CHAPTER 2

EXPERIMENTAL

In this chapter, materials, methods and synthesis procedure for the preparation of alkyl lactates, alkyl lactate acrylates, alkyl lactate methacrylates, poly(alkyl lactate acrylate)s, poly(alkyl lactate methacrylate)s, copolymers of AA with ELA and BLM and SP based nanocomposites of PELA and PBLM were discussed. In addition to this, instrumentation techniques used to characterize the synthesized materials has been reported in detail.

2.1 MATERIALS

D,L-Lactic acid, AA, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, toluene, THF, n-hexane, 3 Å molecular sieves and TLC plates were procured from Merck (India) Pvt. Ltd. MA, CCl$_4$ and SP nanofiller (thick: 5-15 nm, wide: 10-30 nm, long: 500-5000 nm in size) were purchased from Sigma-Aldrich chemicals. Methanol, conc. H$_2$SO$_4$ and aluminum oxide were obtained from Fisher Scientific (India) Pvt. Ltd. AIBN and ethyl acetate were procured from Spectrochem (India) Pvt. Ltd. Both AA and MA were used as such for the preparation of alkyl lactate acrylates and alkyl lactate methacrylates. All other chemicals were used as received except AA, methanol, ethanol, toluene, THF and AIBN.
2.2 PURIFICATION OF REACTANTS, SOLVENTS AND REAGENTS

2.2.1 Acrylic Acid

Hydroquinone inhibitor from AA (10 g) was removed by stirring aluminum oxide (0.5 g) into the monomer for 2 h. The aluminum oxide was allowed to settle down at the bottom of the container. Syringe (Whatmann 0.2 mm PTFE membrane filters) was used to filter the AA from the oxide (Leary & Paul 2004). Later, AA was vacuum distilled to remove moisture and used for copolymerization reactions.

2.2.2 Methanol

Methanol was refluxed over anhydrous calcium oxide (5 % w/v) for 6 h and distilled. Then distilled methanol was refluxed with magnesium metal (5 g) for 30 min. and re-distilled. The fraction boiling at 65 ºC was collected and stored over 3 Å molecular sieves till further use (Furniss et al 1989).

2.2.3 Ethanol

Ethanol was refluxed with calcium oxide (5 % w/v) for 6 h, set aside overnight and distilled. The fraction distilling at 80 ºC was collected and stored over 3 Å molecular sieves till further use (Furniss et al 1989).

2.2.4 Toluene

Toluene was treated with 15 % of its volume of conc. H₂SO₄ below 30 ºC, until the acid layer was colourless followed by washing with water. Further it was treated with 10 % w/v of sodium carbonate solution, followed by washing with water. The resulting mixture was collected and stored over 5 Å molecular sieves (Furniss et al 1989).
2.2.5 THF

THF was treated with sodium hydroxide (25 g) for 3 h and distilled. The distillate was dried using sodium wire and re-distilled, then it was stored over 3 Å molecular sieves (Furniss et al 1989).

2.2.6 AIBN

AIBN was recrystallized twice from chloroform.

2.3 SYNTHESIS

Alkyl lactates, alkyl lactate acrylates and alkyl lactate methacrylates were synthesized through acid catalyzed esterification reaction by azeotropic distillation using Dean-Stark apparatus. Esterification is a reversible reaction in the presence of acid catalyst. To avoid the reversible reaction and facilitate the forward reaction, the simultaneous removal of byproduct water from the reaction mixture is important to promote forward reaction.

2.3.1 Synthesis of Alkyl Lactates

D,L-Lactic acid (45 g, 0.5 mol), methanol (32 g, 1.0 mol) and toluene (100 mL) were taken in a 250 mL 3-necked round-bottomed flask fitted with a Dean-Stark apparatus, thermometer and water condenser. The schematic representation of reaction setup is shown in Figure 2.1 for the separation of water using toluene as solvent. The esterification reaction was carried out by gradual heating. When the reaction mixture reached a temperature of 60 °C, few drops of concentrated sulfuric acid were added. Azeotropic distillation was carried out until there was no further collection of water. The reaction lasted for an hour and a half. The reaction scheme is shown in Figure 2.2. The unreacted methanol and toluene was removed by vacuum distillation and subsequently ML was distilled out. ML, a colorless liquid (94 % yield, 1.5 h) was thus prepared and stored over 3 Å molecular sieves.
Figure 2.1  Schematic representation of azeotropic distillation setup for the removal of water from reaction mixture using toluene

Figure 2.2  Preparation of alkyl lactates

\[
\text{CH}_3\text{CHCOOH} + R\text{OH} \xrightarrow{\text{Toluene} / H^+} \Delta \text{CH}_3\text{CHCOR} \\
\text{Lactic acid} \quad \text{alcohol} \quad \text{alkyl lactate}
\]

For ML, R = CH$_3$;  
For i-PL, R = -CH(CH$_3$)$_2$

For EL, R = CH$_3$CH$_2$;  
For BL, R = CH$_3$(CH$_2$)$_3$-

For PL, R = CH$_3$(CH$_2$)$_2$;  
For i-BL, R = -CH$_2$-CH(CH$_3$)$_2$
Other alkyl lactates namely ethyl lactate (EL), n-propyl lactate (PL), isopropyl lactate (i-PL), n-butyl lactate (BL) and isobutyl lactate (i-BL) were prepared using the same procedure as discussed above. Further, the alkyl lactates were analyzed by TLC using silica coated on glass plate (pore diameter of 60 Å, a pore volume of 0.8 ml/g and a specific surface of 520 m$^2$/g). $R_f$ was calculated by using hexane and ethyl acetate (4:1 v/v) as a eluent. Iodine and UV chamber were used to identify the mobility of substance. The polarity difference of the alkyl lactates accounted for the variation in $R_f$ values. Presence of single spot confirmed that the prepared alkyl lactates were free from reactants. The molar ratio of reactants, reaction time, $R_f$ value and yields are tabulated in Table 2.1.

The synthesized alkyl lactates were characterized by EI-MS, LC-MS, FT-IR, $^1$H-NMR and $^{13}$C-NMR spectroscopic techniques and the results are discussed in chapter 3.

Acid catalyzed reactions of lactic acid with various alcohols have been well documented in literature (Hwang et al 2012). A series of alkyl lactates using lactic acid and various alcohols ranging from methanol to butanol and their corresponding acrylates were synthesized by azeotropic distillation. The molar ratio of the reactants and the respective reaction time were tabulated in Table 2.1. The molar ratio of the reactants was chosen depending upon the solubility of alcohol in water. Methanol, ethanol, n-propanol and isopropanol are soluble in water at room temperature, whereas n-butanol and isobutanol is insoluble in water. That is why, higher molar ratio was used in the case of methanol, ethanol n-propanol and isopropanol to compensate the weight loss of alcohols upon azeotropic distillation, when compared to n-butanol and isobutanol.
# Table 2.1 Synthesis data of alkyl lactates

<table>
<thead>
<tr>
<th>Alkyl lactate</th>
<th>Alcohol</th>
<th>Molar ratio of Lactic acid: Alcohol</th>
<th>Reaction time (h)</th>
<th>Yield (%)</th>
<th>R&lt;sub&gt;f&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>ML</td>
<td>Methanol</td>
<td>1.0 : 2.0</td>
<td>1.5</td>
<td>94</td>
<td>0.48</td>
</tr>
<tr>
<td>EL</td>
<td>Ethanol</td>
<td>1.0 : 2.0</td>
<td>3.0</td>
<td>92</td>
<td>0.51</td>
</tr>
<tr>
<td>PL</td>
<td>n-Propanol</td>
<td>1.0 : 2.0</td>
<td>3.0</td>
<td>91</td>
<td>0.50</td>
</tr>
<tr>
<td>i-PL</td>
<td>Isopropanol</td>
<td>1.0 : 2.0</td>
<td>3.0</td>
<td>66</td>
<td>0.47</td>
</tr>
<tr>
<td>BL</td>
<td>n-Butanol</td>
<td>1.0 : 1.5</td>
<td>4.5</td>
<td>95</td>
<td>0.53</td>
</tr>
<tr>
<td>i-BL</td>
<td>Isobutanol</td>
<td>1.0 : 1.5</td>
<td>5.0</td>
<td>84</td>
<td>0.51</td>
</tr>
</tbody>
</table>

It has been reported that in the case of esterification reaction, methanol is more reactive than other primary alcohols and secondary alcohols (Carey 2000). Methanol takes lesser time for esterification with lactic acid compared to other alcohols which can be attributed to the high reactivity of methanol than other alcohols. Secondary alcohols such as isopropanol and isobutanol takes more time for esterification with lactic acid compared to primary alcohols. This was attributed to the bulkiness of secondary alcohols (Carey 2000).

## 2.3.2 Synthesis of Alkyl Lactate Acrylates

Alkyl lactate (0.25 mol), AA (0.25 mol) and dry toluene (80 mL) were taken in a 250 mL 3-necked round-bottomed flask. The azeotropic distillation was carried out similar to the synthesis of alkyl lactates as discussed in section 2.3.1. Toluene was separated by vacuum distillation and subsequently alkyl lactate acrylate was distilled out. Synthetic route for alkyl lactate acrylates is shown in Figure 2.3. Alkyl lactate acrylates, namely methyl lactate acrylate (MLA), ethyl lactate acrylate (ELA), n-propyl lactate acrylate (PLA), isopropyl lactate acrylate (i-PLA), n-butyl lactate acrylate...
(BLA) and isobutyl lactate acrylate (i-BLA) are colorless liquids. Appearance of single spot in TLC confirmed that the prepared alkyl lactate acrylates were free from reactants. The reaction time, yield and \( R_f \) values are tabulated in Table 2.2. Hydroquinone inhibitor was added and stored over 3 Å molecular sieves.

![Reaction scheme](image)

**Figure 2.3** Preparation of alkyl lactate acrylates

<table>
<thead>
<tr>
<th>Alkyl lactate acrylate</th>
<th>Reaction time (h)</th>
<th>Yield (%)</th>
<th>( R_f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MLA</td>
<td>9</td>
<td>91</td>
<td>0.75</td>
</tr>
<tr>
<td>ELA</td>
<td>11</td>
<td>93</td>
<td>0.74</td>
</tr>
<tr>
<td>PLA</td>
<td>16</td>
<td>81</td>
<td>0.78</td>
</tr>
<tr>
<td>i-PLA</td>
<td>18</td>
<td>63</td>
<td>0.74</td>
</tr>
<tr>
<td>BLA</td>
<td>24</td>
<td>72</td>
<td>0.80</td>
</tr>
<tr>
<td>i-BLA</td>
<td>32</td>
<td>68</td>
<td>0.73</td>
</tr>
</tbody>
</table>

The synthesized alkyl lactate acrylates were characterized by EI-MS, FT-IR, \(^1\)H-NMR and \(^{13}\)C-NMR spectroscopic techniques and the results are discussed in chapter 3.
Reaction time for the formation of alkyl lactate acrylate monomers increased with an increase in the side-chain length of alkyl lactates. Also, reaction time increased from 9 to 24 h as alkyl chain length of n-alkyl lactate increased from methyl to butyl group. Presence of isoalkyl groups such as isopropyl and isobutyl takes more time for esterification with AA compared to its respective primary alkyl group which was attributed to the bulkiness of secondary alkyl group (Carey 2000).

### 2.3.3 Polymerization of Alkyl Lactate Acrylates

Hydroquinone inhibitor was removed from the liquid monomers MLA, ELA, PLA, i-PLA, BLA and i-BLA by passing over aluminum oxide and the monomers were distilled under vacuum (Leary & Paul 2004). Alkyl lactate acrylate (5 g) and THF (25 mL) were charged into a 100 mL 3-necked round-bottomed flask. AIBN (0.05 g) was added as a free radical initiator into a reaction mixture at about 60 °C. The reaction was conducted in dry N₂ atmosphere at 60 °C. The reaction scheme is shown in Figure 2.4. After a certain period of time, the reaction mixture was slowly added into a large volume of n-hexane to precipitate the poly(alkyl lactate acrylate)s.

![Reaction scheme](image)

**Figure 2.4 Preparation of poly(alkyl lactate acrylate)s**
The synthesized polymers namely poly(methyl lactate acrylate) (PMLA), poly(ethyl lactate acrylate) (PELA), poly(n-propyl lactate acrylate) (PPLA), poly(isopropyl lactate acrylate) (P(i-PLA)), poly(n-butyl lactate acrylate) (PBLA) and poly(isobutyl lactate acrylate) (P(i-BLA)) were dried for about 12 h at 60 °C under vacuum (yield > 90 %).

The synthesized poly(alkyl lactate acrylate)s were characterized by FT-IR, \(^1\)H-NMR, \(^{13}\)C-NMR, GPC, WAXS, moisture absorption ability, DSC and TGA and the results are discussed in chapter 3.

### 2.3.4 Synthesis of Alkyl Lactate Methacrylates

Alkyl lactate (0.25 mol), MA (0.25 mol), CCl\(_4\) (80 mL) and few drops of conc. H\(_2\)SO\(_4\) were taken in 250 mL round bottomed flask equipped with modified Dean-stark apparatus. The schematic representation of reaction setup is shown in Figure 2.5 for the separation of water using CCl\(_4\). The azeotropic distillation was carried out until there was no further collection of water. Synthetic scheme for alkyl lactate methacrylates is shown in Figure 2.6. CCl\(_4\) followed by alkyl lactate methacrylates were vacuum distilled. Alkyl lactate methacrylates, namely methyl lactate methacrylate (MLM), ethyl lactate methacrylate (ELM), n-propyl lactate methacrylate (PLM), isopropyl lactate methacrylate (i-PLM), n-butyl lactate methacrylate (BLM) and isobutyl lactate methacrylate (i-BLM) are colorless liquids. Appearance of single spot in TLC confirmed that the prepared alkyl lactate methacrylates were free from reactants. The reaction time, yield and R\(_f\) values are tabulated in Table 2.3. Hydroquinone inhibitor was added and stored over 3 Å molecular sieves.
Figure 2.5  Schematic representation of azeotropic distillation setup for the removal of water from reaction mixture using CCl₄

Figure 2.6  Preparation of alkyl lactate methacrylates
Table 2.3 Synthesis data of alkyl lactate methacrylates

<table>
<thead>
<tr>
<th>Alkyl lactate methacrylate</th>
<th>Reaction time (h)</th>
<th>Yield (%)</th>
<th>( R_f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MLM</td>
<td>8</td>
<td>68</td>
<td>0.70</td>
</tr>
<tr>
<td>ELM</td>
<td>9</td>
<td>73</td>
<td>0.73</td>
</tr>
<tr>
<td>PLM</td>
<td>13</td>
<td>77</td>
<td>0.74</td>
</tr>
<tr>
<td>i-PLM</td>
<td>14</td>
<td>58</td>
<td>0.76</td>
</tr>
<tr>
<td>BLM</td>
<td>17</td>
<td>81</td>
<td>0.81</td>
</tr>
<tr>
<td>i-BLM</td>
<td>21</td>
<td>64</td>
<td>0.71</td>
</tr>
</tbody>
</table>

The synthesized alkyl lactate methacrylates were characterized by EI-MS, FT-IR, \(^{1}\)H-NMR and \(^{13}\)C-NMR spectroscopic techniques and the results are discussed in chapter 4.

Synthesis of alkyl lactate methacrylates by azeotropic distillation technique using toluene as a solvent led to thermal polymerization. This was attributed to lower heat of polymerization of MA when compared to AA (56.3 vs 76.9 kJ/mol) (Kine & Novak 1985) and high boiling temperature of toluene azeotrope. Due to ease of polymerization of MA in toluene, \( \text{CCl}_4 \) was chosen as a solvent for the synthesis of alkyl lactate methacrylates as the boiling temperature of its azeotrope was lower than that of toluene (66.8 vs 84.1 °C) (Horsley 1973).

Reaction time for the formation of alkyl lactate methacrylate monomers increased with an increase in the side chain length of alkyl lactates. Also, reaction time increased from 8 to 17 h as alkyl chain length of n-alkyl lactate increased from methyl to butyl group. Presence of isoalkyl groups such as isopropyl and isobutyl takes more reactive time for esterification with MA when compared to its corresponding primary alkyl group. This was attributed to the bulkiness of secondary alkyl group (Carey 2000).
2.3.5 Polymerization of Alkyl Lactate Methacrylates

Hydroquinone inhibitor was removed from the liquid monomers MLM, ELM, PLM, i-PLM, BLM and i-BLM by passing over aluminum oxide and the monomers were distilled under vacuum (Leary & Paul 2004). Alkyl lactate methacrylate (5 g) and THF (25 mL) were charged into a 100 mL 3-necked round-bottomed flask. AIBN (0.05 g) was added as a free radical initiator into a reaction mixture at about 60 °C. A typical procedure for the polymerization of alkyl lactate methacrylates is similar to the preparation of poly(alkyl lactate acrylate)s which was discussed in 2.3.3 section. The reaction scheme is shown in Figure 2.7.

\[ \text{alkyl lactate methacrylate} \quad \text{Poly(alkyl lactate methacrylate)} \]

For PMLM, R = CH₃; For P(i-PLM), R = -CH(CH₃)₂
For PELM, R = CH₂CH₂₋; For PBLM, R = CH₃(CH₂)₃₋
For PPLM, R = CH₃(CH₂)₂₋; For P(i-BLM), R = -CH₂-CH(CH₃)₂

Figure 2.7 Preparation of poly(alkyl lactate methacrylate)s

The synthesized polymers namely poly(methyl lactate methacrylate) (PMLM), poly(ethyl lactate methacrylate) (PELM), poly(n-propyl lactate methacrylate) (PPLM), poly(isopropyl lactate methacrylate) (P(i-PLM)), poly(n-butyl lactate methacrylate) (PBLM) and poly(isobutyl lactate methacrylate) (P(i-BLM)) were dried for about 12 h at 60 °C under vacuum (yield > 90 %).
The synthesized poly(alkyl lactate methacrylate)s were characterized by FT-IR, $^1$H-NMR, $^{13}$C-NMR, GPC, WAXS, moisture absorption ability, DSC and TGA and the results are discussed in chapter 4.

2.3.6 Copolymerization

The highest moisture absorption was observed in the series of poly(alkyl lactate acrylate)s and poly(alkyl lactate methacrylate)s are PELA about 10 % w/w and PBLM about 24 % w/w respectively. Further to increase and tune the moisture absorption properties of PELA and PBLM, the monomers of ELA and BLM was copolymerized with AA.

Two series of copolymers were synthesized using ELA with AA and BLM with AA using free-radical solution polymerization technique. ELA (17.4 mmol, 2.99 g) or BLM (17.4 mmol, 3.72 g), AA (69.6 mmol, 5 g) and pre-dried THF (43.6 mL) were taken in a 100 mL 3-necked round bottomed flask. Solution polymerization was carried out in dry N$_2$ atmosphere at 60 °C using AIBN (1 % w/w) as a free radical initiator (Figures 2.8 and 2.9). After 4 h, the reaction mixture was added into a large volume of n-hexane to precipitate the poly(ELA-co-AA) or poly(BLM-co-AA). The above procedure is for the preparation of copolymer having molar ratio of 0.2 ELA or BLM : 0.8 AA in feed. Similarly, ELA or BLM and AA were copolymerized in different molar ratio of 0.4 : 0.6, 0.6 : 0.4 and 0.8 : 0.2 in feed and copolymer codes are given in Table 2.4. The polymers were dried for about 12 h at 60 °C under vacuum.

The prepared copolymers of poly(ELA-co-AA) and poly(BLM-co-AA) were characterized by FT-IR, $^1$H-NMR, $^{13}$C-NMR, GPC, WAXS,
moisture absorption ability, DSC and TGA and the results are discussed in chapter 5.

**Figure 2.8** Copolymerization of ELA with AA

**Figure 2.9** Copolymerization of BLM with AA
Table 2.4 Monomer and comonomer feed ratio and sample codes

<table>
<thead>
<tr>
<th>Alkyl lactate (meth)acrylate (feed ratio)</th>
<th>AA (feed ratio)</th>
<th>Sample code</th>
</tr>
</thead>
<tbody>
<tr>
<td>ELA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>0.8</td>
<td>2E8A</td>
</tr>
<tr>
<td>0.4</td>
<td>0.6</td>
<td>4E6A</td>
</tr>
<tr>
<td>0.6</td>
<td>0.4</td>
<td>6E4A</td>
</tr>
<tr>
<td>0.8</td>
<td>0.2</td>
<td>8E2A</td>
</tr>
<tr>
<td>BLM</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>0.8</td>
<td>2B8A</td>
</tr>
<tr>
<td>0.4</td>
<td>0.6</td>
<td>4B6A</td>
</tr>
<tr>
<td>0.6</td>
<td>0.4</td>
<td>6B4A</td>
</tr>
<tr>
<td>0.8</td>
<td>0.2</td>
<td>8B2A</td>
</tr>
</tbody>
</table>

2.3.7 Synthesis of Polymer Nanocomposites

PELA and PBLM polymers were used to prepare nanocomposites by solution casting method using the SP nanofiller of 0.5, 1.0, 1.5 and 2.0 % w/w with respect to polymer content. Initially, PELA or PBLM (0.995 g) was dissolved in THF (25 mL) and followed by the gradual addition of SP (0.005 g) using magnetic stirrer at 1000 rpm. Later, the solution was sonicated for about 30 min at room temperature using an ultrasonicator. Frequency and amplitude used for dispersion of SP were 33 ± 3 kHz and 100 %, respectively. The resulting mixture was solution casted on a clean glass plate and kept in vacuum oven at 40 °C for 12 h to get 0.5 % w/w nanocomposite (Krishnan et al 2007). Similarly, other nanocomposites were prepared for the remaining concentration of SP nanofiller. Block diagram for the preparation of nanocomposites is shown in Figure 2.10 and sample codes are given in Table 2.5.
Figure 2.10  Block diagram for the preparation of nanocomposites

Table 2.5  Nanocomposites and sample codes

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Sepiolite (% w/w)</th>
<th>Sample code</th>
</tr>
</thead>
<tbody>
<tr>
<td>PELA</td>
<td>0.5</td>
<td>0.5-PELA</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>1.0-PELA</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>1.5-PELA</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>2.0-PELA</td>
</tr>
<tr>
<td>PBLM</td>
<td>0.5</td>
<td>0.5-PBLM</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>1.0-PBLM</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>1.5-PBLM</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>2.0-PBLM</td>
</tr>
</tbody>
</table>
The prepared nanocomposite samples were characterized by FT-IR, WAXS, SEM, TEM, moisture ability, DSC and TGA and the results are discussed in chapter 6.

2.4 CHARACTERIZATION

2.4.1 Mass Spectrometry

A mass spectrometer is an instrument designed to measure the mass-to-charge ratio \((m/z)\) of analyte ions. To be analyzed by a mass spectrometer, the desired species must be charged in the gas phase. Once the charged particle is in the gas phase, mass spectrometers use electric and/or magnetic fields to control the paths of the ions. The detected ion particles of species exhibited unique fragmentation pattern, which is used to identify the molecular mass and structure. EI-MS and LC-MS mass spectrometry were used to confirm the formation of alkyl lactates and EI-MS was used to confirm the formation of monomers namely alkyl lactate acrylates and alkyl lactate methacrylates.

2.4.1.1 LC-MS analysis

Two-dimensional analyzes, both the chromatography and the mass spectrometry can be optimized to solve the particular problem upon fragmentation pattern of molecules. Presence of byproducts can able to find easily by means of different retention time. Perkin Elmer Flexar SQ 300 MS was used to analyze the alkyl lactates. Silica and chloroform were used as a stationary phase and eluent respectively. A high performance Single Quadrupole analyzer was used to detect the fragmentated ion peaks. The formation of \(M^+\) or \(M+1\) fragmentation peaks of alkyl lactates, which confirmed their formations.
2.4.1.2 EI-MS analysis

EI-MS techniques required gas phase ions for a successful analysis of molecules. Spectra were recorded using a Micromass VG 7035 and 70 eV was used for ionizing the materials. Formation of M⁺ or M+1 peaks and parent fragmentation peaks of alkyl lactates, alkyl lactate acrylates and alkyl lactate methacrylates, which confirmed their formations.

2.4.2 FT-IR Spectroscopy

FT-IR spectroscopy is multidisciplinary analytical tool that yields information pertaining to the structural details of a material. FT-IR involves the absorption of electromagnetic radiation in the infrared region by a material. It is a valuable and formidable tool to identify the functional groups of molecules. Since every functional group has unique vibrational energy, the IR spectra can be seen as their fingerprints. FT-IR spectrometer (Thermo Scientific Nicolet 6700 FT-IR spectrometer) was used to substantiate the formation of products in this study. The spectra recorded for all samples were directly placed on diamond disc. All the spectra were recorded in the range 4000 to 400 cm⁻¹ at a resolution of 4 cm⁻¹ with a maximum of 124 scans. A background spectrum was run before recording the spectra for each sample. The spectral calibration of the instrument was made using a polystyrene film at regular intervals of time.

2.4.3 NMR Spectroscopy

NMR is a spectroscopic method to identify the position of molecules in its structure. Many nuclei may be studied by NMR techniques, but hydrogen and carbon are most commonly investigated. Infrared spectroscopy reveals the types of functional groups present in a molecule, whereas NMR gives information about the number of magnetically distinct atoms of the type being studied.
High-resolution $^1$H and proton decoupled $^{13}$C-NMR spectra were recorded using Bruker AV-III 500 MHz NMR spectrometer. Deuterated dimethylsulphoxide (Aldrich, DMSO-$d_6$, 99.8 % containing 0.03 % v/v tetramethylsilane) was used as solvents for recording NMR spectra. The proton NMR spectra were recorded using broadband inverse probe where the inner coil for the protons and outer coil for ‘X’ nuclei. Solvent suppression was applied in some cases where the solvent signal is very strong compared to the sample signals. $^{13}$C spectra were recorded in the dual ($^{13}$C/$^1$H) probe where the inner coil for $^{13}$C and the outer coil for protons.

2.4.4 Solubility

Solubility of homopolymers and copolymers was tested using various polar and non-polar solvents such as DMF, DMSO, THF, chloroform, toluene, n-hexane, n-heptane. The polymer samples were taken in a solvent at the concentration of 1 % w/v and continuously stirred for 10 min at room temperature.

2.4.5 Inherent Viscosity

Viscosity of a polymer solution depends on concentration and molecular weight of the dissolved polymer. By measuring the solution viscosity one will be able to get an idea about molecular weight. $\eta_{inh}$ was measured by Ubbelohde viscometer at 30 ± 0.1 °C in THF at 0.5 g/dL concentration for poly(alkyl lactate acrylate)s and poly(alkyl lactate methacrylate)s and THF/0.1 M NaNO$_3$ at 0.5 g/dL concentration for copolymers of ELA and BLM with AA comonomer using Equations (2.1) and (2.2).

$$\text{Relative viscosity} \quad (\eta_{rel}) = \frac{t}{t_0} \quad (2.1)$$

where $t_0$ = time taken for pure solvent

$t$ = time taken for solution
From the relative viscosity, $\eta_{inh}$ was measured

\[
\text{Inherent viscosity} \quad (\eta_{inh}) = \frac{\ln \eta_{rel}}{c} \quad (2.2)
\]

where \(c\) = concentration of polymer in solution (g/dL)

2.4.6 GPC Analysis

GPC also known as size exclusion chromatography, it separates analytes on the basis of size. The technique is often used for the analysis of polymers. Molecular weights and molecular weight distributions of the prepared homopolymers were determined using GPC (PL-GPC 220, Agilent Technologies. Inc.,) with a 1260 Quat pump, differential refractive index (DRI) detector and PL gel column (10 \(\mu\)m mixed-B 300 x 75 mm). Polystyrene was used as standards. THF was used as a mobile phase at a flow rate of 1 mL/min. Injection volume of 100\(\mu\)L and a sample concentration of 2 mg/mL were used. Number average molecular weight ($M_n$), weight average molecular weight ($M_w$) and poly dispersity index ($M_w/M_n$) of poly(alkyl lactate acrylate)s and poly(alkyl lactate methacrylate)s and PAA and its copolymers with ELA and BLM were determined.

2.4.7 WAXS Analysis

WAXS measurements were carried out to obtain diffraction pattern of the homopolymers, copolymers and nanocomposites. WAXS measurements were performed at room temperature (about 30 °C) by Shimadzu Lab XRD-6000 using X-ray diffractometer and Ni filtered CuK\(_\alpha\) radiation. The X-rays were generated by a 40 kV rotating anode generator. The beam was monochromated to obtain a radiation of wavelength 1.54 Å (CuK\(_\alpha\) radiation) by using a graphite crystal. A double slit arrangement was used to collimate the beam, which subsequently interacted with the sample in
a sample holder. The diffraction pattern of the polymers was collected on a two-dimensional image plate detector. The scanning rate was 2º/min over a range of 2θ = 10 to 70º for homopolymers and copolymers and 2-70º for polymer nanocomposites.

For amorphous materials, the average molecular interchain spacing \( \langle R \rangle \) was determined using the Equation (2.3) (Shobhana 2012),

\[
\langle R \rangle = \frac{5}{8} \left( \frac{\lambda}{\sin \theta} \right)
\]

where \( \langle R \rangle = \text{Average molecular interchain spacing} \)

\( \lambda = \text{Wavelength of radiation (Cu K}_\alpha, \lambda = 1.5418 \text{ Å)} \)

\( \theta = \text{Diffraction maximum angle obtained from amorphous halo} \)

2.4.8 Moisture Absorption

The moisture absorption of materials from humid atmosphere can be measured using various equipments namely permeation analyzer (Sacher & Susko 1981), dynamic vapor sorption instrument (Kim et al 2003), infrared near-field scanning optical microscope (McDonough et al 2003), stress analyzer (Ree et al 1993), quartz crystal microbalance (Tamirisa & Hess 2006) and electro-micro balance (Hernandez & Gavara 1994). In this study, samples were kept in a glass chamber that was pre-conditioned at specific RH and the samples were weighed periodically. Different percentages of RH such as 69, 86 and 97 % was maintained inside a glass chamber using saturated solutions of potassium iodide, potassium chloride and potassium chromate respectively. About 2-3 g of pre-dried polymer was taken in petridish which was housed in closed glass chambers and RH was continuously monitored by digital hygroscopic meter. Temperature was maintained at 30 ± 1 ºC. The
moisture absorption percentage was calculated from the weight gain by Equation (2.4),

\[
\text{Moisture absorption at time 't' (\%) = } \left( \frac{M_t - M_d}{M_d} \right) \times 100
\]  

(2.4)

where \( M_d \) = weight of the dried sample

\( M_t \) = weight of the sample at time ‘t’ after moisture absorption

2.4.9 Contact Angle Measurement

Wettability studies usually involve the measurement of contact angle, which indicates the degree of wetting when a solid and liquid interact. Small contact angles correspond to high wettability, while large contact angles correspond to low wettability. Contact angle measurement is a direct measurement of the tangent angle at the three-phase contact point on a sessile drop, monitored by telescope-goniometer.

The wettability of the polymeric materials was characterized by contact angle measurements. The contact angles were measured using a Drop Shape Analyzer (DSA) (Kruss GmbH, Germany). The volume of water droplet was approximately 4 µL and the average of three measurements is reported as the contact angle at zero time (\( t = 0 \)).

2.4.10 SEM Analysis

SEM was used to investigate the surface morphology of the prepared SP based polymer nanocomposites. SEM micrographs were obtained with the help of Carl Ziess SMT (EVO MA15). The prepared nanocomposites were dried and then sputtered with gold to achieve SEM images. The samples were conditioned for 1 h and sputter coated with gold before imaging using an accelerating voltage of 5-20 kV.
2.4.11 TEM Analysis

TEM analysis was used to get the visual information of the SP based polymer nanocomposites. It gives information about the size and dispersion of nanofillers in polymer matrix. TEM images were recorded using a JEM 1400 (JEOL JAPAN) instrument, with an acceleration voltage of 100 kV. The samples were trimmed by ultra microtome using diamond knife of about 70 nm thickness and ultrathin sections were placed on 300 mesh carbon coated copper grids for observations.

2.4.12 DSC Analysis

DSC was used to analyze the thermal transition of polymers. Generally, DSC measures the heat released or absorbed by polymers upon thermal treatment. The measurement is performed by comparing the temperature of the samples and that of the reference material. The instantaneous heat flux is computed from this temperature difference using instrumental calibration constants. Indium was used for the calibration of DSC measurements. The measuring cell of a calorimeter includes the sample and reference materials enclosed in a single furnace. The DSC furnace is made of silver and separated from the DSC sensor by a ceramic plate. The temperature of each of the two containers (pans) is measured by thermocouples connected in series and located around each of them.

DSC was performed using the heat flux Perkin Elmer Diamond DSC-7 model. The experiments were carried out in nitrogen atmosphere at a heating rate of 10 °C/min from -70 to 200 °C and a nitrogen flow of 10 mL/min.
2.4.13 TGA Studies

TGA was performed to assess the relative thermal stability of the homopolymers, copolymers and nanocomposites. Thermograms were obtained using a Perkin Elmer Pyris1 TGA thermogravimetric analyzer. The sample weight was in the range of 4-6 mg. All the runs were carried out under N\textsubscript{2} atmosphere with a gas flow rate of 10 mL/min. All the experiments were carried out at a heating rate of 10 °C/min except thermal degradation kinetic study of poly(n-alkyl lactate methacrylate)s. The pans used in thermogravimetric analyser made of α-Alumina. α-Alumina exhibited a linear calorimetric trace with no thermal transition in the temperature range from 100 to 700 °C. The instrument was calibrated using calcium carbonate as a standard. Measurements are used primarily to determine the composition of materials and to predict their thermal stability at temperatures up to 700 °C in N\textsubscript{2} atmosphere.