ABSTRACT

In recent years, biocompatible, biodegradable materials (linear polylactic acid-based urethanes) in the solid and/or liquid form have attracted tremendous attention in biomedical application particularly in stent coating. Low molecular weight poly (lactic acid) s (PLA), having narrow molecular weight distribution was by dehydrochlorination method using tetraphenyltin as a catalyst. Hydroxyl terminated linear polylactic acid was prepared reacting PLA with aliphatic diol compounds. The hydroxyl end groups were determined by $^{31}$P NMR. PLA oligomers containing both hydroxyl and carboxylic groups were also synthesized by the ring opening polymerization using stannous octoate as an initiator and water as a coinitiator and their structures were confirmed by spectral techniques. The tin modified solid cloisite-30B catalyst was prepared and characterized. The reaction of PLA oligomers and isocyanates (4,4’ methylene bis (phenylisocyanate), toluenediisocyanate, 4,4’ methylelenbis (cyclohexylisocyanate), hexamethylene diisocyanate) was carried out using tin modified solid cloisite-30B catalyst. The effect of the reaction conditions, i.e. the reaction temperature, molar ratio, isocyanates and catalyst on the molecular weight were explored. The structure of the polymer samples was determined with FT IR, $^1$H NMR, $^{13}$C NMR, matrix-assisted laser-desorption ionization time-of-flight mass spectroscopy (MALDI– TOF MS) and TEM. The present work will highlight the synthesis and characterization of various linear polylactic acid-based urethanes using tin modified solid cloisite catalyst. Copyright © 2012 VBRI press.

Keywords: Biodegradable, biocompatible, linear polylactic acid-based urethanes, MALDI– TOF MS, TEM.

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Introduction

Polyurethanes form a class of industrially useful materials because of their excellent properties. An isocyanate terminated prepolymer which are often reacted with diols, [1] diamines [2] and water [3]. Hydroxyl terminated polyesters[4-5] are also starting material for many of the urethane polymers.

Polyurethanes have found a number of useful industrial applications in diverse areas such as coatings, adhesives, sealants, defoamers, and textile dyes[6-14]. In this area, biodegradable polymers such as polylactide, polycaprolactone, polycarbonate, poly (amino acid) have found interesting uses in biomedical application area such as drug delivery, stent, packing materials because of their relatively good mechanical properties, biodegradability and biocompatibility[15-19].

PLA oligomers were prepared and converted into polyurethane with the addition of isocyanates [20]. Harkonen et al. [21] reported the synthesis of similar polyurethane’s with the treatment of a PLA polyol prepolymer with HDI in an inert atmosphere, but no exact description of the procedure has been given. Seppala et al. [22] had mainly used HDI and toluene diisocyanate (TDI) with PLA in solutions for 10-13 h and/or some day at high temperatures and obtained yellow, stiff and fragile foam. Borda et al. [5] showed that Stannous Octoate is better catalyst so far in comparison with other catalysts in ROP of lactones. However, it has certain drawbacks: (i) Stannous Octoate is a viscous liquid and its quantitative addition for homogeneous mixing in the reaction is achieved through dilution with some solvents (ii) As such Stannous Octoate allows the formation of some amount of Octanoic acid during storage time. (iii) During reaction, Octanoic acid reacts with isocyanate group and forms amide linkage. Again, the formation of tin hydroxides, stannoxane is unavoidable when water is present or formed during reaction process. (iv) It has also been reported that the catalyst was effective for the polyurethane formation at 120 °C. The reactive species might be SnO instead of Sn (II) 2-ethylhexanoate. (v) Stannous Octoate-based catalyst is a complex dynamic system which responds to all changes of the reaction condition by a change of structure and concentration of the active species.

Therefore, we have prepared tin modified solid cloisite catalyst for the first time to overcome all these above mentioned encountered problems. The catalyst structure is cyclic and its presence within the foam matrix will give a harder, more thermally stable structure. It is also well documented in the literature report that cyclic structure within the foam matrix is harder, more thermally stable structures. Poly (D, L-lactic acid) had been found to be amorphous in nature and contained both hydroxyl and carboxyl as the end groups. Therefore, both urethane and amide linkages had been observed [5].

The literature report reveals that the mechanical properties are influenced by the functionality and the molecular architecture. Therefore, hydroxyl terminated Poly (L-Lactic acid) (PLA) oligomers were prepared from L-lactic acid and 2, 5-hexane diol using dehydropolycondensation method. Hydroxyl and carboxyl terminated PLA oligomers were also prepared using ring opening polymerization of L,L-lactide using stannous octoate as a initiator and water as a coinitiator.

The elastomeric properties of these materials are derived from the phase separation of the hard and soft copolymer segments of the polymer, such that the urethane hard segment domains serve as cross-links between the amorphous polyester soft segment domains.

The choice of chain extender, 2, 5 hexane diol behaves as soft segments in polyurethane polymers. The hard segments, which are formed from the isocyanate, L-lactic acid and chain extenders, are stiff and immobile, covalently coupled to the soft segments (2, 5 hexane diol), inhibit plastic flow of the polymer chains, thus creating elastomeric resiliency. The polyester urethane prepared by us can certainly contribute better mechanical properties such as high tensile strength, elongation, and tear resistance values according to its molecular architecture.

Literature report reveals that upon mechanical deformation, a portion of the soft segments are stressed by uncoiling, and the hard segments become aligned in the stress direction. This reorientation of the hard segments and consequent powerful hydrogen bonding contributes to high tensile strength, elongation, and tear resistance values.

Since there is no detailed study of polylactic acid esterurethane linkages reported in the literature, therefore we report the synthesis of a series of novel biocompatible and biodegradable poly (esterurethane) s (PEU) via in-situ melt polymerization of hydroxyl terminated poly(lactic acid) (dil) using tin modified solid cloisite-30B catalyst. PLA oligomers (containing both hydroxyl and carboxylic groups) and various isocyanates such as toluenediisocyanate (TDI), 4, 4’methylenebis (cyclohexyl diisocyanate) (HMDI), 4, 4’methylenebis (phenyl diisocyanate (MPDI), hexamethylene diisocyanate (HDI) were reacted to obtain polyuretherane linkage. The effect of reaction temperature, time and novel cloisite modified catalyst were discussed. The present study will focus a better understanding of the synthesis of biodegradable and biocompatible polyurethane materials with improved properties, making them widely applicable.

Experimental

Materials and Instrumentation

4,4’ Methylenedis(phenylisocyanate) (98%) , Toluene 2,4-diisocyanate, (95%), 4, 4’ methylene bis cyclohexyl isocyanate, (90%) , Sn(Oct)2, (95%), PbSn(97%), Dibutyl tin oxide (98%) were procured from Aldrich. Hexamethylene diisocyanate, (98%) and Cloisite 30B were purchased from Fluka and Southern Clay respectively. L-lactic acid and L, L-lactide (purity higher than 99.5%) were obtained from Purac. All the materials were used without further purification. Polylactides (PLA) were prepared using ring opening polymerization technique as well as condensation technique.

Synthesis and characterization of linear PLA oligomers of controlled number average molecular weight and with both carboxylic and hydroxyl end groups

Synthesis by ring opening polymerization (ROP) of L-lactide: Sn (Oct)2-initiated ring opening polymerization
(ROP) of lactonic monomers, including L-lactide, in presence of water co-initiator proceeds via a coordination-insertion mechanism of initiation and propagation (Scheme-1).

Synthesis of diol-ended telechelic PLA prepolymer

In a reactor vessel of glass, passivated using trimethylsilylchloride and fitted with a Dean and Stark type condenser, L-lactic acid (20 g, 0.196 M), as 88 % aqueous solution obtained from PURAC and 2,5-hexanediol (HDO) (2.3 g, 0.0196 M) were simultaneously with p-xylene for 6 h and cooled to 50 °C under argon atmosphere, following which tetraphenyltin (0.0855 g, 0.04 mM, that is about 0.02 M % of L-lactic acid) was added and refluxed in p-xylene for 15 h. The xylene was finally evaporated and obtained polymer was dissolved in DCM (50 mL), precipitated into petroleum ether (250 mL), filtered, washed with petroleum ether and dried under reduced pressure at room temperature, and characterized.

Synthesis of clay modified catalyst (Catalyst 1)

Catalyst 1 was prepared by condensing 1.443 gm (0.0040M) cloisite 30B, where T is Tallow (65% C18; 30% C16; 5% C14) and 1 gm (0.0040 M) di-n-butyltin oxide in toluene at 110 °C for 7h. The reaction mixture was cooled at room temperature and filtered. Crude product was washed with n-hexane several times and dried using vacuum to obtain constant weight. The yield was ~ 95%. The catalyst was schematically represented below (Scheme-2).

Preparation of poly esterurethanes (PEU): The reaction of hydroxyl terminated PLA with isocyanates was performed in a two-necked reactor equipped with a reflux condenser, a stirrer. The reaction was carried out over the blanket of nitrogen atmosphere. The hydroxyl terminated PLA, equivalent amount of isocyanates and the modified clay catalyst were mixed thoroughly at requisite temperature and reaction time. The completion of the reaction was monitored by GC and IR. The optimum reaction time was found to be 0.5 h. Therefore, all the esterurethane reactions were carried out for 0.5 h.

Molecular weights

The molecular weights [number-average molecular weight \(\bar{M}_n\) and weight-average molecular weight \(\bar{M}_w\)] and polydispersity \((\bar{M}_w/\bar{M}_n)\) were determined with respect to polystyrene standards by SEC on a Waters 150 C machine at 25 °C with eluting PEU solutions (10 mg/mL of CHCl3), with toluene as an internal standard, through a series of five 30-cm-long -Styrage columns with pore sizes of 105, 104, 103, 500, and 100 Å. CHCl3 was used as the mobile phase (flow rate -1 mL/min), and a refractive-index detector was used for the detection of different molecular weight fractions. The \(\bar{M}_w\) and intrinsic viscosity (\(\eta\)) values were determined with the help of a Knauer K-7000 Vapor pressure osmometer (25 °C) and a three arm Ubbelohde viscometer (Schott Gerate) at 30 °C.

NMR

For the NMR measurements, the samples were dissolved in chloroform-\(d\) in 5-mm-diameter NMR tubes at room temperature. The sample concentration for the \(^{13}\)C NMR measurements was 10 wt %. Proton-decoupled \(^{13}\)C NMR spectra (nuclear Overhauser effect) were recorded on a Bruker DRX 500-MHz NMR spectrometer working at 125 MHz for \(^{13}\)C.

Thermal analysis

Differential scanning calorimetry (DSC) measurements were performed on a PerkinElmer DSC-7 thermal analyzer in a nitrogen atmosphere. The measurements were run from -40 to 200 °C at a heating rate of 10 °C/min and at a cooling rate of 100 °C/min. The glass-transition temperature (\(T_g\)) and the crystallinity data were recorded from the second and first heating curves, respectively. Crystallinity values for different polymers were calculated through the integration of the normalized area of the melting endotherm, the determination of the heat involved, and the rating of it to the reference 100% crystalline polymer (93.6 J/g).

X-Ray analysis

Wide-angle X-ray scattering patterns of the samples were obtained in the reflection mode with a Rigaku Dmax 2500 diffractometer and Ni-filtered copper radiation. The samples were scanned in the 20 range of 10–35 °, and the generator was operated at 40 kV and 150 mA. The full width at half-maximum of the 110 peak was determined with peak-fitting software available with the diffractometer.

MALDI-TOF MS analysis

MALDI-TOF MS analysis was performed on a Kratos Kompact MALDI IV spectrometer equipped with 0.7-m linear and 1.4-m reflection flight tubes as well as a 337-nm nitrogen laser with a pulse width of 3 ns. All experiments were carried out at an accelerating potential of 20 kV. In general, mass spectra from 200 shots were accumulated to produce a final spectrum. The obtained data were smoothened to reduce the spikiness by the average method; the smoothening filter moved along the collected data channels, adding together a number of channels and dividing by that number to give an average signal. This smoothening, however, did not eliminate or hide minor signals distinct from the baseline noise. The samples were dissolved in tetrahydrofuran (1 mg/mL) and mixed with the matrix (15 mg/ml of tetrahydrofuran) before being dried on the sample plate. 2, 4, 6-Tritylhydroxyacetophenone was used as the matrix. The sample plate was inserted into the apparatus under a high vacuum (10^{-5} Pa).

TEM

Sample preparation: The sample was dispersed in isopropyl alcohol solvent to understand the aggregation behavior. The solutions were collected on 300 mesh carbon coated copper grids. The copper grids were kept overnight on filter paper for drying. TEM imaging was performed using a FEI Tecnai 20 TEM operating at an accelerating voltage of 200 kV with 1.7Å² point resolution. Images were
capture d using charged couple detector camera and viewed using Gatan Digital Micrograph software.

Results and discussion

Hydroxyl ended telechelic PLA polymer was prepared by dehydropropylenecondensation of L-lactic acid with 2, 5-hexanediol in presence of tetraphenyltin using xylene at 144 °C. The product was purified, characterized and used for the synthesis of PLA-based esterurethanes. The other telechelic PLA polymer was also prepared using stannous octoate as an initiator and water as a co-initiator. To support the structure and functionality of the telechelic PLA polymer formed by dehydropropylenecondensation and ROP techniques, $^1\text{H}$, $^{13}\text{C}$, $^{31}\text{P}$, GPC, DSC and XRD characterizations were performed. The results confirmed the desired structure and functionality of the telechelic PLA polymers which are the precursor of linear PLA-based ester-urethanes. The reaction products of the hydroxyl terminated telechelic PLA polymers were shown in Scheme 1. L-lactide was thoroughly dried under vacuum and all precautions were taken to avoid ingress of moisture during the reactions. Water was used as the co-initiator, so that carboxylic acid end groups found in the Scheme-1 could be generated at the terminal of each PLA oligomer chain.

![Scheme 1. Coordination-insertion mechanism of ROP of L-lactide.](image)

The number average molecular weight and degree of polymerization, $\bar{M}_n$ and $\bar{D}_n$, respectively, of PLA oligomers thus prepared were calculated as:

$$\bar{M}_n = ([M] / [I]) \times M_L \times \text{conversion}$$

$$\bar{D}_n = ([M] / [I]) \times \text{conversion}$$

where [M] = moles of monomer, [I] = moles of co-initiator (water) and $M_L$ = molecular weight of L-lactide. Conversion was determined from yield of PLA oligomer.

Synthesis of diol-ended telechelic PLA prepolymer

Diol-ended telechelic PLA prepolymer was obtained from L-lactic acid and 2, 5-hexanediol (HDO) by polycondensation technique using xylene as a solvent and tetraphenyltin as a catalyst. $^1\text{H}$-NMR (500 MHz); δ (ppm, CDCl$_3$ at 7.25) 5.20 – 5.05 (qt, CH-a attached to ester in the repeating unit, extra shoulders due to different environments and/or different degrees of polymerization), 4.65 – 4.60 and 4.55 (m and m, CH-b attached to ester, different environments), 4.25 – 4.12 (m, CH-b attached to terminal hydroxyl and CH-b attached to penultimate ester linkage, for those chains where HDO was at the end), 4.36 – 4.29 (qt, CH-a attached to terminal hydroxyl), 1.87 – 1.78 (m, CH$_2$-CH$_2$ due to HDO), 1.61 – 1.49 (d, CH$_2$-a), 1.22 – 1.49 (double d, CH$_3$-b + CH$_3$-b'). The diol-ended PLA telechelic was confirmed by $^1\text{H}$-NMR (500 MHz) spectrum alone.

Determination of molecular weights of oligomers

The achieved degree of polymerization and number average molecular weight was determined from the ratio of integral of the ester carbonyl carbon to that of the carboxylic acid carbonyl carbon in the $^{13}\text{C}$-NMR spectrum, as shown in Fig. 1. Number average molecular weights of these oligomers were also determined by vapor pressure Osmometry (VPO). Both theoretically calculated and experimentally obtained values of these parameters are organized in the data shown in Table 1, where samples 1 and 2 are the two PLA oligomers synthesized in this procedure with different [M]/ [I] ratios and different Sn (Oct)$_2$ concentrations in proportion to the lactide monomer, to obtain oligomers of different degrees of polymerization and hence different number average molecular weights. The theoretical and experimental values were found to be in good agreement, thereby indicating successful use of water as a co-initiator in the ROP of L-lactide.

Table 1. Number Average Molecular Weights of the PLA Oligomers Synthesized by ROP of L-lactide with Water as Co-initiator and Sn(Oct)$_2$ as initiator.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[Sn(Oct)$_2$]</th>
<th>[H$_2$O]</th>
<th>Yield (%)</th>
<th>$\bar{M}_n$, NMR</th>
<th>$\bar{M}_n$, VPO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>200</td>
<td>32</td>
<td>86</td>
<td>55</td>
<td>60</td>
</tr>
</tbody>
</table>
| 2      | 400           | 45        | 87         | 77             | 5774           | 5692

![Fig. 1. $^{13}\text{C}$-NMR spectrum of PLA oligomer synthesized by ROP of L-lactide: inset showing ester carbonyl region (ester as well as carboxylic acid) as enlarged.](image)


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Both oligomers had similar values of $T_m$ and $T_g$. Effect of $D_p$ on $T_m$ is also evident from the result.

**Table 2.** Thermal Characterization and Crystallinity Values of PLA Oligomers Synthesized by ROP of 1-lactide

<table>
<thead>
<tr>
<th>PLA Sample</th>
<th>Tg (°C)</th>
<th>Tm (°C)</th>
<th>$\Delta H_{\text{melting}}$ (J.g⁻¹)</th>
<th>XRD Powder (%Crystallinity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>48</td>
<td>141</td>
<td>53.4</td>
<td>85.52</td>
</tr>
<tr>
<td>2</td>
<td>51</td>
<td>162</td>
<td>59.7</td>
<td>85.73</td>
</tr>
</tbody>
</table>

**XRD**

The powder XRD patterns of the two oligomers are shown in Fig. 3, where it can be found that the two polymers had almost identical patterns, as expected. The % crystallinity values of the oligomers calculated from these XRD patterns are shown in Table 2, and they were also found to be similar. XRD is a method capable of probing long-range order in polymer crystals, and it is therefore used to follow changes in the crystallinity of PLA monofilaments. The crystallinity of a lactic-acid-based polymer is typically expressed as a percentage of theoretical maximum crystallinity of high-molar-mass PLA. The melting enthalpy value for 100% crystalline PLA is 93.1 J/g and used for calculation of % crystallinity, shown in Table 2. The increase in % crystallinity values from 57.4 to 64.2 is attributed due to the increase in molar mass from 4320 to 5544 Da.

The diol-ended telechelic PLA was confirmed by $^1$H-NMR (500 MHz) spectrum alone (shown in Fig. 4a). The OH end group concentration of the telechelic PLA prepolymer was determined by $^{31}$P-NMR (shown in Fig. 4b) was found to be $2.49 \times 10^{-3}$ M/g, and the number average molecular weight was calculated as 820, which matched closely with the values determined by SEC, as shown in Table 3.

**Table 3.** Results of Characterization of the Diol-ended PLA Telechelic prepolymer

<table>
<thead>
<tr>
<th>Oligomer Type</th>
<th>Synthesis Method</th>
<th>[η] (dL/g)</th>
<th>$M_n$ (NMR)</th>
<th>$M_n$ (VPO)</th>
<th>$M_n$ (SEC)</th>
<th>$M_w$ (SEC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Telechelic</td>
<td>Co-condensation of LLA with 2,5 hexane diol HDO</td>
<td>0.085</td>
<td>820</td>
<td>830</td>
<td>900</td>
<td>1200</td>
</tr>
</tbody>
</table>

The telechelic PLA prepolymer was prepared from dehydropolycondensation of L-lactic acid (LLA) in presence of small amount of 2, 5-hexanediol, so that both ends of the telechelic contained similar, secondary hydroxyl groups.

**Synthesis of cloisite modified catalyst catalyst 1**

The clay modified catalyst was prepared, characterized and confirmed the structure by $^{13}$C and $^{119}$Sn NMR. $^{13}$C CP/MAS (Cross-Polarization/Magic Angle Spinning) NMR of the clay modified catalyst show peaks at 23.65, 25.28, and 27.28 ppm which are attributed due to the presence of dibutyl groups attached to the tin atom. The disappearance of the peak at ~70 ppm is due to the absence of hydroxyl group and appearance of methylene and methyl groups at 

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**Fig. 2.** Thermal characterization (DSC) first and second heating showing $T_g$ and $T_m$, respectively of PLA oligomers: (a) 1, first heating; (b) 2, first heating; (c) 1, second heating and (d) 2, second heating.

**Fig. 3.** Powder XRD patterns of PLA oligomers: (a) 1 and (b) 2.

**Fig. 4a.** $^1$H-NMR spectrum (500 MHz) of the diol-terminated telechelic PLA. **b.** $^{31}$P-NMR spectrum of the diol-terminated telechelic PLA.
23.65 and 16.04 ppm confirmed the structure of the catalyst as shown in Scheme 2.

Scheme 2. Synthesis of clay modified catalyst 1.

The typical example of $^{119}$Sn NMR spectra of modified clay catalyst and results with probable assignment are given in Scheme 2. The high field signals at -176.15 ppm is attributed to Sn (1) coordinated by two oxygen atoms and two butyl groups. The catalyst gives rise to an unusually low field signal (- 86.82) which may be attributed due to presence of anionic species coordinated with tin atom. Thermal stability of the catalyst was carried out using thermo gravimetric analysis. TGA curve of the Cloisite-30B shows two decomposition temperatures 298.9 and 405.8 °C respectively. The weight losses are 5 and 30.30 % and became steady.

TGA curve of the catalyst shows that the clay modified catalyst started decomposition at 293.96 °C. The weight loss was calculated as 51.52 % and became steady. The remaining 48.48 % is due to the presence of tin as well as clay.

All four types of diisocyanates i.e. toluene diisocyanate (TDI), bis (cyclohexyl diisocyanate), (HMDI), 4, 4’ methylene (phenyl diisocyanate) (MPDI) and hexamethylene diisocyanate (HDI) and their reaction products of the hydroxyl terminated telechelic PLA polymers were shown in Scheme 3 and 4 respectively. These products were soluble mostly in all chlorinated solvents. The dynamic light scattering measurements showed no particles larger 3nm. The results clearly focus the complete dissolution of the urethane polymers.

Scheme 3. Synthesis of poly (ester-urethane) using diisocyanates where A: 1. (4, 4’ methylenebis (phenylisocyanate); 2. Toluene 2,4 diisocyanate; 3. 4,4’methylenebis (cyclohexyl isocyanate); 4. hexamethylene diisocyanate).

Infra-Red spectroscopy(IR)

The IR investigations of TDI and all three products the PLA-TDI, PLA-HMDI, and PLA-MPDI) reactions were shown in Fig. 5(a-d) and the spectra confirmed the completion of the reaction.

The infrared spectra of the poly(L-lactic acid) polymers showed characteristic absorption bands around 3400 cm$^{-1}$ ($\nu$ OH), 1740 cm$^{-1}$($\nu$ C=O) and intense absorption at 1100 cm$^{-1}$($\nu$ CO). Fig. 5a showed the peak at 2266 cm$^{-1}$which is a characteristic peak of $–$N= C=O group. The disappearance of the peak at 2266 cm$^{-1}$ due to $–$N= C=O group occurred in all the three respective spectra (Fig. 5 b, c and d) and the peaks due to esterurethane linkage appeared.

The structures of the prepared polyesterurethanes were established by studying their IR spectra. The infrared spectrum of the polyesterurethane (Fig. 5 b, c, d) showed characteristic absorption bands around 3400 cm$^{-1}$($\nu$ NH) and an intense absorption at 1100 cm$^{-1}$($\nu$ C=O). The carbonyl absorption appeared as a strong band at 1740 for ester group.

NMR

$^1$H-NMR (500 MHz): δ (ppm, CDCl$_3$ at 7.25) - The $^1$H NMR spectra of the polyesterurethane (PLA-TDI) showed peak at 7.8-7.0 due to the aromatic protons and $–$NH groups. The peaks were appeared at 5.12 -5.18 (qt, $–$CH attached to urethane in the repeating unit, extra shoulders due to different environments and /or different degrees of polymerization), 4.37 -4.29 (qt, $–$CH attached to terminal hydroxyl), 2.4-1.9 (m, CH$_3$ attached to aromatic ring), 1.6-1.4 (d, CH$_3$ attached to CH) and 1.3 -1.19 (CH$_3$ attached to CH) respectively.

Fig. 5. Characteristic IR spectrum of the products obtained : (a) TDI, (b) PLA-TDI, (c)PLA-HMDI, and (d) PLA-MPDI.
In this study, $^{13}$C NMR technique was used to determine the structure of polyester urethane using various isocyanates ranging from aliphatic, alicyclic and aromatic containing groups. The $^{13}$C NMR spectra corresponding to polyesterurethanes such as PU-1, PU-2 and PU-3, PU-4 are shown in Fig. 6(a, b) and 7(a, b) respectively.

In the spectrum, PU-1 (Fig. 6a), the peaks appearing from 168.5 to 169.5 ppm are due to ester carbonyl groups. The peaks at 128.32 and 125.80 ppm are due to the presence of aromatic ring. The peak arises at 66.75 ppm is due to CH adjacent to hydroxyl end groups. The peak at 69.05 is due to CH group attached to ester group of the repeating unit of PLA. The peaks at 28.89 and 31.66 are due to methylene groups. The peaks at 19.77 and 16.67 ppm are due to methyl group attached to aromatic ring and methyl group attached to CH group of the repeating unit of PLA. The peak at 111 ppm is due to TDI protonated ring between urethane linkages. The peak arising at 101 ppm is due to the CH attached to the urethane linkage.

$^{13}$C NMR spectra (500 MHz) of polyesterurethanes; (a) PU-1 and (b) PU-2

The $^1$H NMR spectra of the polyurethane (PLA-HMDI) showed at 7.8 and 6.72 ppm due to the NH groups. The peaks were appeared at 5.3 -5.1 (qt, CH attached to the urethane in the repeating unit, extra shoulders due to different environment and/or different degrees of polymerization), 4.96-4.7, (m, CH-b attached to ester) and 4.37-4.29 (qt, -CH attached to terminal hydroxyl group respectively. The peaks were appeared at 3.73 and 3.37 ppm are due to equatorial and axial hydrogen of cyclohexane ring respectively. The line width of peak calculated at 3.37 (axial-axial) is 10 Hz in comparison with peak at 3.73 (equatorial – axial and 4.8 Hz). The peaks were shown at 2.4 to 1.9 (m CH$_3$ attached to cyclohexane ring), 1.6-1.4 (d, CH$_3$ attached to CH) and 1.3-1.11 (d, CH$_3$ attached to CH) respectively.

The $^1$H NMR spectra of the polyurethanes (PLA-MPDI) displayed bands at 7.7-7.0 due to protons of phenyl CH=CH and NH groups. The methylene attached to both aromatic rings appeared at 4.1-3.6 ppm. The peaks were aroused at 5.12 -5.18 (qt, -CH attached to urethane in the repeating unit, extra shoulders due to different environments and/or different degrees of polymerization), 4.37 -4.29 (qt, -CH attached to terminal hydroxyl), 2.4-1.9 (m, CH$_3$ attached to aromatic ring), 1.6-1.4 (d, CH$_3$ attached to CH) and 1.3 -1.19 (CH$_3$ attached to CH) respectively.

$^{13}$C NMR of PU-3 (PLA-MPDI) is shown in Fig. 7b. The peaks appearing from 119.08 to 129.42 ppm are due to aromatic region. The peak at 169.86 ppm is due to ester group of the repeating unit of PLA. The peaks at 69.07 and 16.67 ppm are due to the methine and methyl group of repeating group. The peak at 41 ppm is due to methylene group between two aromatic rings.

$^{13}$C NMR of (PLA-HDI) is shown Fig. 7b. The peaks appearing at 169.67, 69.08 and 15.66 ppm are due to ester carbonyl, methine and methyl carbon of PLA repeating unit. The peak at 66.78 ppm appears due to methine carbon attached to hydroxyl end group. The peaks ranging from 28.90-19.78 ppm are due to methylene groups.

**Molecular weights**

The results of characterization of the polyesterurethanes (PU-1 to PU-12) were tabulated in Table 4, 5 and 6 respectively. All polyesterurethanes are soluble in organic solvents and molecular weights data correspond to polystyrene standards, with a refractive index detector and so are only apparent values. PU-1, PU-2, PU-3 and PU-4 polyesterurethanes were prepared using telechelic polymer (diol ended PLA) with four different isocyanates i.e. TDI, HMDI, MPDI and HDI at 80 $^\circ$C using reaction time (30 min.) in all the cases. PU-1 showed maximum weight average molecular weight. $M_n$=8500 with number average molecular weight $M_n$=3900 with a molecular weight distribution (PDI-2.2). PU-2 showed $M_n$=5400, $M_s$=2400
and molecular weight distribution (PDI=2.2). PU-3 showed \( M_w=2600, M_n= 1300 \) and molecular weight distribution 2.01 which are comparatively smaller than PU-1 and PU-2. PU-4 showed \( M_w=2200 \) with narrower distribution 1.5. A similar observation was made by Borda et al. 5 for TDI which contributed more molecular weight polyurethane products in comparison with other isocyanates.

TDI is most industrially important diisocyanate although other types are now being developed and adopted industrially. Therefore, kinetic parameters were varied using TDI.

It is apparent that the temperatures have greater impact on the molecular weight. Table 5 illustrates the \( M_w, M_n \), and MD values from PU-5 to PU-8 which were prepared using diol ended PLA with toluene diisocyanate. The following parameters were systematically investigated reaction time, reaction temperature and catalyst for the optimization of the reaction conditions. At the outset, the reaction time was varied. Low viscous liquid was observed till 25 min of reaction time. The product was formed in case of all four isocyanates, when the reaction time was increased gradually up to 30 min, optimized and kept constant for all reactions.

After the reaction time was fixed, the effect of the temperature was studied and the related results were shown in Table 5. With increasing reaction temperatures, the molecular weights also increased, but at higher temperature the molecular weights further decreased. The maximum molecular weight i.e. \( M_w=9000 \) was obtained at 100 °C. A catalyst was always needed to speed up the reaction; the catalyst concentration of novel cloisite catalyst was varied from 1–4 wt%. The results were tabulated in Table 6. The highest molecular weight; \( M_n=11000 \) was obtained at 2 wt% catalyst. Thereafter, the molecular weight remained constant and the molecular distribution was obtained ~2 in all the polyester urethane polymers (PU-8 to PU-11).

Table 4. Results of Characterization of the Polyesterurethanes from Diol-ended PLA Telechelic Prepolymer and Diisocyanate

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Mn (g/M)</th>
<th>Mw (g/M)</th>
<th>PDI</th>
<th>Tg (°C)</th>
<th>Tm (°C)</th>
<th>ΔHmelting (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU-1</td>
<td>3900</td>
<td>8500</td>
<td>2.17</td>
<td>27</td>
<td>77</td>
<td>0.90</td>
</tr>
<tr>
<td>PU-2</td>
<td>2430</td>
<td>5400</td>
<td>2.22</td>
<td>50</td>
<td>117</td>
<td>18</td>
</tr>
<tr>
<td>PU-3</td>
<td>1300</td>
<td>2620</td>
<td>2.01</td>
<td>13</td>
<td>144</td>
<td>18</td>
</tr>
<tr>
<td>PU-4</td>
<td>1450</td>
<td>2200</td>
<td>1.51</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
</tbody>
</table>

Thermal characterization

Thermal analysis of some polyurethanes showed that the polymers were stable up to 300-350 °C. TG and DTA curves of polymers were recorded. These high thermal stability values obtained for the prepared polyesterurethanes are in agreement with those reported for polyester based polyurethanes [20].

The results of the thermal characterization are shown in Table 4 and Fig. 8 (e-g). \( T_g \) varied from 27 to 13°C for polyesterurethanes (PU-1 and PU-3). The decrease of \( T_g \) value in case of PU-3 is attributed to the incorporation of methylene group between two aromatic rings and resulted flexibility in the polymer chain and increase of mobility. The \( T_g \) value in case of PU-2 is 50°C which is superior to PU-1 and PU-3. PU-2 polyesterurethane contains two cyclohexyl rings attached with methylene group. The cyclohexyl ring forms different conformation such as chair and boat form. The motion of the chair form experiences restriction in the mobility which enhanced the \( T_g \) value.

Table 5. Effect of the Temperature on the PLA based Polyurethane Using Toluene Diisocyanate (TDI)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Temp. (°C)</th>
<th>Mn (g/M)</th>
<th>Mw (g/M)</th>
<th>PDI</th>
<th>Tg (°C)</th>
<th>Tm (°C)</th>
<th>ΔHmelting (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU-5</td>
<td>80</td>
<td>3870</td>
<td>8520</td>
<td>2.20</td>
<td>-12</td>
<td>77</td>
<td>0.90</td>
</tr>
<tr>
<td>PU-6</td>
<td>100</td>
<td>3810</td>
<td>8860</td>
<td>2.32</td>
<td>-9</td>
<td>59</td>
<td>7</td>
</tr>
<tr>
<td>PU-7</td>
<td>120</td>
<td>900</td>
<td>2480</td>
<td>2.75</td>
<td>-19</td>
<td>55</td>
<td>6</td>
</tr>
<tr>
<td>PU-8</td>
<td>140</td>
<td>996</td>
<td>2500</td>
<td>2.51</td>
<td>-19</td>
<td>56</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 6. Effect of the Novel Cloisite Catalyst on the PLA Based Polyurethane Using Toluene Diisocyanate (TDI)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Catalyst Conc. (wt %)</th>
<th>Mn (g/M)</th>
<th>Mw (g/M)</th>
<th>PDI</th>
<th>Tg (°C)</th>
<th>Tm (°C)</th>
<th>ΔHmelting (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU-9</td>
<td>1</td>
<td>3330</td>
<td>7000</td>
<td>2.10</td>
<td>-36</td>
<td>63</td>
<td>6</td>
</tr>
<tr>
<td>PU-10</td>
<td>2</td>
<td>5490</td>
<td>11400</td>
<td>2.08</td>
<td>-32</td>
<td>61</td>
<td>12</td>
</tr>
<tr>
<td>PU-11</td>
<td>3</td>
<td>4470</td>
<td>10890</td>
<td>2.43</td>
<td>-14</td>
<td>59</td>
<td>8</td>
</tr>
<tr>
<td>PU-12</td>
<td>4</td>
<td>5390</td>
<td>10600</td>
<td>1.96</td>
<td>-17</td>
<td>68</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 5 shows the \( T_g \) values of PU-1 at four different temperatures i.e. 80, 100, 120 and 140 °C and the samples are designated as PU-5, PU-6, PU-7 and PU-8. \( T_g \) value is increasing by 3 °C by enhancement of reaction temperature from 80 to 100 °C. This may be interpreted as the molecular weight increased, \( T_g \) value also increased. The number of hard segment i.e. phenyl ring are more which results the restriction of polymer chain mobility. Therefore, \( T_g \) values in case of PU-7 and PU-8 are 19 °C because of low molecular weight.

Fig. 8. DSC thermograms of polyesterurethanes; (e) PU-1, (f) PU-2 and (g) PU-3.

The wide angle X-ray scans are shown in Fig. 9. The crystalline structure of PLA has been investigated by XRD and found that four characteristic peaks appeared at \( 2θ = 14.6^0, 16.68^0, 19.14^0 \) and 22.27°[23].

In case of PU-1 (Fig. 9, X1) and PU-3 (Fig. 9, X2), there is a single peak appeared at 18° is shown in Fig. 9 The crystallinity may be attributed due to the lamellar superstructure as revealed by SAXS [21]. The peaks of PU-2 as shown in Fig. 9 (X3) appeared at 2θ =17°, 19° and 32°.
The difference in \( \theta \) values between Fig. 9 (X3) and PLA polymer clearly indicates the formation of different kind of crystallinity.

**MALDI-TOF MS analysis**

MALDI-TOF MS has been employed for the determination of molecular weights and the nature of the groups\[22-23\]. With dehydropolycondensation reactions; only low molecular weight PLA can be prepared. Such oligomers were subjected to further reaction with various diisocyanates. The polyesterurethanes prepared during this study were subjected to MALDI-TOF MS analysis. The results of the analysis are shown in Fig. 10 (a-d). Fig. 10a presents the MALDI-TOF mass spectrum of PU-1. The polyesterurethane contained chain terminated hydroxyl groups in both sides. The MALDI spectrum is dominated by a series of intense peaks ranging from mass 2000 to 6000 Da corresponding to polyesterurethanes doped with Na\(^+\) ions of type

\[
\text{OH} \rightarrow \text{CO-NH-} \Phi \text{-NH-CO-O} \rightarrow \text{[CH(CH$_3$)$_2$-CO-O]} \rightarrow \text{[CH(CH$_3$)$_2$]} \rightarrow \text{[CH(CH$_3$)$_2$]} \rightarrow \text{[CO-CH(CH$_3$)]-OH Na$^+$}
\]

(mass =72n+168+90+23); n values from 4 to 8 were detected, 23 being the mass no of sodium. The group \( \Phi \) also varies from 1 to 7. The symbol \( \Phi \) represents the aromatic ring. The spectrum also displays other peaks of lower intensity, which desorbed as polyurethanes doped with K\(^+\) ions. (K\(^+\) adduct molecular ions, mass= 72n+168+90+39); see the peaks at 3190, 4897 in the inset. The spectrum displays peaks of higher intensity ranging from 2171 to 5600 Da corresponding to polyesterurethanes doped with H\(^+\) ions of type

\[
\text{OH} \rightarrow \text{CO-NH-} \Phi \text{-NH-CO-O} \rightarrow \text{[CH(CH$_3$)$_2$-CO-O]} \rightarrow \text{[CH(CH$_3$)$_2$-CH(CH$_3$)$_2$]} \rightarrow \text{[CH(CH$_3$)$_2$-]} \rightarrow \text{[CO-CH(CH$_3$)]-OH H$^+$}
\]

(mass =72n+84+280m+23), where n values varies from 3 to 8 and m varies from 1 to 2, 23 being the mass number of sodium. Here \( \Phi \) represents dicyclohexyl methane group. The corresponding sodium ion doped peak appears at 533.6, 610 and 683.0 Da respectively. The two important peaks belonging to this series are observed, corresponding to polyesterurethanes of the same structure. (mass= 72n+84+280m+23) where n values varies from 3 to 8 and m varies from 1 to 2, 23 being the mass number of sodium. Fig. 10c represents the MALDI-TOF mass spectrum of polyesterurethane prepared from PLA oligomers with 4, 4’ methylenedis (phenylisocyanate). The polyesterurethane contained chains terminated hydroxyl groups at both the chain ends.

**Fig. 10b** shows the MALDI TOF spectra of polyesterurethane PU-2. The MALDI spectrum is dominated by a series of intense peaks ranging from a mass of 500 to mass 1300 Da, corresponding to polyesterurethanes doped with Na\(^+\) of types

\[
\text{OH} \rightarrow \text{[-CO-NH-} \Phi \text{-NH-CO-O]} \rightarrow \text{[CH(CH$_3$)$_2$-CO-O]} \rightarrow \text{[CH(CH$_3$)$_2$-CH(CH$_3$)$_2$]} \rightarrow \text{[CH(CH$_3$)$_2$-]} \rightarrow \text{[CO-CH(CH$_3$)]-OH Na$^+$}
\]

Fig. 10a, MALDI-TOF spectra of polyesterurethane (PLA-TDI) (PU-1). b. MALDI-TOF spectra of polyesterurethane (PLA-HMDI (PU-2). c. MALDI-TOF spectra of polyesterurethane (PLA-MPDI) (PU-3). d. MALDI-TOF spectra of polyesterurethane (PLA-HDI) (PU-4).
The MALDI is dominated by a series of intense peak ranging of 2050 to 4500 Da corresponding oligomers doped Na⁺ ions of type

\[ \text{OH} \rightarrow \left( -\text{CO-NH-} \Phi_2 \text{-CO-O} \right)_n \left( \text{CH(CH}_3\text{)-CO-O} \right)_n \left( \text{CH} \left( \text{CH}_3\right)\text{-(CH}_2\text{) }_2\text{-CH(CH}_3\text{-}[O-CO-CH}(\text{CH}_3)\text{)]n-OH-Na^+ \right. \]

(mass = \(72n+84+102+166+23\)), where \(n\) varies from 1 to 4 and 23 being the mass number of sodium. \( \Phi_2 \) represents biphenyl methylene group. The corresponding peaks due to the polyurethane doped with \(K^+\) ions (\(K^+\) adduct molecular ions, mass \((72n+84+102+166+39)\), see the peak at 2188, 4075 and 4386 Da respectively. Fig. 10d depicted the MALDI TOF spectra of polyesterurethane of PU-4 prepared from hydroxyl terminated PLA with hexamethylene diisocyanates. The MALDI spectrum is dominated by a series of intense peaks ranging from a mass of 500 Da to a mass of 1100 Da, corresponding to oligomers doped with Na⁺ ions of the type

\[ \text{OH} \rightarrow \left( -\text{CO-NH-} \Phi_2 \text{-CO-O} \right)_n \left( \text{CH(CH}_3\text{)-CO-O} \right)_n \left( \text{CH} \left( \text{CH}_3\right)\text{-(CH}_2\text{) }_2\text{-CH(CH}_3\text{-}[O-CO-CH}(\text{CH}_3)\text{)]n-OH-Na^+ \right. \]

(mass = \(72n+84+102+23\)), where \(n\) varies from 1 to 5 and 23 being the mass number of sodium. The corresponding additional peaks are due to the polyurethanes doped with \(K^+\) ion (\(K^+\) adduct molecular ions, \(m=72n+84+102+84+39\)), the peaks at 2187.9, 4074.7 and 4385.7 respectively.

**Transmission electron microscopy (TEM)**

The thermal characteristic result showed the aggregation behavior of hydroxyl end groups, which was further examined by TEM. Functionalized interfacial organic and polymer layers fabricated from molecular segments with different amphiphilicity can be designed to act as a smart or switchable surface. These surfaces are capable of responding to various suitable changes in the surrounding environment such as \(\text{pH}\), surface pressure and temperature, light and solvent quality. In the present study, PU-1, PU-2, PU-3 and PU-4 aggregate in isopropyl alcohol solvent and their structures are slightly different from each other. These structures are responsible for controlling physical properties in term of application such as drug delivery and biomimetic materials. PU-1, PU-2, PU-3 and PU-4 used in this study is hydroxyl terminated PLA and four different isocyanates, which were synthesized to obtain different polyesterurethanes. The \(M_n\) and polydispersity indices of the polyesterurethanes were estimated by gel permeation chromatography. \(T_g\), \(T_m\) and \(\Delta H\) values were calculated from DSC curves and illustrated in Table 4.

From the MALDI TOF spectrum, it was observed that all four polyesterurethanes contain hydroxyl terminated end group at both ends. Invariably, a single polyesterurethane polymer contains two hydroxyl groups. The hydrophilic and hydrophobic group will be placed on the opposite sides of the polyesterurethane backbone in isopropyl alcohol. Fig. 11(a-d) showed the morphologies of the aggregates of PU-1, PU-2 and PU-4 in isopropyl alcohol. However, PU-3 showed the entirely different morphology in comparison with PU-1, PU-2, and PU-4 and showed précised narrow distribution of micelle-like aggregates in isopropyl alcohol. They consist of a hydrophobic units core covered with hydrophilic units (hydroxyl groups) forming corona. The hydrophobic units’ core is covered with hydrophilic units forming the corona. Similar observation has been made by Lifeng Zhang et. al.[22]

The hydroxyl and carboxyl ended telechelic polylactic acid (PLA) oligomers were also subjected to a chemical reaction with above four isocyanates at similar reaction conditions as mentioned above. The obtained polyesterurethanes are mixture of linear and insoluble crosslinked products. In some of the reaction conditions, the insoluble crosslink products are around 30 %.

**Conclusion**

Hydroxyl terminated PLA oligomers were synthesized by the reaction of L-lactic acid with 2, 5-hexane diol via dehydropropycondensation technique. They were mainly characterized by \(\text{H, } ^1\text{C and } ^3\text{P NMR and confirmed that both ends contain secondary hydroxyl groups (CH (CH}_3\text{)}}\text{OH). PLA oligomers containing both hydroxyl and carboxylic groups were also synthesized by the ring opening polymerization using stannous octoate as an initiator and water as a coinitiator and their structures were confirmed by spectral techniques. All the reactions were monitored precisely in a quantitative manner. The optimum reaction conditions were determined for the synthesis of linear PLA-based polyurethanes. The reaction time, reaction temperature, the concentration of modified cloisite catalyst was varied to obtain optimum result. The reaction time is much reduced in comparison with earlier literature report. The Tin modified solid cloisite catalyst had a fundamental impact on the molecular weight of the polyesterurethanes. The desirable linear polyesterurethanes were exclusively obtained from diol ended PLA oligomers and various aliphatic, alicyclic and aromatic disiocyanates. The polyester-urethane product (~100 % yield) is white and completely soluble in organic solvents such as chloroform, N, N-dimethyl formamide etc. There is exclusively urethane linkage when diol ended PLA oligomers are used. The final telechelic polyurethane polymers contain hydroxyl groups at both ends. It can react with any telechelic polymer preferably containing isocyanate groups at both ends.
The similar white product (~100 % yield) was obtained from hydroxyl and carboxyl ended PLA oligomers and diisocyanates compounds and soluble to some extent in organic solvents such as chloroform, N, N-dimethyl formamide etc. The urethane and amide linkage are observed when both hydroxyl and carboxyl ended PLA oligomers are used. However, around 30% crosslinked polyestereurathane products were obtained when PLA oligomers containing both hydroxyl and carboxylic groups reacted with various aliphatic, alicyclic and aromatic diisocyanates at identical condition. On the basis of the MALDI-TOF-MS, $^{13}$C nmr and IR investigations, the functionality of the various polyesterurethanes synthesized was determined, the presence of hydroxyl groups at the both ends were supported. TEM picture showed the morphologies of the aggregates of polyurethanes (PU-1, PU-2, PU-3 and PU-4) in isopropyl alcohol because of hydroxyl-hydroxyl self association.

This prepared polyester urethane has the advantages of good biocompatibility, simple preparation method, low preparation cost, environmental friendliness and suitability for industrial production, can be absorbed by human body, and has good application prospect in the field of medicine.

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