LOW TEMPERATURE BIOPLASTIC FOR MEDICAL APPLICATION

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ABSTRACT

In this study, PLA was synthesized by bulk ring opening polymerization in the presence of Sn(Oct)\textsubscript{2} as catalyst and cardanol as plasticizer. Furthermore cardanol which containing a hydroxide group was also expected to react with Sn(Oct)\textsubscript{2} to form the actual initiator in this system. The obtained synthesized PLA products were mixed with commercial PLA at different contents for the low temperature splinting materials. The effect of plasticizer content, polymerization time, and polymerization temperature on the glass transition temperature, molecular weight, percentage of yield and percentage of monomer conversion were studied. In addition, the physical and mechanical properties of products for splinting materials were also investigated.

INTRODUCTION

Polymers have been widely applied in health rehabilitation as substitutes for plaster to correct and support body structures after surgery over the past decades. Polymers differ from traditional plaster in that they are lighter, easily molded to fit the body of the patient and can be removed for cleaning and patient bathing. These polymers are classified into two types base on the molding temperature of the material which compose of high temperature thermoplastic polymers and low temperature thermoplastic polymers. Most of the splinting materials today are referred to as low temperature thermoplastics (LTTPs) because we can activate them at low heat (60-70\textdegree C) when compared to other high temperature thermoplastics which require higher activation temperatures (greater than 100\textdegree C). We can also place these LTTPs directly on the patients while we are molding, unlike the previous generations had to create molds first (Meng, Q. et al., 2009).

There are so many types and varieties of LTTPs splinting materials available today such as polyurethane impregnated fiberglass bandages which have more advantages when compared to plaster of Paris (Gypsona) bandages such as greater strength, lighter weight, better X-ray transmission, cleaner application and much faster curing time (Wytch, R. et al., 1987). However, the increasing in environmental concern has provided an active impetus in research leading to the synthesis of biodegradable polymers and also the consideration about toxicity during processing (Gowda, R.R. et al., 2011). Poly(lactic acid) (PLA) is one such polymer, with biodegradability, biocompatibility, good mechanical properties, processability and widely used as biomedical materials in absorbable sutures, orthopaedic devices, tissue scaffolds or drug delivery (Yuan, Y. et al., 2016 & Cabezas, L.I. et al., 2013). The preferred route for synthesis PLA is the bulk ring opening polymerization of the lactide cyclic monomer in the presence of an initiator (Schwach, G. et al., 1997). However, PLA is still pretty brittle for using in some applications.
The most widespread used approach in order to improve polymer ductility is the use of plasticizer, potentially able to reduce the glass transition temperature of polymer. Cardanol is an industrial grade oil obtained by vacuum distillation of cashew nut shell liquid (CNSL), which represents a by-product of cashew nut shell industry. Cardanol and its derivatives have been proven to be efficient plasticizer in many works (Greco, A. et al., 2016). Synthesized cardanol derivative glycidyl ether (CGE) incorporated with PVC (CGE/PVC) showed the decreasing of glass transition temperature and increasing of elongation at break of PVC when compared with PVC incorporated with two kinds of commercial phthalate ester plasticizer DOTP and DINP (Chen, J. et al., 2015). Cardanol acetate (CA), as plasticizing agent of poly(lactic acid) (PLA). The plasticizing effectiveness of cardanol acetate was confirmed by the decrease of glass transition temperature and flexural modulus, which were comparable to those obtained by the use of conventional oil based plasticizers, such as DEHP (Greco, A. et al., 2016).

The aim of this work is to find the suitable condition for synthesized PLA by bulk polymerization. The obtained synthesized PLA products were mixed with commercial PLA at different contents for the low temperature splinting materials. The physical and mechanical properties of products for splinting materials were investigated.

EXPERIMENTAL

Materials

L-lactide monomer (99.5% purity) was purchased from Shenzhen Bright China Industrial Co., Ltd, commercial PLA in pellet form (Natureworks PLA 2003D) and tin(II) 2-ethylhexanoate (stannous octoate, Sn(Oct2)) from Sigma-Aldrich Corp, and cardanol from Satya Cashew Chemicals® PVT. LTD. Tetrahydrofuran, isopropyl alcohol, dichloromethane, and methanol were of HPLC grade from RCI Labscan LTD.

Synthesis PLA

Ring opening polymerization of lactide was conducted in the bulk phase using stannous octoate (Sn(Oct)2) as catalyst. First, L-lactide monomer 25 g, catalyst 0.0625 wt% and cardanol at varied contents (3, 5, 10, 15 wt%) were placed together in a glass round bottom flask and were dried under vacuum. To make sure that in the system not has any moisture, nitrogen gas was also purged into a glass round bottom flask and then it was sealed by rubber stopper. The contents were heated with stirring at varied temperatures (140, 160 and 180°C) in an oil bath. During the reaction at a given temperature, samples were collected along the reaction time and were quenched to room temperature around 25°C to stop polymerization. The polymerization product was dissolved in dichloromethane and precipitated with methanol, which this process was twice repeated to purify the polymer. After filtration, the polymer was dried in a vacuum oven at 40°C for 24 hrs.

Mixing synthesized PLA with commercial PLA

The obtained synthesized PLA products from first part were mixed with commercial PLA at varied contents (10, 20 and 30 wt%) in internal mixer at 180°C for
10 min with a rotor speed 60 rpm. After mixing, the products were ground into small size for easier using in further characterization.

**Characterization**

The functional group of synthesized PLA was analyzed by Thermo Nicolet Nexus 670 FT-IR spectrometer. The spectra were recorded from 650 to 4000 cm\(^{-1}\) with number of scans 16 and a resolution of 4 cm\(^{-1}\).

The molecular weight (MW) and molecular weight distribution (MWD) of synthesized PLA were determined by gel permeation chromatography (GPC) on a SHIMADZU GPC instrument equipped with Styragel columns and a refractive index detector. Tetrahydrofuran (THF) was used as eluent at 40°C with flow rate of 1 mL/min and injection volume of 60 μL. All samples were dissolved in THF and filtered before injection with a pore size of 0.45 μm. The molecular weight was calibrated according to polystyrene standard calibration curve.

The percentage of yield of synthesized PLA was determined by using gravitational method. The monomer conversion of samples was determined by thermo gravimetric analysis on a TGA Perkin-Elmer instrument with a refrigerated cooling system. Samples weights were between 3-10 mg and the measures were run in aluminum pan from 25 to 400°C at a heating rate of 10°C/min under nitrogen purge with flow rate of 100 mL/min.

Differential scanning calorimetry was performed using a Perkin Elmer under nitrogen gas at flow rate of 20 mL/min. The samples (4-8 mg) were placed in aluminum pan. The testing temperature ranged from 25 to 200 °C at a heating rate of 10°C/min. To reduce the influence of thermal history, all samples were first heated to 200 °C. After that they were cooled to 25°C at a cooling rate of 10°C/min, and then reheated to 200°C at same condition to record the heat flow for analysis.

Melt flow indexer (Dynisco) was used to check melt flow index (MFI) of the samples. The tests were carried out following ASTM D1238 at 190°C and the 2.16 kg load was applied to extrude the melt. The units of measure are grams of material/10 minutes (g/10 min).

The mechanical properties were determined by using an Instron testing machine. The samples were prepared in the dumbbell shape. The tensile tests were carried out following with ASTM D638-04 at a stretching speed of 10 mm/min.

**RESULTS AND DISCUSSION**

**Chemical analysis of synthesized PLA**

FTIR technique was employed to study the functional of synthesized PLA. The spectra were recorded from 650 to 4000 cm\(^{-1}\) with 16 scans at a resolution of 4 cm\(^{-1}\). Figure 1 shows the FTIR spectra of lactide monomer and synthesized PLA with cardanol (CD) content 3 wt% at 160°C for 8 h. The synthesized PLA spectra shows the band at 2998.29 and 2931.07 cm\(^{-1}\) from symmetric and asymmetric valence vibration of C-H from CH\(_3\), respectively. It is possible to observe a band shift related to the C=O stretch in monomer in 1752.30 to 1756.65 cm\(^{-1}\) in the synthesized PLA. In addition, it can be observed that the ring specific vibration of lactide monomer at about 650 and 930 cm\(^{-1}\) are decreased in synthesized PLA.
Figure 1  FTIR spectra of lactide monomer and synthesized PLA with cardanol content 3 wt%.

Figure 2 shows FTIR spectra of CD and synthesized PLA with CD contents 3 and 15 wt% at 160ºC for 8 h. The CD spectra shows many typical peaks. The phenolic hydroxyl group at 3332.99 and 1348.45 cm\(^{-1}\). The C-H in -CH=CH- on benzene ring and unsaturated alkyl chains at 3008.25 and 998.87 cm\(^{-1}\), respectively. The methyl, methylene and methane groups at 2923.54, 2852.97, and 1455.19 cm\(^{-1}\), respectively. The C=C on aromatic ring at 1588.41 cm\(^{-1}\), symmetric and asymmetric stretching of C=C at 1263.16 and 1153.22 cm\(^{-1}\), respectively. The vibration of the four hydrogen atoms adjacent to the benzene ring at about 780 and 690 cm\(^{-1}\). In the spectra of synthesized PLA, the phenolic hydroxyl group (3332.92 cm\(^{-1}\)) of CD is not observed, while the vibration of the four hydrogen atoms adjacent to the benzene ring (about 780 and 690 cm\(^{-1}\)) is observed and the intensity of peak at CD content 15 wt% is higher than at 3 wt%. These results indicate that CD may be has some form complexes with PLA.

Figure 2  FTIR spectra of cardanol and synthesized PLA with cardanol contents 3 and 15 wt%.

Effect of polymerization time and temperature

In this part, cardanol content and polymerization time were fixed at 3 wt% and 6 h, respectively. The polymerization temperatures were varied in 140, 160 and 180ºC to determine the suitable temperature for synthesis PLA. The effect of polymerization temperature on molecular weight of synthesized PLA is shown in Table 1.
Table 1 The molecular weight of synthesized PLA at different temperatures.

<table>
<thead>
<tr>
<th>Temperature (˚C)</th>
<th>Time (h)</th>
<th>Mn (g/mol)</th>
<th>Mw (g/mol)</th>
<th>MWD</th>
</tr>
</thead>
<tbody>
<tr>
<td>140</td>
<td>6</td>
<td>11,272</td>
<td>14,367</td>
<td>1.27</td>
</tr>
<tr>
<td>160</td>
<td>6</td>
<td>16,760</td>
<td>25,472</td>
<td>1.53</td>
</tr>
<tr>
<td>180</td>
<td>6</td>
<td>13,646</td>
<td>20,551</td>
<td>1.51</td>
</tr>
</tbody>
</table>

From Table 1, it is clearly seen that the highest molecular weight of synthesized PLA was obtained at 160˚C. At 140˚C provided the lower molecular weight because this temperature is lower than the melting point of PLA so when the reaction was carried out until certain time, viscosity in the system was increased and the further reaction was limited. However, if the polymerization temperature is too much (180 ˚C), the depolymerization can occur and then the molecular weight will decrease. The results confirmed that the suitable polymerization temperature in this system is 160˚C.

The effect of polymerization time and cardanol contents on molecular weight of synthesized PLA, monomer conversion and percentage of yield were also investigated. In this study cardanol contents were varied in 3, 5, 10, and 15 wt% of lactide monomer and polymerization temperature was fixed at 160˚C. The polymerization times were varied in range of 1-8 h. The results are shown in Figure 3-6.

![Figure 3](image1.png) **Figure 3** The effect of polymerization time on Mn of synthesized PLA.

![Figure 4](image2.png) **Figure 4** The effect of polymerization time on Mw of synthesized PLA.

![Figure 5](image3.png) **Figure 5** The effect of polymerization time on monomer conversion.

![Figure 6](image4.png) **Figure 6** The effect of polymerization time on percentage of yield.

From Figure 3-6 shows the time dependence of molecular weight of synthesized PLA and monomer conversion. It is clearly seen that both molecular weight and
monomer conversion increase with time in the first interval of reaction time, due to the relatively high propagation rates induced by the higher concentration of monomer in the mixture at the beginning. As the monomer concentration decreases, the propagation rate is diminishing and the molecular weight tends to stabilize. However, if the reaction takes place for a long time, the molecular weight presents a decreasing trend due to the process reversibility same as in the case of using high temperature. The suitable polymerization time that provided high molecular weight of synthesized PLA is about 6 h. The effect of cardanol contents on molecular weight and percentage of yield are also considered. From the data shows that both molecular weight and percentage of yield decreased with increasing cardanol contents because cardanol has hydroxyl group which also can act as initiator in this system so when initiator concentration increase, it will provide more number of polymer chains but low molecular weight.

**Effect of cardanol contents on thermal properties**

The thermal properties of synthesized PLA were investigated by means of differential scanning calorimetry. From figure 7 shows that when synthesized PLA was cool from 200 to 25°C at a rate 10°C/min to eliminate thermal history, evidence of crystallization was observed and no cold crystallinity phenomenon was observed in the secondary heating curve. The degree of crystallinity ($X_c$) of synthesized PLA could be calculated from the melting enthalpy ($\Delta H_m$) in the second heating curves according to the following equation:

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} \times 100 \%$$  \hspace{1cm} (1)

where $\Delta H_m^0$ is the standard melting enthalpy of the PLA crystalline (93 J/g). The thermal characteristics of synthesized PLA with all cardanol contents are also given in Table 2.

![Figure 7](image.png)  
*Figure 7 DSC curves of synthesized PLA at different cardanol contents: a) 3 wt%, b) 5 wt%, c) 10 wt%, and d) 15 wt%.*

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As shown in Figure 7 and Table 2, the addition of cardanol provided chain mobility in synthesized PLA so evidence of crystallization can be observed in the cooling step as mentioned before. However, with the increasing of cardanol contents, $X_c$ of synthesized PLA slightly decreased and $T_m$ decreased dramatically, especially at cardanol contents 10 and 15 wt%.

The obtained synthesized PLA with different cardanol contents from first part were mixed with commercial PLA at ratio 10:90, 20:80 and 30:70. The thermal properties of the mixing products were also investigated.

![Figure 8: DSC curve of synthesized PLA at cardanol content 3 wt% mixed with commercial PLA at different ratios.](image1)

![Figure 9: DSC curve of synthesized PLA at different cardanol contents mixed with commercial PLA at ratio 30:70.](image2)

### Table 3 DSC data of synthesized PLA mixing with commercial PLA.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_g$ (°C)</th>
<th>$T_{cc}$ (°C)</th>
<th>$\Delta H_{cc}$ (J/g)</th>
<th>$T_{m1}$ (°C)</th>
<th>$T_{m2}$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$X_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial PLA</td>
<td>54.8</td>
<td>122.8</td>
<td>14.27</td>
<td>150.2</td>
<td>-</td>
<td>14.78</td>
<td>0.55</td>
</tr>
<tr>
<td>PLACD3_10</td>
<td>55.8</td>
<td>109.3</td>
<td>32.17</td>
<td>148.4</td>
<td>157.1</td>
<td>38.14</td>
<td>6.42</td>
</tr>
<tr>
<td>PLACD3_20</td>
<td>53.2</td>
<td>103.5</td>
<td>30.47</td>
<td>147.8</td>
<td>157.0</td>
<td>39.08</td>
<td>9.26</td>
</tr>
<tr>
<td>PLACD3_30</td>
<td>52.9</td>
<td>101.8</td>
<td>31.53</td>
<td>149.1</td>
<td>158.3</td>
<td>42.39</td>
<td>11.68</td>
</tr>
<tr>
<td>PLACD5_10</td>
<td>58.4</td>
<td>107.4</td>
<td>29.78</td>
<td>148.3</td>
<td>156.7</td>
<td>36.78</td>
<td>7.53</td>
</tr>
<tr>
<td>PLACD5_20</td>
<td>51.8</td>
<td>100.8</td>
<td>31.35</td>
<td>145.8</td>
<td>155.0</td>
<td>40.45</td>
<td>9.78</td>
</tr>
<tr>
<td>PLACD5_30</td>
<td>50.6</td>
<td>99.6</td>
<td>30.26</td>
<td>141.2</td>
<td>155.0</td>
<td>41.05</td>
<td>11.60</td>
</tr>
<tr>
<td>PLACD10_10</td>
<td>57.9</td>
<td>110.2</td>
<td>29.84</td>
<td>148.3</td>
<td>155.9</td>
<td>34.79</td>
<td>5.32</td>
</tr>
<tr>
<td>PLACD10_20</td>
<td>53.5</td>
<td>106.2</td>
<td>31.59</td>
<td>146.1</td>
<td>155.0</td>
<td>39.39</td>
<td>8.39</td>
</tr>
<tr>
<td>Samples</td>
<td>( T_g ) (°C)</td>
<td>( T_{cc} ) (°C)</td>
<td>( \Delta H_{cc} ) (J/g)</td>
<td>( T_{m1} ) (°C)</td>
<td>( T_{m2} ) (°C)</td>
<td>( \Delta H_m ) (J/g)</td>
<td>( X_c )</td>
</tr>
<tr>
<td>----------</td>
<td>----------------</td>
<td>----------------</td>
<td>---------------------------</td>
<td>----------------</td>
<td>----------------</td>
<td>----------------</td>
<td>-------</td>
</tr>
<tr>
<td>PLACD10_30</td>
<td>47.6</td>
<td>100.4</td>
<td>30.29</td>
<td>142.9</td>
<td>152.8</td>
<td>40.77</td>
<td>11.27</td>
</tr>
<tr>
<td>PLACD15_10</td>
<td>51.7</td>
<td>101.6</td>
<td>32.07</td>
<td>143.8</td>
<td>153.4</td>
<td>36.75</td>
<td>5.03</td>
</tr>
<tr>
<td>PLACD15_20</td>
<td>48.6</td>
<td>106.4</td>
<td>32.40</td>
<td>142.7</td>
<td>152.5</td>
<td>38.93</td>
<td>7.02</td>
</tr>
<tr>
<td>PLACD15_30</td>
<td>45.6</td>
<td>100.4</td>
<td>32.84</td>
<td>139.6</td>
<td>150.4</td>
<td>39.54</td>
<td>7.20</td>
</tr>
</tbody>
</table>

As shown in Figure 8-9 and Table 3, the mixing of synthesized PLA with commercial PLA affected the glass transition temperature, melting temperature and degree of crystallinity of the mixing products. When the contents of cardanol and synthesized PLA increased, the glass transition temperature and melting temperature slightly decreased due to the effect of chain mobility. In case of the degree of crystallinity, when synthesized PLA contents increased, the degree of crystallinity also increased but if we considered about cardanol contents, found that at cardanol contents 10 and 15 wt% provided the lower degree of crystallinity when compared with cardanol content at 3 and 5 wt%.

**Physical properties**

The variation of melt flow index (MFI) of the mixing products was showed in Figure 10.

![Figure 10 Melt flow index (MFI) of the mixing product at different ratios.](image)

MFI data shows that all formulations have higher MFI than commercial PLA. The addition of synthesized PLA increases the polymer chain mobility which implies a reduction in viscosity and increase of MFI of the mixing products.

In addition, physical appearance of the mixing products was also studied. As show in Figure 11, all formulations still have transparent properties but the color become more yellow with increasing cardanol contents and synthesized PLA contents in the mixing products.
Mechanical properties

It is well known that commercial PLA has poor flexibility and presents a typical fragility. It has a high tensile strength and modulus but low elongation at break. With the addition of synthesized PLA, changes in mechanical properties were identified by tensile tests. The tensile properties and stress-strain curves of the mixing products are shown in Figure 12.

![Figure 12 Stress-strain curve of the mixing product at different synthesized PLA contents; a) 10 wt%, b) 20 wt% and c) 30 wt%.

The results show that the synthesized PLA with cardanol content at 3 wt% and mixing content at 10 wt% slightly improved elongation at break, whereas tensile strength and modulus decreased. In case of the other formulations, even though they can also provide the low glass transition temperature and the increasing of the degree of crystallinity but the mechanical property of the mixing products still bad and tended to worse than commercial PLA. This was the result of the molecular weight. From previous results, the molecular weight of synthesized PLA was relatively low when compared with commercial PLA so the immiscible between both of them can occur when mixing together and the synthesized PLA may acted as like a defect in the mixing products resulted in decreased the mechanical properties.

CONCLUSIONS

The synthesized PLA was characterized by FTIR to analyze its functional groups. The effect of polymerization time and temperature, the effect of cardanol
contents on thermal properties, the physical properties, and the mechanical properties were studied. The results show that at 160˚C with polymerization time around 6 h and cardanol content 3 wt% provide the highest molecular weight of synthesized PLA. Molecular weight of synthesized PLA decreases with increasing cardanol contents. The glass transition temperature and melting temperature slightly decrease with increasing cardanol and synthesized PLA contents in the mixing products. For physical properties, MFI of the mixing products increases with increasing cardanol and synthesized PLA contents. The mixing products still have transparent properties. Synthesized PLA with cardanol content at 3 wt% and mixing content at 10 wt% provide the good mechanical properties when compared with the other formulations.

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