDPE nanocomposites, there was a gradual decrease of strain at break values and not a significant difference was observed at 30 and 60 weight percent clay loading.
4.5 Conclusions

This study successfully examined the synthesis of LDH-PTS and its nanocomposites with LDPE, flammability studies and mechanical properties. The LDH-PTSNi was characterized by XRD, FTIR, TGA, DSC and SEM. The morphology of the nanocomposites was studied by optical microscopy, SEM and XRD techniques. The material shows dispersion as well as formation of agglomerates in some areas.

TGA studies of thermal properties indicated a decrease in weight loss percentage with the increase in nanoclay concentration. DSC results shows shifts in endothermic peak indicating the effect of LDH on the polymer matrix with about 17% increase in melting temperature. About 10% increase in the crystallization temperature was also observed in the materials and LDH imparted crystallinity to the polymer.

Mechanical behavior of the material was also studied. Increase in LDH concentration shows improved stiffness in the composites indicating the effect of the LDH and results of flammability test indicated that the 60LDH shows the best flame retarding properties and high stiffness in the nanocomposites. In addition, the LDH/LDPE nanocomposites show a steady decrease in the linear burn rate with an increase in LDH concentration. Thus, the potential utility of LDH as an effective flame retarding agent for polyethylene has been successfully studied.

4.6 References


5. Romeo, V.; Gorras, G.; Chronakis, V.; Chronakis, I. S. Biomacromolecules 2007, 8, 3147.


CHAPTER 5
POLY (L-LACTIC ACID)-LDH NANOCOMPOSITES: DRUG RELEASE AND DECREASED TOXICITY

5.3 Introduction

Synthetic materials are increasingly being used in clinics and hospitals for surgical sutures, in guided tissue regeneration,\(^1\) as bone filler,\(^4\,5\) and in drug delivery systems.\(^6\) The deployment of biopolymers such as poly lactic acid (PLLA) as implants in the body has been an area of some concern.\(^10\) Concerns include possible inflammation of the tissue around the biopolymers leading to increased cell adhesion, and mechanical performance of the implant. Decreased cell proliferation have been found in prior efforts based on incorporating drugs into inorganic materials such as montmorillonite and layer double hydroxide (LDH) clays.\(^11\) The biocompatibility of the LDH\(^14\) makes them an ideal choice for safe drug delivery. The use of polymers as hosts for drug delivery has also been of considerable interest. In particular, studies of bio-implants with ibuprofen-modified PLLA have shown that ibuprofen inhibits the smooth muscle cells (SMCs) proliferation and demonstrated ibuprofen’s role in reducing implant-associated restenosis in arteries.\(^17\)

Generally, clays have also been found to increase the mechanical properties of polymers. Nanocomposites based on dispersion of smectite clays have proven to be

---

particularly useful because improved properties can be obtained with the addition of a few percentages by weight. The driving parameter for improved mechanical performance is the enhanced interfacial area afforded by expanding and dispersing nanoplates in the medium. The nanoplates can either be cation exchanging or anion exchanging. Montmorillonite, for instance, is the commonly investigated cation exchanged clays. LDHS have a general formula \([\mathrm{M}^{\mathrm{II}}_{1-x}\mathrm{M}^{\mathrm{III}}_x(\mathrm{OH})_2]^x^-\mathrm{A}^{n^-}_{\times/n}\mathrm{mH}_2\mathrm{O}\), where \(\mathrm{M}^{\mathrm{II}}\) represents a divalent metal, \(\mathrm{M}^{\mathrm{III}}\) a trivalent metal, and \(\mathrm{A}^{n^-}\) an anion. They have a brucite-like structure in which a fraction of the divalent metal is replaced with a trivalent metal. The replacement gives the layers a positive charge, and anions are intercalated between these layers to maintain the electro-neutrality. Intercalation of organic compounds into LDHs provides a useful synthetic route to prepare organic-inorganic hybrids that contain properties of both the organic guest and the inorganic host in a single material. The resulting properties can be tailored to a specific requirement needed to serve specific purposes.

A dual functionality of decreased cell proliferation and enhanced mechanical properties may be possible if the LDH is functionalized by non-steroidal anti-inflammatory drugs (NSAIDs) such as ibuprofen. In this paper, we present the possibility of using nanoclay fillers functionalized with a noninflammatory drug (ibuprofen) for a combined benefit of decreased cell adhesion and improved mechanical performance. No study of LDH ibuprofen with PLLA nanocomposite has been reported to our knowledge. Films were spun-cast; and dispersion, thermophysical characterization, cell proliferation and drug release measurements were conducted using various analytical methods.
5.4 Experimental

5.4.1 Materials

Poly (L-lactic acid) or PLLA ($M_n = 98,600$, $M_w = 194,799$ Daltons) was supplied by NatureWorks LLC (MN, USA) and dried in oven for 48 hours at 35°C. Dichloromethane (>99.8% purity, EMD), sodium hydroxide (50% NaOH solution, Sigma-Aldrich), aluminum nitrate hexahydrate ($\text{Al(NO}_3\text{)}_3 \cdot \text{H}_2\text{O}$, Alfa Aesar), zinc nitrate hexahydrate ($\text{Zn(NO}_3\text{)}_2 \cdot \text{6H}_2\text{O}$, Alfa Aesar), sodium salt of ibuprofen (Sigma) were used as received for the synthesis of different layered double hydroxides.

5.4.2 Preparation of Zn-Al LDH Nitrate

To prepare 2 gm of 2:1 Zn-Al LDH Nitrate, 4.08 gm of $\text{Al(NO}_3\text{)}_3 \cdot \text{6H}_2\text{O}$, and 11.87 gm of $\text{Zn(NO}_3\text{)}_2 \cdot \text{6H}_2\text{O}$ were dissolved in 133 ml of freshly drawn deionized water (Millipore MilliQ Academic, 18.2 MΩ cm$^{-1}$). The solution was neutralized with 4.2 ml of NaOH to precipitate 2:1 Zn-Al LDH Nitrate under dry nitrogen. The water used for the preparation of the Zn-Al LDH Nitrate was heated to around 40 °C before the metal nitrates and sodium hydroxide were added and was stirred constantly to minimize the presence of CO$_2$. The precipitate was then aged in the mother liquor for 24 hours at a temperature of about 90 °C to 100 °C under a nitrogen gas blanket, after which it was allowed to cool and centrifuged to separate the precipitate. It was washed two more times with deionized water to remove any remaining ions from the mother liquor. This crystalline white solid, designated as LDH NO$_3$ (Zn-Al LDH Nitrate), was used for the exchange with sodium salt of ibuprofen. A nitrate precursor was made because the nitrate
anion is easier to exchange with the desired anion, ibuprofen here, than other general choices such as chloride and carbonate.

5.4.3 Preparation of Zn-Al LDH Ibuprofen

A solution of sodium salt of ibuprofen 3.64 gm in 50 ml of deionized water was added to a suspension of the nitrate precursor prepared as described above. The mixture was stirred under a nitrogen gas blanket for 1 hour before the precipitate was separated and washed twice with deionized water by centrifugation. The molar ratio of the sodium salt of ibuprofen to the LDH NO$_3$ was 1.2. This slight excess, in the place of 1:1, was used to facilitate the anion exchange. The crystalline white solid thus obtained was dried in a hot air oven at 70°C and is designated as LDH Ibu (Zn-Al LDH Ibuprofen).

5.4.4 Preparation of PLLA/LDH Ibu Nanocomposites

Nanocomposites were prepared by the solution casting route. Initially, the LDH Ibu powder was dispersed in 75 ml of dichloromethane and stirred for 10 minutes. Then 3.0 gm of PLLA was added and the mixture was heated at 40°C under vigorous stirring for 4 hours. The resulting dispersion was allowed to age for 24 hours. Nanocomposite films were prepared by spin casting and the samples were dried under vacuum at 35°C for 2 days to remove residual solvent. The LDH Ibu amounts corresponded to effective weight percentages of 1, 3 and 5% nanocomposites, which are referred to as 1LDH Ibu, 3LDH Ibu, and 5LDH Ibu, respectively. For the cell proliferation measurements, 1 ml of the resulting dispersion was collected in several cylindrical glass vials specially made with a volume capacity of about 2 ml. The solvent was allowed to evaporate from the vials, leaving a thin film of PLLA/LDH Ibu nanocomposite. Control samples of PLLA,
PLLA with ibuprofen (PLLA/Ibu) and PLLA with LDH NO$_3$ (PLLA/LDH NO$_3$) were also prepared as needed for control experiments.

5.5 Characterization

5.5.1 LDH Characterization

5.5.1.1 Metals and C, H, N Analyses of LDH Ibu

The metals analysis was conducted on the LDH NO$_3$ and LDH Ibu sample using a Perkin-Elmer Analyst 300, with Perkin-Elmer supplied standards and element lamps. The sample was dissolved in a 5% HNO$_3$ solution. The C, H, N analysis was performed by Elf Analytical Services, Inc.

5.5.1.2 Fourier Transform Infrared (FTIR) Analysis

To ensure that the nitrate anions were successfully exchanged by ibuprofen anions, FTIR measurements of LDH NO$_3$, LDH Ibu and sodium salt of ibuprofen (Ibu) samples were performed using a Nicolet Nexus 6700 FT-IR spectrometer (Nicolet, USA) having a resolution of 4 cm$^{-1}$, a scan range of 4000 to 400 cm$^{-1}$. A total of 64 scans per sample were performed.

5.5.1.3 Wide Angle X-ray Diffraction (WAXD) Analysis

To confirm the success of the functionalization process, WAXD measurement was conducted on the LDH NO$_3$ and LDH Ibu samples. For all samples, diffractograms were obtained with a Rigaku model D/Max–Ultima III X-ray Diffractometer (generated at 44 mA and 40 kV). Each sample was scanned from 2° to 70° (2θ), with a step size of 0.05° and a dwell time of 1.34 seconds, using CuKα radiation ($\lambda = 1.540562$ Å).
5.5.2 PLLA/LDH Nanocomposites

5.5.2.1 Dispersion

5.5.2.1.1 Wide Angle X-ray Diffraction (WAXD) Analysis

WAXD measurement was also conducted on the PLLA/LDH Ibu nanocomposites in order to study the dispersion of the nanofiller in the PLLA matrix. For all samples, diffractograms were obtained with a Rigaku model D/Max–Ultima III X-ray Diffractometer (generated at 44 mA and 40 kV). Each sample was scanned from 2° to 70° (2θ), with a step size of 0.05° and a dwell time of 1.34 seconds, using CuKα radiation (λ =1.540562Å).

5.5.2.1.2 Transmission Electron Microscopy (TEM) Analysis

TEM was used to complement WAXD results on nanoplatelet dispersion. Bright field TEM images were recorded on Philips EM 420 equipment at an accelerating voltage of 120 kV. Prior to the analysis, samples of pure PLLA and PLLA/LDH Ibu nanocomposites were sandwiched and glued between two sheets of epoxy resin. The sandwiched samples were then cut into slices of a nominal thickness of 90 nm with a diamond knife on RMC MT 6000 ultra microtone at room temperature. The sections were transferred from water at room temperature onto a 200-mesh copper grid.

5.5.2.2 Thermal analysis

5.5.2.2.1 Thermo-gravimetric Analysis (TGA)

Thermal stability of the neat LDH Ibu, neat sodium salt of ibuprofen, neat PLLA and the nanocomposites was performed with a Perkin-Elmer TGA6. Around 15 mg of each sample was weighed in a standard ceramic pan and run under nitrogen atmosphere.
The measurements were performed from 30 to 700 °C at 10°C/min. All TGA measurements were done in duplicate.

5.5.2.2 Differential Scanning Calorimetry (DSC)

Thermal properties of the parent PLLA and the nanocomposites were recorded on a DSC 6 Perkin-Elmer apparatus under a nitrogen atmosphere. The system was calibrated using elemental indium. The samples were run from 30 to 200 °C, held at 200 °C for 5 minutes to erase their thermal history and then cooled to 30 °C. The heating and cooling rates were maintained at 10 °C/min. Two runs were conducted and each sample was tested in duplicate.

5.5.2.3 Mechanical Properties

5.5.2.3.1 Dynamic Mechanical Analysis (DMA)

The viscoelastic properties of the parent PLLA and its nanocomposites were measured using a dynamical mechanical analyzer (DMA), Rheometric solids analyzer 3 (RSA III TA Instruments, NJ, USA), operating in the tensile mode. The mean sample dimensions are 5 mm × 25 mm with a mean thickness of 140 µm. Samples were scanned from -50 to 100 °C at a heating rate of 3 °C/min, a frequency of 1 Hz and a strain amplitude of 0.25% (determined from a separate strain amplitude sweep at 1 Hz to establish the linear viscoelastic region). All DMA measurements were done in triplicate.

5.5.2.3.2 Tensile Testing

Tensile properties of the neat PLLA and its nanocomposites were measured using a dynamical mechanical analyzer (DMA), Rheometric solids analyzer 3 (RSA III TA Instruments, NJ, USA), operating in the tensile mode with a strain rate of 0.04 min⁻¹.
Three samples of $25 \times 5 \text{ mm}^2$ with a thickness of $0.15 \pm 0.01 \text{ mm}$ were taken to get the average tensile properties.

5.5.2.4 Biofunctionalities

5.5.2.4.1 Smooth Muscle Cells (SMCs) Proliferation Studies

Human aortic smooth muscle cells (SMCs) obtained from Cascade Biologics were cultured in a complete medium consisting of Dulbecco’s modified eagle medium (DMEM) supplemented with 10% fetal bovine serum (FBS) and 1% penicillin-streptomycin. Cells were incubated in a humid environment at $37^\circ \text{C}$ and 5% CO$_2$. Upon 80-90% confluency, the cells were passaged or used for experiments. Cells up to passage 9 were used in the experiments. Before cell studies, all glass sample vials were sterilized under UV for 30 minutes. For proliferation studies, SMCs were harvested after trypsinization from culture flasks and seeded onto glass vials (controls) and glass vials containing pure PLLA, and 1, 3 and 5wt% LDH Ibu-PLLA, Ibu-PLLA, LDH Ibu, LDH NO$_3$ or Ibu (pure ibuprofen) samples at an approximately seeding density of 9000 cells/$\text{cm}^2$. After 5 days of seeding, cells were washed with PBS and then lysed with 1 ml of the 1% Triton X-100 for 30 minutes at $37^\circ \text{C}$. Concentration of total cell sample DNA ($\mu$g of DNA/ml) as an equivalent to the cell number or the number of proliferation cells was determined by using PicoGreen DNA assay kits (Molecular Probes, Eugene, OR) following the manufacturer’s instructions.

5.5.2.4.2 Statistical Analysis

Analysis of the results was performed using ANOVA with post hoc comparisons (StatView 5.0 software, SAS Institute). For each study, the sample size was 4 ($n=4$) and
all the results are presented as mean ± standard deviation (SD). Results are considered as significantly different with p < 0.05.

5.5.2.4.3 High Performance Liquid Chromatography (HPLC) Drug Release

Drug release experiments were performed using HPLC (Thermo Scientific’s Finnigan Surveyor). The ibuprofen-loaded PLLA and PLLA/LDH Ibu films (35 × 20 mm) made in glass vials as described previously were incubated 37 °C with phosphate-buffered saline (PBS) having a pH of 7.4. The vials were capped for up to 5 days with mild shaking. At appropriate times, the PBS was collected and replaced with fresh buffer. Triplicate aliquot samples (20-µl of the PBS solution) were injected into the HPLC to determine the Ibu concentration released from the films. The HPLC conditions were as follows: column, Thermo C18 (150 × 4.6 mm); mobile phase, 60:40 acetonitrile: 0.1% trifluoracetic acid in water (pH of 2.55); flow rate of 1.5 ml/min; 20-µl injection; UV/vis detection at 220 nm. Ibuprofen eluted at these HPLC conditions at a retention time of 3.9 min. The peak areas were used to calculate the concentrations of ibuprofen released from the films. Triplicate analysis was done for each injection to obtain a relative standard deviation for each point in the Ibu release curves. Modified Freundlich plots of the experimental data match a diffusion controlled process for the release of Ibu.

5.6 Results and Discussion

5.6.1 Structural Characterization

Figure 5.1 represents the chemical structure of ibuprofen and Figure 5.2 shows the FTIR spectra of the pure LDH NO$_3$, sodium salt of ibuprofen (Ibu), and LDH Ibu. The spectrum of the salt$^{22, 23}$ shows alkyl stretching peaks around 3000 to 2800 cm$^{-1}$, carbonyl
stretch mode at 1703 cm\(^{-1}\), and the asymmetric and symmetric RCOO\(^-\) stretches at 1550 and 1380 cm\(^{-1}\). The peaks around 3380, 1384 cm\(^{-1}\), and 426 cm\(^{-1}\) in the spectrum of the parent nitrate material indicate the presence of nitrate interlayer anion and also confirm the Zn-Al LDH structure, as do the other broad peaks below 1000 cm\(^{-1}\). The loss of the characteristic nitrate peak (1384 cm\(^{-1}\)) and the presence of the ibuprofen anion peaks demonstrate the replacement of nitrate by this anion in the exchanged material. The C-H stretching vibrations at 2963 cm\(^{-1}\), shows the presence of the methyl group of the ibuprofen, and confirms the intercalation of the ibuprofen into the Zn-Al LDH layers. The band at 845 cm\(^{-1}\) corresponds to the C-H bend (\(\rho\)-substituted for the aromatic group), the absorption band at 1559 cm\(^{-1}\) corresponds to C=C stretch, the absorption band at 845 cm\(^{-1}\) corresponds to CH\(_2\) bend of the alkyl group for the substituted aromatic group, the absorption region at 744 cm\(^{-1}\) corresponds to CH out-of-plane bending of the aromatic ring, and the region from 410 to 500 cm\(^{-1}\) corresponds to X-O and to O-X-O (X = Mg, Zn, Al, Cu).\(^{24,25}\)

![Chemical structure of ibuprofen.](image)

**Figure 5.1 Chemical structure of ibuprofen.**

The WAXD pattern of the exchanged material LDH Ibu shows an interlayer spacing of 22.95 Å at a 2\(\theta\) of 3.84° for the (003) reflection peak (Figure 5.2).
This d-spacing is an increase from approximately 8.3 Å d-spacing of the nitrate precursor, which confirms intercalation of ibuprofen between the layers. The size of the ibuprofen molecule is 10-11 Å, and the d-spacing fits well with an interpenetrating double-layer arrangement model of the molecules in the gallery space. The other reflections (006), (009), and (0012) can also be seen clearly in the pattern, indicating the superior crystallinity of the material. For each reflection peak of LDH Ibu, the angle (2θ), d-spacing and the full width half maximum (FWHM) values are given in Table 5.1.
Table 5.1 WAXD characteristic peaks of LDH Ibu.

<table>
<thead>
<tr>
<th>LDH Ibu</th>
<th>(003)</th>
<th>(006)</th>
<th>(009)</th>
<th>(0012)</th>
<th>(0015)</th>
<th>(110/113)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reflection angle $2\theta$ (°)</td>
<td>3.84</td>
<td>7.94</td>
<td>11.94</td>
<td>15.95</td>
<td>20.10</td>
<td>60.50</td>
</tr>
<tr>
<td>Interlayer spacing (Å)</td>
<td>22.95</td>
<td>11.11</td>
<td>7.40</td>
<td>5.55</td>
<td>4.41</td>
<td>1.52</td>
</tr>
<tr>
<td>FWHM</td>
<td>0.69</td>
<td>0.57</td>
<td>0.58</td>
<td>0.62</td>
<td>0.56</td>
<td>0.80</td>
</tr>
</tbody>
</table>

Metal and elemental analyses showed a presence of 25.9% Zn, 5.4% Al, 29.6% C, 5.48% H, and 0.06% N in LDH Ibu. When compared to the theoretical percentages derived from the formula $\text{Zn}_2\text{Al(OH)}_6(\text{C}_{13}\text{H}_{17}\text{O}_2).2\text{H}_2\text{O}$ of 26.8% Zn, 5.56% Al, 31.1% C, 5.43% H, these amounts suggest a nearly complete exchange of the nitrate for ibuprofen. The negligibly small amount of nitrogen (0.06%) and the similarity between the theoretical and observed percentages of carbon provide proof for successful exchange and absence of carbon dioxide intercalation. We note that for every gram of LDH Ibu, 0.409 grams corresponded to ibuprofen.

5.6.2 Dispersion of the LDH Ibu in PLLA Matrix

Table 5.2 Effect of PLLA on the (003) reflection peak of LDH Ibu showing intercalated structure.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$2\theta$ (°)</th>
<th>d (Å)</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDH NO$_3$</td>
<td>9.80</td>
<td>9.01</td>
<td>0.23</td>
</tr>
<tr>
<td>LDH Ibu</td>
<td>3.84</td>
<td>22.95</td>
<td>0.69</td>
</tr>
<tr>
<td>1LDH Ibu</td>
<td>3.17</td>
<td>27.82</td>
<td>0.48</td>
</tr>
<tr>
<td>3LDH Ibu</td>
<td>3.15</td>
<td>27.99</td>
<td>0.81</td>
</tr>
<tr>
<td>5LDH Ibu</td>
<td>3.25</td>
<td>27.16</td>
<td>0.62</td>
</tr>
</tbody>
</table>

When the LDH Ibu was dispersed in the PLLA matrix, there was a slight additional intercalation of PLLA in between the nanofiller layers, resulting in a shift to lower $2\theta$ of the (003) reflection peak and increased d-spacing as shown in Figure 5.2 and Table 5.2.
The TEM micrographs of the PLLA/LDH Ibu nanocomposites are shown in Figures 5.3, 5.4 and 5.5, intercalated as well as exfoliated structure of LDH Ibu component can be observed. The images were analyzed using Image-J®. The dark lines are sections of the LDH Ibu layers of about 1.3 to 1.5 nm thickness. The distance between each dark line has an average distance of 14 to 17 nm. It is clear, however, that the localized structure shows an intercalated/exfoliated dispersion and that aggregation and clustering of the intercalated/exfoliated regions exist. Thus, uniform dispersion of the LDH Ibu in the PLLA matrix is limited as the nanofillers concentration increases.

Figure 5.3 TEM micrograph of PLLA/1LDH Ibu nanocomposites.
Figure 5.4 TEM micrograph of PLLA/3LDH Ibu nanocomposites.

Figure 5.5 TEM micrograph of PLLA/5LDH Ibu nanocomposites.
5.6.3 Thermal Stability

![TGA traces of neat Ibu, neat LDH Ibu, neat PLLA, and PLLA/LDH Ibu nanocomposites.](image)

The TGA curves (TG) of the neat PLLA, LDH Ibu, sodium salt ibuprofen (Ibu), and PLLA/LDH Ibu nanocomposites and their first derivative plots (DTG) are shown in Figure 5.6 and 5.7, respectively.

The thermal stability of the samples shows weight-loss behavior as a function of temperature. TGA and DTG curves of the Ibu show the total weight loss of nearly 80%, which corresponds to the loss of water (around 80 °C), and of ibuprofen between 380 and 545 °C. The TG curve of the LDH Ibu sample indicates 50% weight loss, which corresponds well with theoretical loss of water and the interlayer anion (ibuprofen) and formation of a mixture of ZnO and ZnAl$_2$O$_4$ residue.
Figure 5.7 DTG traces of neat Ibu, neat LDH Ibu, neat PLLA, and PLLA/LDH Ibu nanocomposites.

The residue was black, indicating the presence of some carbonaceous char. The DTG trace shows one bimodal weight loss zone centered at around 100 and 190 °C, respectively, and a single one centered at 450 °C. The weight loss zone at 100 °C is due to the evaporation of water molecules, both physically adsorbed and chemically bound; whereas that at 190 and 470 °C can be attributed to the collapse of hydroxide layers and the escape of the ibuprofen anion in the gaseous form, respectively. The presence of only three distinct thermal decomposition steps, of which two correspond to loss of water and collapse of hydroxide layers, suggests that there is only one interlayer anion (which corresponds to the only remaining step) and hence that the exchange can be considered nearly complete.
The thermal degradation of PLLA is very complex and includes intramolecular transesterification leading to lactic acid and cyclic oligomers, cis-elimination leading to acrylic acid oligomers, and fragmentation producing acetaldehyde and carbon dioxide.\textsuperscript{27} The DTG curve of PLLA shows two single weight-loss zones centered at 100 and 385 °C, respectively. The lower-temperature weight loss zone corresponds to moisture content (less than 3%), whereas the higher-temperature one can be attributed to the temperature of maximum decomposition (T\textsubscript{p}) of PLLA. Indeed, pure PLLA starts degrading at about 285 °C and completely decomposes (0% wt. char residue) at around 430 °C. For the PLLA/LDH Ibu nanocomposites, the shape of the TG curves is very similar to that of the parent PLLA, although the temperature of the decomposition step is lower. From the DTG curves, the T\textsubscript{p} decreased from 387 °C for pure PLLA to 331, 317, and 311 °C for 1LDH Ibu, 3LDH Ibu, and 5LDH Ibu, respectively, indicating the decrease in the thermal stability of the neat PLLA with increasing the LDH Ibu content. This behavior is due to the fact that the increase of the LDH Ibu loading thermally destabilizes the polymer matrix, thus decreasing the temperature of the maximum decomposition. Therefore, it might be concluded that the PLLA/LDH Ibu interfaces are the possible weak points of the nanocomposites. The thermal degradation of our nanocomposites left between 0.3-2% residues. Assuming that PLLA has been completely volatilized and the ibuprofen anions have been degraded, the weight residue remaining after 550 °C can be regarded as the real carbonaceous char content.
5.6.4 Thermal Transitions

The effect of the addition of LDH Ibu on the thermal transitions of PLLA was investigated by DSC (Figures 5.8 and 5.9).

![DSC traces for the second heating of neat PLLA and its nanocomposites showing the effect of the LDH Ibu on the glass transition, cold crystallization and melting temperature.](image)

Figure 5.8 DSC traces for the second heating of neat PLLA and its nanocomposites showing the effect of the LDH Ibu on the glass transition, cold crystallization and melting temperature.

The glass transition temperature ($T_g$), heat capacity ($\Delta C_p$), melting temperature ($T_m$), melting enthalpy ($\Delta H_m$), cold crystallization temperature ($T_{cc}$), cold crystallization enthalpy ($\Delta H_C$), melt crystallization temperature ($T_{mc}$), melt crystallization enthalpy ($\Delta H_{mc}$) and the degree of crystallinity ($X_c$) were obtained from the thermograms. The thermal properties of the cooling and second heating curves are summarized in Table 5.3.
Figure 5.9 DSC traces for the cooling of neat PLLA and its nanocomposites indicating the slight crystallization promoting effect of the LDH Ibu.

Table 5.3 Thermal properties of the cooling and second heating of PLLA and PLLA/LDH Ibu nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ ($^\circ$C)</th>
<th>$\Delta C_p$ (J/g.$^\circ$C)</th>
<th>$T_{cc}$ ($^\circ$C)</th>
<th>$\Delta H_{cc}$ (J/g)</th>
<th>$T_m$ ($^\circ$C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$\chi_c$ (%)</th>
<th>$T_{mc}$ ($^\circ$C)</th>
<th>$\Delta H_{mc}$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLLA</td>
<td>54.3</td>
<td>0.674</td>
<td>125.7</td>
<td>-37.3</td>
<td>-</td>
<td>164.2</td>
<td>39.5</td>
<td>29.3</td>
<td>-</td>
</tr>
<tr>
<td>1LDH Ibu</td>
<td>47.0</td>
<td>0.564</td>
<td>101.7</td>
<td>-41.4</td>
<td>154.8</td>
<td>163.8</td>
<td>60.4</td>
<td>45.2</td>
<td>93.7</td>
</tr>
<tr>
<td>3LDH Ibu</td>
<td>43.9</td>
<td>0.397</td>
<td>99.1</td>
<td>-33.8</td>
<td>152.0</td>
<td>161.0</td>
<td>54.0</td>
<td>41.2</td>
<td>96.7</td>
</tr>
<tr>
<td>5LDH Ibu</td>
<td>40.1</td>
<td>0.386</td>
<td>94.0</td>
<td>-30.0</td>
<td>145.3</td>
<td>156.4</td>
<td>51.2</td>
<td>39.9</td>
<td>98.1</td>
</tr>
</tbody>
</table>

The thermal transitions of PLLA in composite systems have been widely investigated.\textsuperscript{27-30} As seen in Figure 5.8, neat PLLA showed a $T_g$ at around 54.3$^\circ$C, $T_{cc}$ at 125.7, and a $T_m$ at 164.2 on heating. The $T_g$ decreased with increasing the LDH Ibu concentration. It decreased from 54.3$^\circ$C for pure PLLA to 47.0, 43.9 and 40.1 $^\circ$C for 1LDH Ibu, 3LDH Ibu and 5LDH Ibu, respectively. Fujimori et al.\textsuperscript{31} found that the $T_g$
values of the drawn PLLA/clay hybrid films slightly decrease with an increase in the clay concentration, suggesting that the free alkyl ammonium ion may associate with the PLLA chains and play a role in plasticizing the PLLA matrix. Thus, the decrease observed in our nanocomposites could be due to the plasticizing effect of the corresponding ibuprofen anions. Likewise, the heat capacity decreased with increasing the LDH Ibu content. It was found that with respect to the neat polymer, the PLLA/ LDH Ibu nanocomposites showed double endothermic melting points which shifted to the lower temperature with increasing the content of the nanofiller. The decrease in the melting points could indicate an increase in lamella thickness. These peaks could correspond to the $T_m$ of the crystalline phases, suggesting the presence of two crystalline phases in the samples and the fraction of the two $\Delta H_m$ reflect the relative amount of the crystalline phases in the PLLA/LDH Ibu nanocomposites. The values of $\Delta H_m$ in the nanocomposites are higher than that of the pure PLLA. However, in the PLLA/LDH Ibu nanocomposites, $\Delta H_m$ decreased with increased LDH Ibu content. The equilibrium heat of fusion of PLLA used to calculate the degree of crystallinity was 135 J/g.\textsuperscript{31} The degree of crystallinity increases by 54, 41 and 36% for 1, 3 and 5 LDH Ibu, respectively. The increase in the degree of crystallinity coupled to the decrease in melting point could imply that while the lamella thickness increased, the crystal density also increased. On the other hand, $T_{cc}$ showed a significant decrease when the nanofiller is added. It decreased from 125.7°C for the neat PLLA to 101.7, 99.1 and 94.0 °C for 1, 3 and 5 LDH Ibu, respectively. In the context of peak area, neat PLLA showed a noticeable broad cold crystallization peak which became narrow and smaller with increasing LDH Ibu content. The decrease in $T_{cc}$ with increasing
the nanofiller content could indicate some degree of faster crystallization rate in PLLA/LDH Ibu nanocomposites. The change in the crystallization rate is further proved by analyzing the non-isothermal crystallization curves.

The melt crystallization temperatures ($T_{mc}$) during the dynamic cooling were analyzed as a function of the concentration of LDH Ibu (Figure 5.9). The cooling thermograms of the samples showed that the parent PLLA did not reveal any melt crystallization ($T_{mc}$) exotherm peak. The PLLA/LDH Ibu nanocomposites however, did. PLLA broad but shallow melt recrystallization peak can be observed with the addition of LDH Ibu. For 1, 3 and 5LDH Ibu, $T_{mc}$ peaked at 93.7, 96.7 and 98.1, respectively, indicating a slight increase in the $T_{cc}$ with increased nanofiller content. Usually, a lower $T_{cc}$ indicates faster crystallization, whereas a lower $T_{mc}$ indicates slower crystallization. Therefore, the decrease in $T_{cc}$ coupled with the increase in the $T_{mc}$ could be an indicator of crystallization promoting effect of the nanofiller.

5.6.5 Thermo-mechanical and Mechanical Properties

Figure 5.10 showed the relaxation spectrum in terms of storage modulus ($E'$) and the loss tangent ($\tan \delta$) versus temperature at the frequency of 1 Hz for the virgin PLLA and its nanocomposites samples. $E'$ represents the stiffness of a viscoelastic material and is proportional to the energy stored during a loading cycle.

On the other hand, $\tan \delta$ is defined as the ratio of loss modulus $E''$ to storage modulus ($E''/E'$). It is a measure of the energy lost, expressed in terms of recoverable energy, and represents mechanical damping or internal friction in a viscoelastic system.
Figure 5.10 Storage modulus E’ (solid markers) and loss factor tan δ (open markers) curves of the virgin PLLA and PLLA/LDH Ibu nanocomposites showing increase in E’ and a slight shift to the lower temperatures of tan δ peak.

It can be seen from the E’ spectra, that the nanocomposites films showed higher E’ values than that of the virgin PLLA. The higher E’ values of PLLA/LDH Ibu nanocomposites reflect the reinforcement potential of the nanofiller in the biopolymer matrix. The increase in rubbery modulus can be ascribed to the reinforcing effect of the nanofiller. Although E’ generally increased with increasing LDH Ibu content, 5LDH Ibu sample showed E’ less than that of 1LDH Ibu and 3LDH Ibu samples. The decrease in the E’ of 5LDH Ibu sample can be attributed to increased aggregate formation leading to a decrease in the mechanical properties. The glass transition temperature of the virgin
Figure 5.11 Tensile testing results for neat PLLA and PLLA/LDH Ibu nanocomposites showing an increase in UTS and Young’s modulus and decrease in strain to failure with increased LDH Ibu concentration.

The polymer obtained from the maximum tan δ curve is also affected with the addition of the nanofiller. In fact, neat PLLA showed a tan δ peak at around 58 °C and a slight shift to lower temperatures can be observed for all the nanocomposites samples. These results are consistent with the DSC results. The decrease in the tan δ peak can be attributed to the mobility of the amorphous chains promoted by the nanofiller.

Table 5.4 Mechanical properties of PLLA and PLLA/LDH Ibu nanocomposites showing an increase in modulus and ultimate tensile strength but decrease in strain to failure.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elastic Modulus E (GPa)</th>
<th>UTS (MPa)</th>
<th>Strain to failure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLLA</td>
<td>1.31 (±0.09)</td>
<td>41.6 (±0.21)</td>
<td>15.1 (±0.40)</td>
</tr>
<tr>
<td>1LDH Ibu</td>
<td>1.62 (±0.05)</td>
<td>43.2 (±0.15)</td>
<td>10.5 (±0.35)</td>
</tr>
<tr>
<td>3LDH Ibu</td>
<td>1.73 (±0.04)</td>
<td>54.2 (±0.12)</td>
<td>8.2 (±0.75)</td>
</tr>
<tr>
<td>5LDH Ibu</td>
<td>1.52 (±0.06)</td>
<td>44.6 (±0.23)</td>
<td>11.7 (±0.15)</td>
</tr>
</tbody>
</table>
The increase in $E'$ is also supported by increased mechanical properties obtained from tensile testing (Figure 5.11 and Table 5.4). The addition of nanofiller resulted in a 24, 32 and 16% increase in modulus ($E$) for 1LDH Ibu, 3LDH Ibu and 5LDH Ibu, respectively. The ultimate tensile strength (UTS) followed the same trend observed in the modulus. The UTS increased from 4.61 MPa for the virgin PLLA to 43.2, 54.2 and 44.6 MPa for the addition of 1, 3 and 5 wt% LDH Ibu, respectively. This increase indicates the synergistic effect of the nanofiller content on the tensile properties of the PLLA matrix and can be attributed to a high degree of dispersion of the nanoplatelets within the biopolymer matrix leading to a strong interaction between the biopolymer and the layered double hydroxide. Although, $E$ and UTS generally increased with the addition of the nanofiller, the decrease in the $E$ and UTS value of 5LDH sample can be explained by the formation of aggregates that results in decreased mechanical properties due to decreased flow stress. Finally, the hybrids showed a decrease in the strain at break with increasing LDH Ibu content indicating an alteration in plastic deformation of the PLLA matrix with the incorporation of the nanofiller.

5.6.6 Reduction in Cell Proliferation and Release Profile of Ibuprofen

The SMCs proliferation study was conducted on the surface of various samples, and glass and PLLA were used as controls. Samples with and without PLLA prepared with 1, 3, or 5% LDH Ibu or Ibu were also examined. Similar to previous studies, our results show that cells did not grow well on PLLA surfaces compared to glass surfaces (Figure 5.12, $n = 4$, $p < 0.05$).
Figure 5.12 LDH Ibu blended PLLA films reduced SMC proliferation. Cells were cultured on glass vials (control), PLLA, PLLA/LDH Ibu, PLLA/Ibu, LDH Ibu, or Ibu samples with Ibu concentrations of 1%, 3% and 5%. Cell proliferation was estimated using DNA assays as described in the material and method section (n=4, *significantly difference compared to PLLA, \( p < 0.05 \)).

PLLA with 1wt% LDH Ibu reduced cell proliferation significantly compared to those on PLLA alone. A plateau was formed for 3 and 5 wt% LDH Ibu in PLLA films. This plateau indicates that the inhibition is dose-dependent and that the effective concentration for cell growth inhibition is between 3 and 5wt%. The same behavior was observed when PLLA Ibu was used. However, the cell proliferation was significantly lower when LDH Ibu and Ibu were used without PLLA. This observation might be due to the higher availability of Ibu without PLLA in comparison to Ibu blended with PLLA. The availability of Ibu depends on PLLA degradation, which limits the Ibu released in media at each time point. The inhibition of SMC proliferation observed in our studies is
solely due to Ibu since we observed that the growth of cells on either PLLA with LDH Ibu or LDH samples without Ibu is similar to those of controls (results not shown). In order to determine the release profile of Ibu from the nanocomposite films, we conducted drug release studies with HPLC. The ibuprofen drug release profiles are shown in Figure 5.13.

![Drug Release Profiles](image)

Figure 5.13 Percent cumulative drug release curves of PLLA modified with 1 wt% Ibu, 1LDH Ibu, 3LDH Ibu, and 5LDH Ibu.

The drug release follows a conventional two-stage elution profile, with a quick release (the first 15 h) followed by a slower release (up to 50 h). The initial fast rate of release is due to the diffusion of absorbed drug from the surfaces of the LDH into the solution. A modified Freundlich plot (diffusion kinetic model) gives a linear relationship (R² of 0.96-0.97) for the whole data suggesting the release of ibuprofen is diffusion controlled (similar to the mechanism proposed for drug release from MgAlLDH
functionalized with heparin.\textsuperscript{32} This could be due to the small dimensions of the LDH particles providing short diffusion paths for the Ibu to be released. The percent cumulative drug release increase with the amount of ibuprofen in the nanocomposites: 5LDH Ibu > 3LDH Ibu > 1 LDH Ibu > 1Ibu (1Ibu = 1 wt\% ibuprofen in PLLA). Thus, the cell proliferation results complement the results of the drug release, indicating decreased cell proliferation in samples of higher released Ibu. Noting that 1 gram of LDH Ibu has 0.409 grams ibuprofen, we compare the drug release profile of the PLLA with 1wt\% ibuprofen sample to the 1LDH Ibu which contains 0.409\% ibuprofen. We note that the drug release is higher in the nanocomposite. Thus LDH facilitates the release of the ibuprofen from PLLA. The findings correlate with decreased cell proliferation in PLLA modified with LDH Ibu compared to the PLLA/Ibu samples. Thus LDH works synergistically to strengthen PLLA, facilitate drug release and decrease cell proliferation. The results indicate ranges of release complementary to prior work using ibuprofen. Ibuprofen, has been shown to inhibit vascular smooth muscle cell proliferation in a dose-dependent manner\textsuperscript{33} through a cell cycle arrest (G0/G1 arrest). Ibuprofen also demonstrates to reduce SMC proliferation by both cyclooxygenase-dependent and – independent pathways. A major advantage of ibuprofen is that this drug can be used at very high doses without any cytotoxicity effect.\textsuperscript{33,34} Prior work shows that the release of ibuprofen at much higher doses(>10\% by weight) ranges from 10-80\% depending on the materials in these reports or studies.\textsuperscript{35-37} Thus using ibuprofen on LDH and dispersing the subsequent LDH in biopolymers facilitates drug release in deployable forms (films) and increases the mechanical performance of the biopolymer.
5.7 Conclusions

Simultaneous increase in mechanical performance and inhibition of vascular smooth muscle cell proliferation in PLLA is possible through the use of layer double hydroxides functionalized by non-steroidal anti-inflammatory drugs (NSAID) such as ibuprofen. WAXD and SEM results indicate an intercalated/exfoliated dispersion ensues. The LDH Ibu does not influence the glass and melting transition temperatures of the parent polymer significantly but does increase the cold crystallization temperature. The overall crystallinity decreases when the nanofillers were added. Decreased degradation temperatures are obtained when the LDH Ibu is introduced into the PLLA matrix. Increased moduli and UTS properties are obtained with increased LDH Ibu concentration. LDH Ibu blended PLLA film inhibited the proliferation of SMCs after 5 days of exposure. By comparing pure ibuprofen, ibuprofen in PLLA and LDH functionalized with ibuprofen incorporated into PLLA, we conclude that the ibuprofen component is the dominant cause of the decreased cell proliferation. Incorporating ibuprofen into LDH results in effective drug release that leads to a multi-biofunctional nanocomposite with a significant mechanical advantage.

5.8 References


CHAPTER 6

CONCLUSIONS

The potential of layer double hydroxide (LDH) for multifunctional purposes has been successfully investigated. ZnAl-LDH-NO$_3$ was synthesized and then an anion exchange reaction was performed to synthesize ZnAl-LDH-ST, ZnAl-LDH-STH, ZnAl-LDH-PTS and ZnAl-LDH-Ibu. The matrix choices ranged from LDPE, PS, and ABS to PLLA. LDH like conventional silicate filler with Brucite structure due to its endothermic decomposition process, its surface charge, available surface area as well as potential for functionalization makes them an excellent candidate for several multifunctional purposes such as in catalysis, flame retardation, drug delivery and several other purposes.

Effect of Delamination of LDH Prior to Nanocomposite Formation

The importance of delaminating the LDH prior to polymerization was established but from a comparison of the dispersion obtained in solution versus bulk polymerization, solution polymerization facilitated better dispersion. The Zn Al layer double hydroxides (LDH) were stearate functionalized and then aged in hexadecane to afford delaminated LDH. It is well know that exfoliated nanocomposites are formed when the layer platelets are homogenously dispersed in the polymer matrix resulting in interfacial bonding between the species in contact. The uniform dispersion of clay sheets as well as the huge interfacial area makes delaminated clay/polymer nanocomposites an important utility for many purposes.\textsuperscript{1} The nanometer-scale interaction between the clay sheets and polymers, and the tortuosity through diffusion improve nanocomposites materials such as
mechanical strength, thermal stability, flexibility and durability, impermeability, etc.\textsuperscript{2}.

Styrene was solution polymerized in the presence of delaminated layer double hydroxides. In the same manner, the LDH in concentrations of 1, 3, 5 and 7\%wt were dispersed in styrene monomer which were bulk polymerized using benzoyl peroxide initiator. All nanocomposites were highly exfoliated except in the case of the LDH-NO\textsubscript{3}/PS nanocomposites as determined by the XRD. Complementary TEM showed some evidence of ZnO formed. The glass transition was found to decrease for all nanocomposites as determined by differential scanning calorimetry (DSC) compared to the pure polymer but there was second $T_g$ occurring at higher temperature which started to be evident with 3\% composition. Similarly, the nanocomposites showed no regular pattern with storage modulus.

**Flame Retardant Polymer Nanocomposites**

In a study involving LDH for flame retardancy in LDPE, the effect of incorporating in LDPE matrix was investigated. LDH was added at a specific concentration weight percent into the LDPE matrix and melt processed using a Brabender and compression molding technique. Results of test revealed that the layered clays were immiscible with the LDPE matrix, but well dispersed on the microscale. It was also observed that the thermal properties of the nanocomposites improved. Both clays served as nucleation enhancers with increasing recrystallization temperatures in the composites. Flame retarding properties were tested using the flammability HV UL-94 system. The char structure was analyzed by scanning electron microscopy (SEM). Mechanical properties revealed improved properties as expected.
Moreover, in a further study, layer double hydroxide (LDH) Zn$_2$Al(OH)$_6$PTS, halogen-free compounds that contain an organic anion synthesized through an anion exchange reaction of the nitrate LDH with p-toulene sulfonate in the ABS matrix was investigated. Zn$_2$Al(OH)$_6$NO$_3$.nH$_2$O was prepared by a co-precipitation method followed by functionalization. The flame-retardant properties of LDH/ABS nanocomposites samples were studied by UL-94 flame testing, and the thermal stability was characterized by TGA. The DSC result indicated an increase in the thermogravimetric temperatures of the composites, and XRD shows the microstructure of the composites with appearance of intercalation and evidence for the formation of ZnO in the matrix. Thus a three phase’s structure involving LDH, polymer and ZnO was produced. Complementary TEM showed some evidence of ZnO formed. The presence of ZnO was also rationalized by Uv-Vis study and other studies. The UL-94 test results of LDH with ABS showed that the LDH is an unprecedented flame retardant with improved flame extinction.

Furthermore, the desirability and potential of LDH for drug delivery was also investigated. The potential to decrease cell proliferation while simultaneously increasing mechanical performance with the use of Zn-Al layer double hydroxide (LDH) organically modified with ibuprofen dispersed in poly (L-lactic acid) (PLLA) was explored. Analytical tests on the bio-nanocomposites indicated intercalation and exfoliated nanocomposites. Improved mechanical properties were obtained with these nanocomposites. The LDH affected the cold crystallization and reduces thermal stability of the neat PLLA. Smooth muscle cells were used for in vitro studies of the nanocomposites. It was found that the hybrids reduced cell proliferation, and the amount
of cell reduction was related to ibuprofen release. The detrimental effect of cell adhesion on polymer surfaces has been a limiting factor in the medical deployment of many implants.

6.1 References


