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Full Length Research Paper

Effect of Temperature, Catalyst Concentration and Time, on Polylactic Acid Production from Sisal Boles Juice by Ring Open Polymerization

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ABSTRACT

Polylactic acid (PLA) is a biodegradable and renewable alternative to non-biodegradable petrochemical-based polymers that is environmentally friendly and green. PLA can be made from a variety of agricultural wastes that contain sugars, such as sisal boles. This study aimed at analysing the possibility of producing PLA from lactic acid (LA) produced from sisal bole. A 2^n factorial design was used to analyse the effects of temperature (160-180°C), time (1-2 hrs) and tin octoate catalyst concentration (0.025-0.05%) on the PLA yield during polymerization. Minitab Version 20.2.0 was used to design the experiment and analyse the effects on the responses through ANOVA. It was possible to produce 0.73±0.05 g of lactide per g of sisal bole LA used. More than 99% conversion of lactide into PLA was done for 2 hrs when the system temperature was 180°C regardless of the catalyst ratio used. Temperature and time significantly affected the yield with p-values of less than 0.05 at 95% confidence level. The current findings support sisal bole juice as an alternative feedstock for LA production, a precursor for PLA. The use of sisal bole (SB) waste will protect environment by using waste biomass as an opportunity to participate in a global move to produce biobased plastics and promote the ban on the use of petrochemical-based plastics in packaging.

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INTRODUCTION

More than 270 million tonnes of oil and gas are used annually in the production of traditional, non-biodegradable petrochemical plastics (Msuya *et al.*, 2017). Disposal of non-biodegradable polymer waste has been a major topic of concern for environmental protection (Msuya *et al.*, 2017; Rasal *et al.*, 2010). Use of biodegradable polymers emerges as a promising solution in the preservation of our environment (Hammiche *et al.*, 2019; Dubey *et al.*, 2016).

PLA is a biodegradable and renewably derived thermoplastic polymer (Costa *et al.*, 2016; Rasal *et al.*, 2010), that is green alternative to non-biodegradable petrochemical-based plastics (Ma *et al.*, 2016). Agricultural waste materials like sisal boles contain sugars that can be used to produce Lactic acid (LA) which is a building block for PLA (Msuya *et al.*, 2017). Details of production of pure LA from sisal boles is described in other papers (Msuya *et al.*, 2018c, 2017). This study focuses on using the LA produced from sisal boles to produce PLA using ring open polymerization.

Ring-opening polymerisation (ROP) is a form of chain-growth polymerization, in which the terminal end of a polymer chain acts as a reactive centre where further cyclic monomers can react by opening its ring system and form a longer polymer chain (Lim *et al.*, 2008; Sin *et al.*, 2007; Jacobsen *et al.*, 2000). Ring open polymerization was selected in this study due to its ability to produce high molecular weight polymer (Jamshidian *et al.*, 2010). High molecular weight polymer is easily produced in the presence of catalyst such as aluminium isopropoxide ($Al(OPr)_3$), zinc lactate ($C_6H_{10}O_6Zn$), and tin octoate ($Sn(Oct)_2$) (Balla *et al.*, 2021; Dubey *et al.*, 2016). Tin octoate ($Sn(Oct)_2$) has been approved by Food and Drug Administration (FDA) of United States of America as a safe food additive (Dubey *et al.*, 2016). It is easily soluble in lactide monomer and subsequently allows almost complete conversion (Balla *et al.*, 2021; Dubey *et al.*, 2016). It has low risk of racemisation and can be easily removed from obtained polymer with product yield higher than 90% (Horváth *et al.*, 2021; Pholharn *et al.*, 2019, 2017; Msuya *et al.*, 2017; Pretula *et al.*, 2016).

In ROP, LA is first polymerized to low molecular weight oligomers, which are catalytically depolymerised through internal transesterification to lactide, in an equilibrium reaction that forms the six-member cyclic dimer (lactide ring: 3, 6 dimethyl 1, 4-dioxane 2, 5,-Dione) which together with impurities and presence of water can results into low molecular weight polymer (Nampoothiri *et al.*, 2010; Gupta and Kumar, 2007; Garlotta, 2002). This dimer is prepared by thermal cracking of low molecular weight PLA oligomers at high temperature and low pressure in the presence of catalyst (Nuyken and Pask, 2013; Gupta and Kumar, 2007). The ring of lactide then opens to form high molecular weight PLA (Dusselier *et al.*, 2013; Reddy *et al.*, 2013) .

The ROP reaction is sensitive to experimental conditions including temperature, heating rate, inner pressure, catalyst and reagent. Various researchers have studied the effect of certain variables on the tin octoate catalyst polymerization. It was found that the yield and transesterification is affected by polymerization temperature (160-180°C), catalyst concentration (0.03-0.06%) and polymerization time (2-4 hours) (Lopes *et al.*, 2014; Hagen, 2005; Garlotta, 2002). It is revealed that, higher molecular weight PLA (> 172,000) with optimal yield of 91-93% was obtained using $Sn(Oct)_2$ as a catalyst (0.04%); temperature of 180°C, and reaction time of 2 hrs at atmospheric pressure (Hu *et al.*, 2016). These set of parameters were tested in this study during PLA production.

PLA has numerous interesting properties including good mechanical properties, thermal stability, processability and low environmental impact. PLA can be quite different in chemical and physical properties because of the presence of a pendent methyl group attached to its alpha carbon atom (Gupta and Kumar, 2007). Thermal, mechanical and biodegrability of PLA along with its crystallinity depend strongly on the ratio and distribution of the two stereoisomers in the polymer chain (Cardoso *et al.*, 2013). The ratio of L, D and DL enantiomers influences the properties of PLA such as melting temperature and crystallinity (Ebrahimi and Dana, 2021; Carrasco *et al.*, 2010). Crystalline PLA has L- content higher than D- content; the higher the L the higher the crystallinity.

Since PLA is a thermoplastic polymer, its melting temperature (T_m) and glass-transition temperature (T_g) are strongly dependent on the molar mass and optical purity of the polymer (Ebrahimi and Dana, 2021; Hammiche *et al.*, 2019; Inkinen *et al.*, 2011). The increase in molecular weight produce an increase in the glass transition temperature T_g and crystallinity (Lim *et al.*, 2008), leading to slower degradation since glassy polymers degrade more slowly than rubbery ones (Siracusa *et al.*, 2008). The optical purity of PLA can affect the structural, thermal, barrier and mechanical properties of the polymer. PLA polymers with L- or D- content greater than 90% is said to be crystalline while those with lower values are amorphous (Lim *et al.*, 2008). Different studies have been done on PLA for packaging (Farah *et al.*, 2016; Armentano *et al.*, 2013; Rhim *et al.*, 2013; Sin *et al.*, 2013; Ahmed and Varshney, 2011; Carrasco *et al.*, 2010; Lim *et al.*, 2008). Crystalline high molecular weight Poly(L-Lactic Acid) (PLLA) of more than 100,000 Da with low T_m (170-180ºC), Tg of 55-65ºC and density of 1.25-1.29 g/cc is recommended (Gupta and Kumar, 2007; Garlotta, 2002; Conn *et al.*, 1995).

The crystallinity of PLA, glass-transition temperature (T_g) and melting temperature (T_m) is most commonly determined using differential scanning Calorimetry (DSC) (Lim *et al.*, 2008; Siracusa *et al.*, 2008). Thermal gravimetric analysis (TGA) is used to analyse the thermal properties of the polymer (Cardoso *et al.*, 2013; Lim *et al.*, 2008). Heat flow curves as a function of temperature is obtained under nitrogen flow with specified heating rate if DSC method is used. Thermogravimetric technique is widely used because it is cheap and very precise, it also does not require any specific reagents (Cardoso *et al.*, 2013). Fourier transform Infrared Spectroscopy (FTIR) and high-resolution pyrolysis gas chromatography have been also used to determine thermal degradation and stability of the polymer (Horváth *et al.*, 2021; Carrasco *et al.*, 2010). During the process, the spectra of the monomer and PLA samples can be analysed as films after casting and evaporating polymer solution in chloroform (1%) on an NaCl pellets (Horváth *et al.*, 2021; Cardoso *et al.*, 2013). Hence, these technologies (TGA, DSC, and FTIR) were employed to characterize the PLA produced in this study

METHODS AND MATERIALS

Study descriptions

Raw material for PLA production was LA produced from sisal bole. The extraction of juice, production and purification of LA from extracted sisal bole juice is reported in other papers (Msuya *et al.*, 2018a, 2018b, 2018c). The LA used in this study had an initial concentration of 108 g/L, with residual sugar concentration of 7 g/L (Msuya *et al.*, 2018b, 2018c). PLA production method followed three steps. The first step was water removal (dehydration) of LA. The polymerization methods reported by (Lopes *et al.*, 2014; Lasprilla *et al.*, 2011) was adapted with slight modifications on the equipment setup and experimental design. The water was removed at 160◦C for 2 hours at atmospheric pressure.

The second step involved lactide formation. The system pressure was maintained at 50-100 mbar by means of a Rotary Vane vacuum pump (1003317 3B Scientific® physics). The system temperature was first set at 170ºC for 2 hrs to remove any remaining water and then the temperature was increased gradually to 250ºC in steps of 1.33ºC/min. This was done for almost one hour and then the solution remained at 250ºC temperature for extra 30 minutes. Catalyst used was 0.1 ml of 1% (w/w) solution of tin octoate or stannous octoate (Tin (II) 2-ethylhexanoate ($C_{16}H_{30}O_4Sn$): Lot # SLBP6783V from Sigma Aldrich; 92.5-100%). The condenser temperature was set at 90ºC throughout the lactide formation process to prevent product sub-cooling, which might lead to hardening of the product. Lactide formation laboratory setup is given in Figure 1.

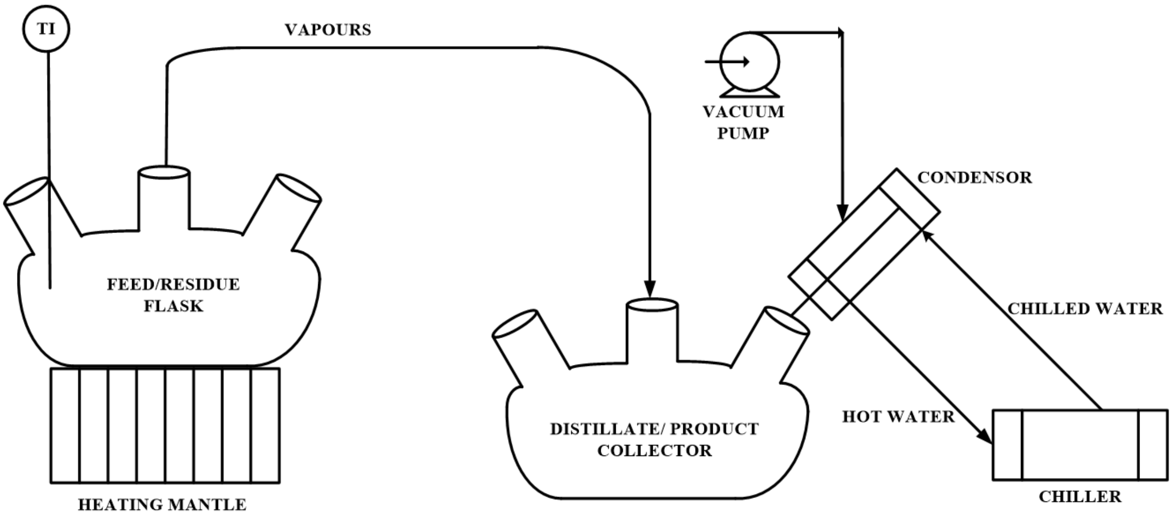

Figure 1: Lactide formation laboratory setup

The crude lactide was then purified before ring opening polymerization in order to obtain high purity and colourless lactide (Hong *et al.*, 2012; Liiu *et al.*, 2008). The lactide was dried in a tarred glass using the vacuum pump at 25 kPa followed by drying in a vacuum oven at 40°C for 12 hrs to remove any remaining moisture before crystallization. The crystallization method by Hyon *et al.*, (1997) was adapted with slight modification. The crude lactide was recrystallised three times while taking precaution not to add moisture into the product. The solvent used was ethyl acetate and the product was dried at 40°C for 12 hours and stored in desiccators with P_2O_5. Ethyl acetate was used due to its capacity to produce higher yield with high molecular weight compared to ethanol and other solvents (Sanglard *et al.*, 2012; Liiu *et al.*, 2008). For every 40 g of lactide crystallized, 100 g of solvent was used.

Third step involved polymerization through LA. A 2^n factorial design was used to design the experiment. Three parameters (Temperature, time and catalyst concentration) were analysed on their response to the yield. Two levels high and low for each factor were obtained from literatures (Hu *et al.*, 2016; Sanglard *et al.*, 2012; Hong *et al.*, 2012; Zhou *et al.*, 2008; Kaihara *et al.*, 2007) and used with their centre points. A design matrix is shown in Table **1** 1. A linear model presented by Equation 1; was used to fit the data and analyse their effects on the responses. Where X_1, X_2 and X_3 are independent variables; β_o, β_1, β_2, β_3 are linear coefficients; β_{12}, β_{13}, β_{23} are two-way interaction coefficients, β_{123} three-way interaction regression coefficients and Y is the response function.

Table 1: Design Matrix for Ring Open Polymerization

Parameters	**Lowest**	**Centre point**	**Highest**
Temperature (◦C)	160	170	180
Time (hrs)	1	1.5	2
Catalyst concentration (%w/w)	0.025	0.0375	0.050

Minitab version 20.2.0 was used to design the experiment and analyse the effects on the responses through ANOVA. The produced PLA was then removed from the polymerization flask, poured into glass plates and immediately quenched in cold water (4-8°) to increase crystallinity (Costa *et al.*, 2016). The product was then stored at less than 4°C to minimize isomerisation (Kaihara *et al.*, 2007) before further analyses. The yield was calculated as the amount of PLA produced (g) per amount of lactide used (g) per time.

The Fourier Transform Infrared spectroscopy (FTIR) was used to determine the functional groups of the produced lactide and PLA. Infrared spectra of lactide and PLA samples were obtained using an Attenuated Total Reflectance (ATR-FTIR) machine (Bruker Platinum-ATR Alpha series, Germany) using an ATR smart Orbit adapter with a diamond disc. For each sample of either LA or PLA a total of 32 scans were done with a wavelength resolution of 4 cm^{-1}. The wavelength used for FTIR experiment was 4000-500 cm^{-1} because the absorption radiation of most organic compounds and inorganic ions is within this region.

The thermal characteristics of the PLA produced were analysed using DSC/TGA. DSC provides information about thermal changes that do not involve a change in sample mass while TGA measures the mass change of a substance as a function of temperature. The thermal stability, melting and glass transition temperature of PLA were measured by Simultaneous Thermal Analyser (LINSEIS: STA PT-1000). Heating rate was set at 5ºC/minutes for both TGA and DSC. All the analyses were carried out in alumina crucible type (which is the best in heat conductivity) from 25-300ºC.

RESULTS AND DISCUSSION

The PLA polymerization yield results are presented in **Error! Reference source not found.**. The result shows clearly that the highest yield was obtained at the reaction temperature of 180ºC, for 2 hours at all catalyst ratios. There was no significant change of yield between 1 hour and 2 hours (0.996 compared to 0.998, respectively). The catalyst effect on the yield was not clearly seen for all runs. This might be attributed to the effect of temperature being too high compared to that of catalyst ratios used in this study. However, it should be noted that increasing amount of catalyst leads to increased number of initiated monomers that leads to shorter chain polymer. Hong *et al*., (2012) reported that it is possible to reduce the molecular weight for almost 37.5% when increasing catalyst content from 0.025% to 0.05%.

ANOVA analysis of the polymerization results, on the effects of temperature, time and catalyst ratio on the PLA yield gave a correlation coefficient of 0.997 confirming that the linear model correlated well with the experimental data. Only linear variables (Temperature and time) significantly affected the yield with p-values of less than 0.05 at 95% confidence level. No effect was seen in a linear variable (Catalyst), 2-way interactions and three-way interactions. This is also well elaborated in a Pareto chart given by Figure 2. Pareto charts are normally used to determine the magnitude and the importance of an effect to the responses. The chart displays the absolute value of the effects and draws a reference line on the chart that corresponds to $\alpha = 0.05$, by default. Any effect that extends past this reference line is statistically significant. It is clearly seen that, temperature has a higher effect on the PLA yield. Increase in temperature increased the PLA yield.

Figure 3 shows the Lactide and PLA formed during ring open polymerization process using sisal boles purified LA. The crude lactide contained yellow-like colour which is attributed to the colour of LA used. The residual sugar composition in the sisal bole LA (only 64% were removed during purification (Msuya *et al*., (2018c)), could have contributed to the colour change as it is concentrated and decomposes when higher temperatures were used during lactide formation. The lactide crystals obtained were whitish in colour which suggests that the solvent used was able to remove the colour containing compounds in the sisal bole crude lactide. From each 1.0 g of sisal bole LA used, it was possible to produce 0.73 g of Lactide. Low yield can also be attributed to the residual sugars in LA used.

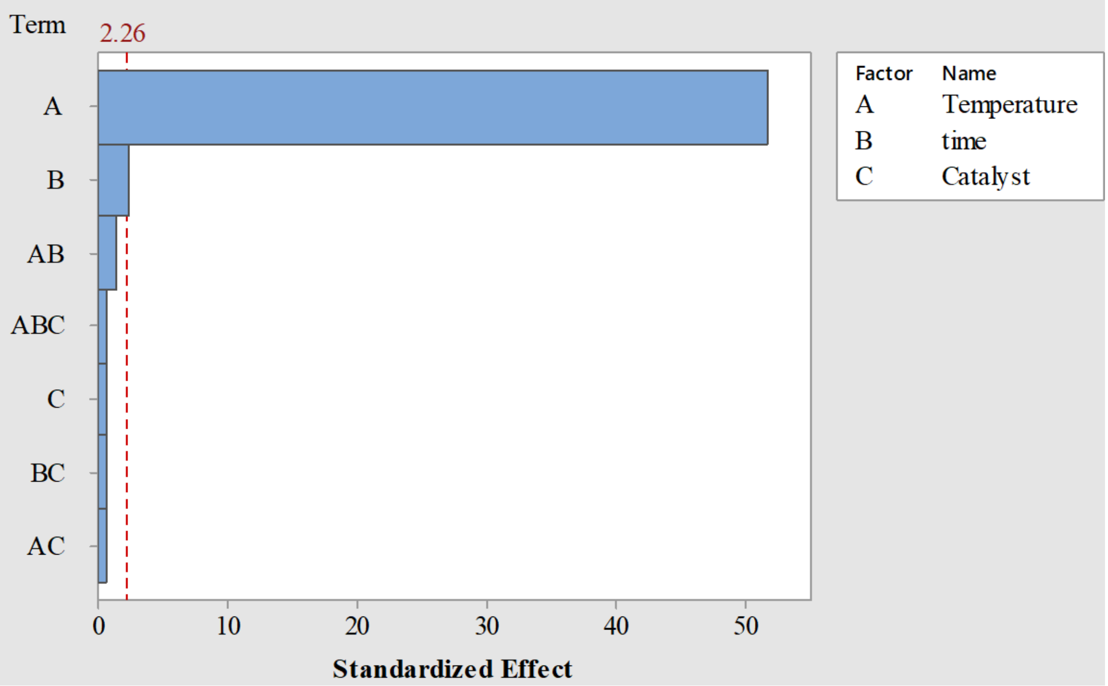

Figure 2: Pareto chart showing effects of variables in PLA yield

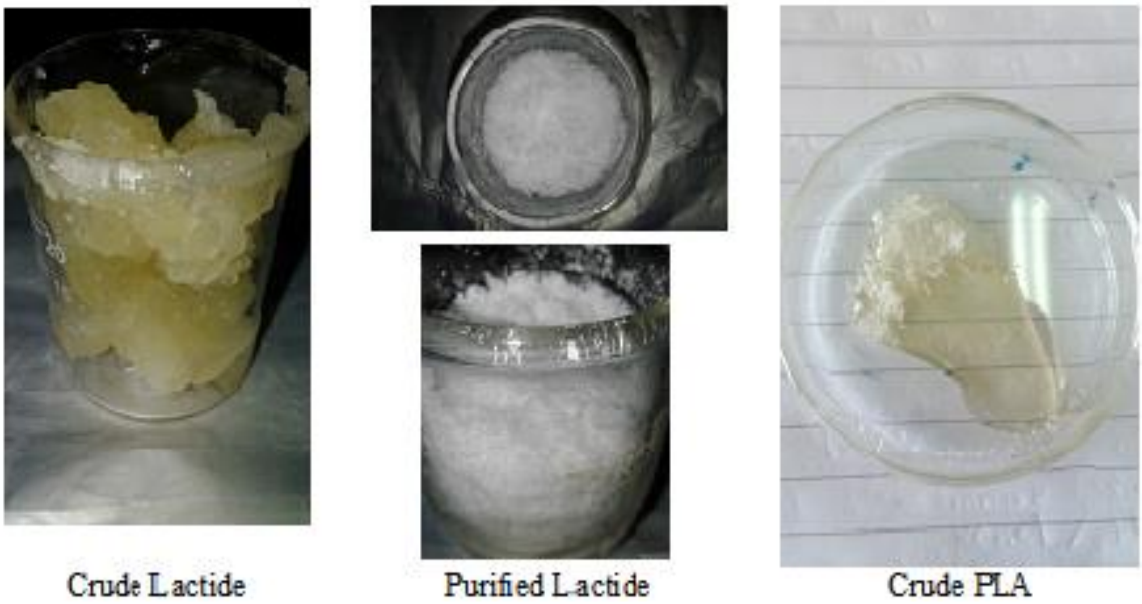

Figure 3: Crude lactide, purified lactide and crude PLA for sisal bole LA

Table 2: Polymerization results for PLA production from sisal bole

StdOrder	RunOrder	Temperature (◦C)	Time (hrs)	Catalyst (%)	Yield (g/g)
1	1	160	1.0	0.0250	0.890
8	2	180	2.0	0.0500	0.998
17	3	170	1.5	0.0375	0.990

StdOrder	RunOrder	Temperature (◦C)	Time (hrs)	Catalyst (%)	Yield (g/g)
16	4	180	2.0	0.0500	0.998
11	5	160	2.0	0.0250	0.890
6	6	180	1.0	0.0500	0.996
15	7	160	2.0	0.0500	0.900
12	8	180	2.0	0.0250	0.998
3	9	160	2.0	0.0250	0.900
18	10	170	1.5	0.0375	0.990
13	11	160	1.0	0.0500	0.890
10	12	180	1.0	0.0250	0.996
9	13	160	1.0	0.0250	0.880
14	14	180	1.0	0.0500	0.996
4	15	180	2.0	0.0250	0.998
5	16	160	1.0	0.0500	0.890
7	17	160	2.0	0.0500	0.890
2	18	180	1.0	0.0250	0.996

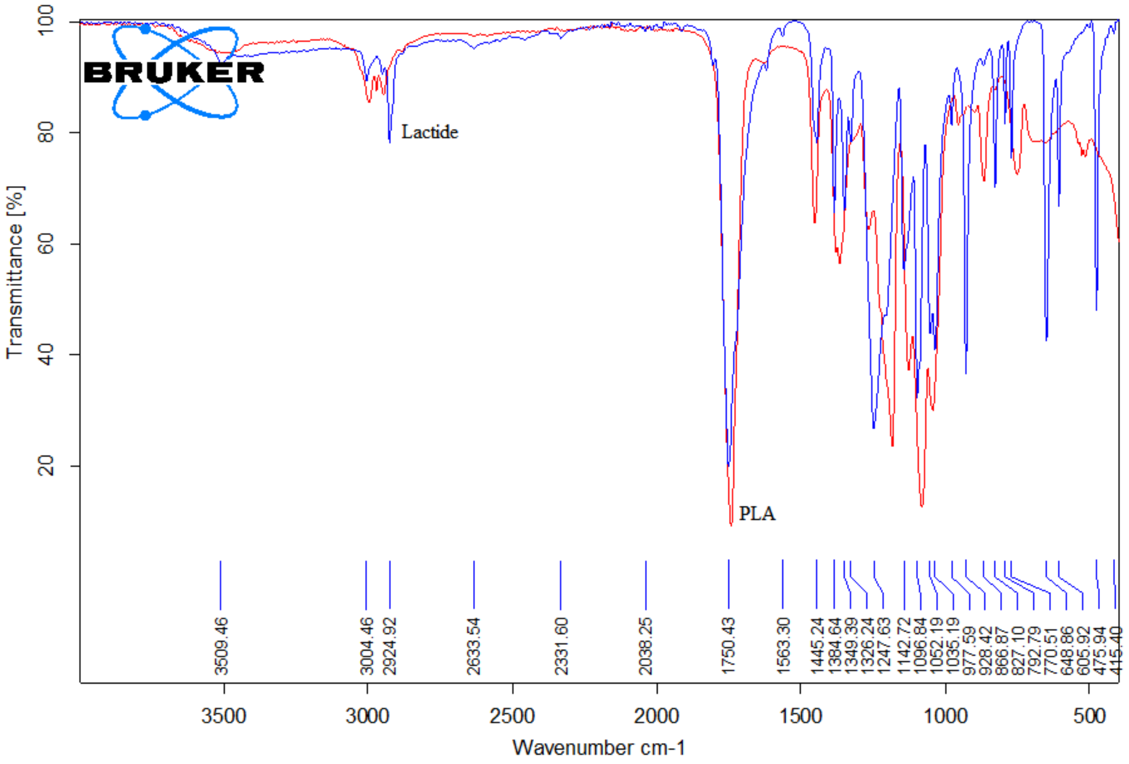

Figure 4: Combined FTIR spectra for sisal bole lactide and PLA

The major focus of IR studies is to observe the spectra changes in the carbonyl (C=O) stretching (Yuniarto *et al.*, 2016; Ahmed & Varshney, 2011; Zhou *et al.*, 2008). The combined functional group analysis spectra for sisal bole lactide and PLA are shown by Figure 4. Main functional groups of produced Lactide and PLA appeared at the frequency region of 1748 cm^{-1} and 1750 cm^{-1} respectively, that is assigned to the C=O group. At this region strong absorption peak of ester-carbonyl group for lactide and PLA were observed. This was expected since PLA is from LA which is rich of carbon chain as C=O groups. This was also reported by Yuniarto *et al.*, (2016) who used FTIR to analyse the functional groups of PLA.

Bending vibrations of CH_3 are found at 1445.24 cm^{-1} and 1349.39 cm^{-1} in the FTIR spectrum while C-O-C asymmetrical vibrations were found at 1052.19 cm^{-1} and 1142.72 cm^{-1} for PLA and at 1247.63 cm^{-1} for the lactide. The spectra show that it was possible to produce lactide and PLA from sisal bole. Formation of PLA and depletion of lactide is clearly observed by the increased vibrations peaks for PLA at 1750.43, 1563.30, 1445.24, 1247.67 and 1096.84 cm^{-1} with disappearance of vibration peaks for lactide at 2924.94, 928.42, 770.51 and 475.94.

It was not very clear in glass transition temperature which appeared before 40ºC and increased rate after 50ºC, hence no conclusion was made on the crystallinity of the product by using T_g. The melting temperature peak of PLA was around 180ºC and reached its peak after 200ºC. The PLA showed a broad melting point which might be attributed to a mixture of different molecular weight with monomer as impurities. Impurities like moisture, residue monomer, catalyst used and solvent used can affect the molecular weight distribution of the polymer (Horváth *et al.*, 2021; Inkinen *et al.*, 2011).

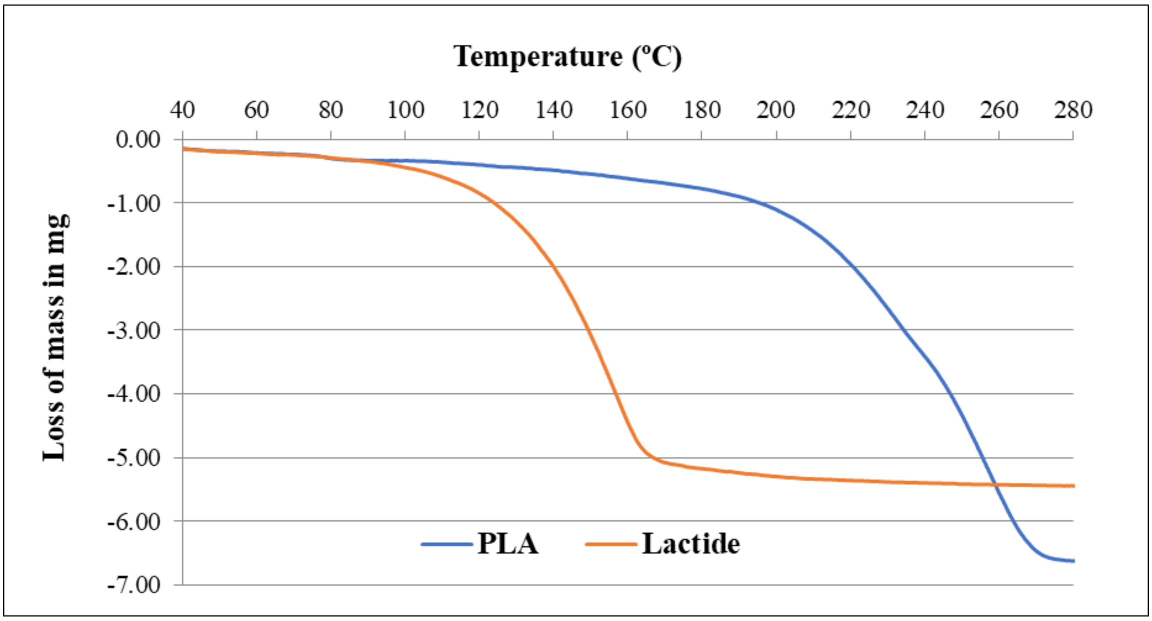

Figure 5: TG Curves for sisal bole produced lactide and PLA

The thermal stability from TG curves for both lactide and PLA in Figure 5 shows clearly that, the PLA mass loss started when the temperature reached 180ºC. The rates reached their plateau at 160 and 260ºC, respectively and started to undergo degradation. The differences in mass loss curves behaviour confirms what has been reported by others that PLA reach its complete degradation at temperatures higher than 250ºC (Sanglard *et al.*, 2012; Mitchell *et al.*, 2009; Kaihara *et al.*, 2007; Mehta *et al.*, 2005). The difference in the plateau of the two polymers confirms that all lactides were converted to PLA and the kinetic equilibrium was reached before thermodynamic equilibrium during polymerization (Sanglard *et al.*, 2012).

CONCLUSION

This study investigated the possibility of producing PLA from lactic acid (LA) produced from sisal bole. One of the key successes was the production of 0.73±0.05 g of lactide per g of sisal bole LA used. More than 99% conversion of lactide into PLA was done for 2 hrs when the system temperature was 180ºC regardless of the catalyst ratio used. Temperature and time significantly affected the yield with p-values of less than 0.05 at 95% confidence level. The current findings support sisal boles juice as an alternative feedstock for LA production, a precursor for PLA. This will protect environment by using sisal bole waste as a resource to produce biobased plastic and it is an opportunity to participate in a global move to ban the use of petrochemical-based plastics in packaging.

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