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Study of Chemical and Thermal Properties of Kenaf Biomass-based Polylactic Acid (PLA)

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ABSTRACT

The development of polylactic acid (PLA) from natural source remains a great challenge. PLA can be produced from its monomer (i.e. lactic acid) via fermentation process. In this study, the production of PLA from kenaf biomass was investigated. It was started with the introduction of kenaf biomass as the renewable source. Since kenaf is a lignocellulosic material, pretreatment process is preferable prior to the fermentation process. Different types of pretreatment methods have been investigated. However, the dilute acid hydrolysis method has been chosen in this project due to its outstanding advantages compared to other processes. After the pretreatment process, kenaf biomass was degraded twice with own isolated *Rhizopusoryzae* strain in the fermentation process. Next, polymerization process was performed to produce PLA. Poly(lactic acid) obtained was analyzed via Fourier transform infrared (FTIR) and differential scanning calorimetry (DSC). From the FTIR analysis, it can be seen that PLA was successfully produced from kenaf biomass especially at $1,741.42\text{ cm}^{-1}$ and the band around the region of $1,650\text{--}1,450\text{ cm}^{-1}$ when compared to the commercial PLA. In terms of thermal properties, the glass transition temperature (T_g) of PLA from kenaf biomass was around 74.83°C , with its melting temperature (T_m) was in the range of $122\text{ to }125^\circ\text{C}$, whereas its crystallization temperature (T_c) was not clearly observed. Low molecular weight ($444\text{ to }543\text{ g/mol}$) and low polydispersity index (PD) (1.2) of PLA produced from kenaf biomass by gel permeation chromatography (GPC) analysis indicated that the polymer has a poor stability state.

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INTRODUCTION

Widespread reliance on petroleum-based polymers that caused serious environmental pollution due to the development of the social and economic sectors has accelerated the utilization of biodegradable polymers such as polylactic acid (PLA), polyhydroxybutyrate (PHB) and polyhydroxyalkanoate (PHA). Among these polymers, PLA has shown obvious advantages as it is easily produced from renewable resources, easily processed using several methods such as electrospinning and melt blending, as well as possessed lower carbon emission during the production [1]. Previous research reported that PLA is commonly prepared by direct polycondensation method and ring-opening polymerization (ROP) of lactide [2]. Between these two polymerization processes, the direct polycondensation polymerization method has a simpler preparation method and it is also more economical since it involves a one-way step [3]. In this process, the monomer is polymerized with a continuous condensation reaction of lactic acid to produce low molecular weight PLA using tin catalysts [4]. However, the purity of the PLA obtained via polycondensation method may not be as good as those obtained using ring opening polymerization (ROP) method as ROP process requires purer monomer.

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The initialization of such polymerization process requires lactic acid, which is the monomer of polylactic acid (PLA). Lactic acid is a biochemical value-added product that has tremendous applications in the industries, such as food and polymer industries. Its demand is increasing especially in the manufacturing of biodegradable polymer products. This has attracted the attention of many researchers who have tried different ways to produce PLA in higher volumes to meet the demands. Commonly, lactic acid is derived from the fermentation of food sources, for instance corn and potato [5].

The largest manufacturer of PLA in the world, NatureWork, produces PLA from corn sources. Additionally, Cereplast Inc. produced impure PLA with the addition of starch from food sources. The production of PLA from such sources is not feasible and economical in the long run as it needs to compete with the food industry, and this has raised the issue of food security particularly for poor country.

The abundance of agricultural biomass in the world can be utilized to identify alternative sources in order to mitigate such problems in the production of PLA. Furthermore, agriculture biomass that contains holocellulose, alpha cellulose, beta cellulose and lignin can be used as the source of lignocellulose material, which includes flax, cotton and jute [6]. Among those materials, kenaf has attracted special attention due to its increasing utilization and fast cultivation in many developed countries. This is because its fibre has widespread applications in the composite industry [7]. Its core part, hereafter called kenaf biomass, is normally thrown away [8]. Additionally, kenaf as a whole composed of holocellulose (77.6 %) and alpha cellulose (45.3 %) [6]. However, there is lack of literature dealing with PLA derived from agriculture biomass.

The main objective of this work is to produce polylactic acid derived from kenaf biomass. The study of its chemical and thermal properties was performed to ensure the successfulness of the PLA produced.

MATERIALS AND METHODS

Preparation of Kenaf Biomass and Lactic acid Production:

Kenaf biomass was procured from Kenaf Fibres Industries Corporation. It was cut into small pieces, grinded and sieved into 149-249 μm of sized. About 2 g of the sieved kenaf biomass was then treated with 2% (w/w) dilute sulfuric acid (H_2SO_4) in 100 ml solution at 180 °C for 60 min in an oven [11].

Lactic Acid Production via Fermentation Process:

Fermentation of lactic acid was started with the growth of *Rhizopusoryzae* which was originally isolated from stale bread and propagated on potato dextrose agar (PDA) at 37 °C for 3 days. Next, it was collected and grown in a 250 ml shake flask containing about 100 ml medium and hydrolysed samples. The fermentation medium consists of (g/L): $(\text{NH}_4)_2\text{SO}_4$, (3.0); $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, (0.25); $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, (0.04), and KH_2PO_4 , (0.30). The fermentation process was conducted for 7 days at 25 °C and stirred at 250 rpm.

Lactic Acid Separation, Purification and Analysis:

After the fermentation step, lactic acid was separated and purified. The purification was done via the dehydration method, where lactic acid was dehydrated with continuous stirring and refluxing at 60 °C for 30 min, performed under reduced pressure of 6 mmHg by using a vacuum pump and without using any drying agent. The obtained lactic acid was then analyzed using high pressure liquid chromatography (HPLC) (Agilent model 1200 series). The column used was a ZORBAX Eclipse XDB-C18 endcapped 5 μm , 4.6x150 mm reverse phase column (Agilent Technologies, USA). The eluent used was buffer, i.e. methanol (9:1 v/v), and the column separation was conducted at a flow rate of 1.0 mL min^{-1} for 15 min. The temperature of the column was maintained at 20 °C.

Polymerization of Polylactic Acid (PLA):

The purified lactic acid was then polymerized using a digital rotary evaporator (IKA RV 10, German). 1% wt stannous octoate and p-toluene sulfonic acid was used with a maximum temperature of about 160 °C and under reduced pressure of 8 mmHg for about 2 h for the polymerization process.

Characterization:

Fourier transform infrared (FTIR) spectroscopy:

PerkinElmer Fourier transform infrared (FTIR) spectroscopy was used to determine the chemical bonding of polylactic acid (PLA) from kenaf biomass. FTIR was done on PLA obtained for comparison with the commercial PLA in order to confirm whether PLA was successfully obtained or not. In this research, commercial PLA was graded as 3051D and produced by NatureWorks®, China. Its specific gravity was measured as 0.998 g/cm^3 , while its melting temperature and glass transition temperature were recorded at 152.3 °C and 57-61 °C, respectively. Samples were analysed via FTIR for 4 scans with resolutions in the spectrum or wavenumber range from 4,000 cm^{-1} to 380 cm^{-1} .

Differential scanning calorimetry (DSC):

In addition, Mettler Toledo differential scanning calorimetry (DSC) 823E was used to acquire the glass transition temperature (T_g), crystallization temperature (T_c) and also the melting temperature (T_m) of the synthesized polylactic acid (PLA). This analytical method was performed using the fast heating ramp to reach 190 °C and the fastest cooling rate to -50 °C to erase the thermal history, and then the heating rate was modulated every minute with a ramp input of 10 °C per min up to 200 °C.

Waters gel permeation chromatography (GPC):

Waters gel permeation chromatography (GPC) was used to determine the molecular weight of polylactic acid obtained. The determination of molecular weight for PLA derived from kenaf biomass cannot be compared with the commercial PLA due to the differences in processing time. This analysis was done using two columns, which are PLgel Mixed B (500-10,000,000 Dalton) and PLgel individual pore (up to 4,000 Dalton) placed in series and operated at flow rate of 0.4ml/min in tetrahydrofuran at 27 °C and equipped with refractive index. The molecular weights were obtained using calibration curve produced from polystyrene standards. Several trials were conducted to establish the suitable correlation for the molecular weight. A measure of the broadness of polymer molecular weight distribution, which is polydispersity index (PD), was also calculated using equation (1) below:

$$PD = \frac{M_n}{M_w} \quad (1)$$

Where M_n is the average molecular weight and M_w is the weight-average molecular weight.

RESULTS AND DISCUSSION*Fourier Transform Infrared (FTIR) Analysis:*

The feasibility of producing PLA from kenaf biomass was investigated through the existence of similar chemical functional groups by comparing the PLA obtained with the commercial PLA, as shown in Figure 1.

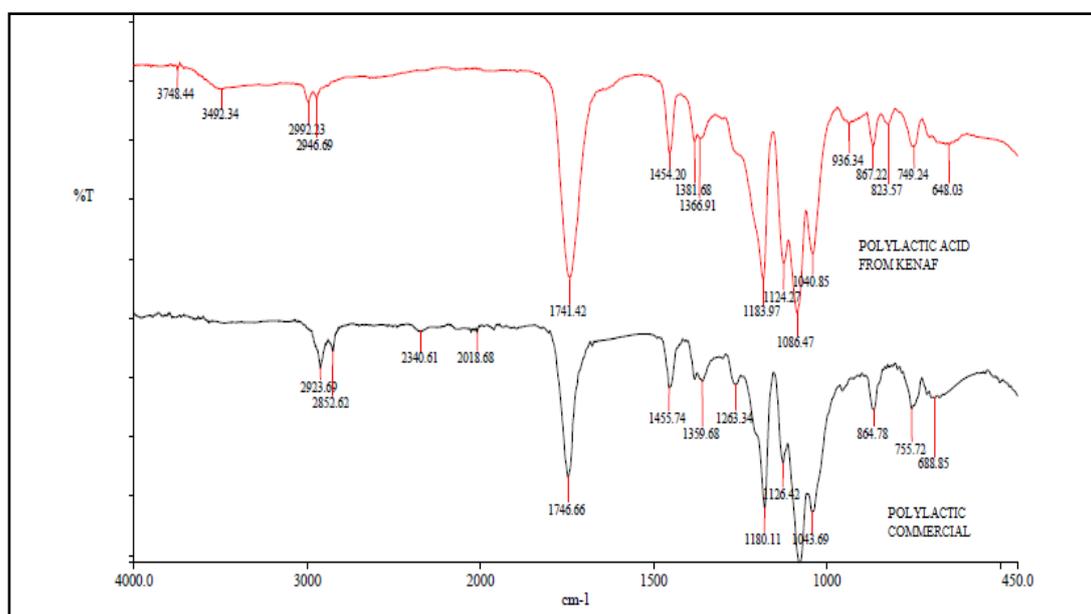


Fig. 1: Comparison of FTIR analysis between PLA from kenaf biomass and PLA from commercial source

Figure 1 depicted the same pattern of both PLAs but differed in terms of the sharpness of the peak. The wavenumber 3,800-2,500 cm^{-1} indicate the existence of O-H bond that actually overlaps with the C-H stretch [10]. These O-H bonds exist in the PLA from kenaf biomass and were indicated by the wavenumber of 3,748.44 cm^{-1} , 3,492.34 cm^{-1} , 2,992.23 cm^{-1} , and 2,946.69 cm^{-1} . As for the commercial PLA, the -OH bonds were non-existent. This may be due to the negligible or decrement of its -OH bonds during the polycondensation reaction process as they react with acid groups to form ester bonds. These findings are similar to those made by Lunelli *et al.* [11] and Nikolic *et al.* [12]. However, PLA commercial spectrum showed bands at 2,923.69 cm^{-1} and 2,852.62 cm^{-1} . This illustrates that the C-H stretch also exists in PLA from kenaf biomass, causing asymmetric

and symmetric stretching vibrations. It can also be seen that peaks occurred at $1,741.42\text{ cm}^{-1}$ and $1,746.66\text{ cm}^{-1}$ for PLA from kenaf biomass and commercial PLA, respectively. This indicates that both PLA has strong carbonyl bonds. Moreover, aromatic bond appeared for both PLAs as both of them showed the band around the region of $1,650\text{-}1,450\text{ cm}^{-1}$. The C–O stretching modes of the ester group and the C–O–C asymmetric mode appear around $1,200\text{ cm}^{-1}$. The amorphous and crystalline phases for both PLA can be attributed at the region between $870\text{-}688\text{ cm}^{-1}$ [10].

Differential Scanning Calorimetry (DSC) Analysis:

The thermal stability of PLA from kenaf biomass was characterized using differential scanning calorimetry. Figure 2 illustrates the glass transition and melting temperatures of PLA from kenaf biomass.

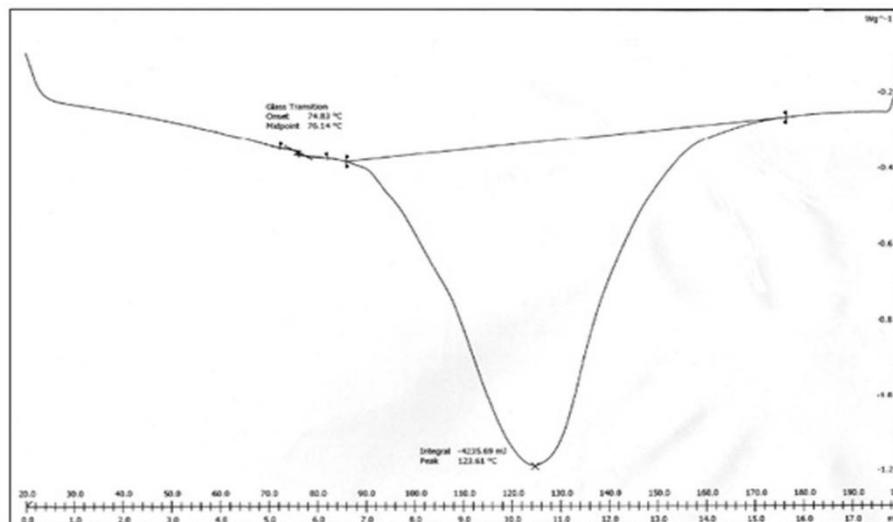


Fig. 2: Glass transition and melting temperatures of PLA from kenaf biomass

Based on Figure 2, the glass transition temperature (T_g) of PLA from kenaf biomass was around $74.83\text{ }^\circ\text{C}$, its melting temperature (T_m) was in the range of $122\text{ to }125\text{ }^\circ\text{C}$, whereas its crystallization temperature (T_c) was not clearly seen. It was found that the T_g and T_m of PLA from kenaf biomass were lower from the PLA that was produced by Dutkiewicz *et al.* [13] and Orozco *et al.* [14]. Both group of researchers claimed that the T_g for their PLA was in the range of $30\text{ to }60\text{ }^\circ\text{C}$, whereas the T_m was in the range of $130\text{ to }150\text{ }^\circ\text{C}$. The lower melting point of PLA from kenaf biomass and the absence of its crystallization temperature may be due to the racemic mixture of lactic acid used. This could be true as the direct polycondensation method production of PLA does not need pure monomer. Thus, the possibility of not having crystallinity may be higher [15]. Additionally, the factor of poor thermal stability may contribute to the absence of crystallinity. This can be supported by the analysis of its molecular weight.

Gel Permeation Chromatography Analysis:

Figure 3 shows the molecular weight chromatograph for PLA from kenaf biomass obtained via polycondensation method.

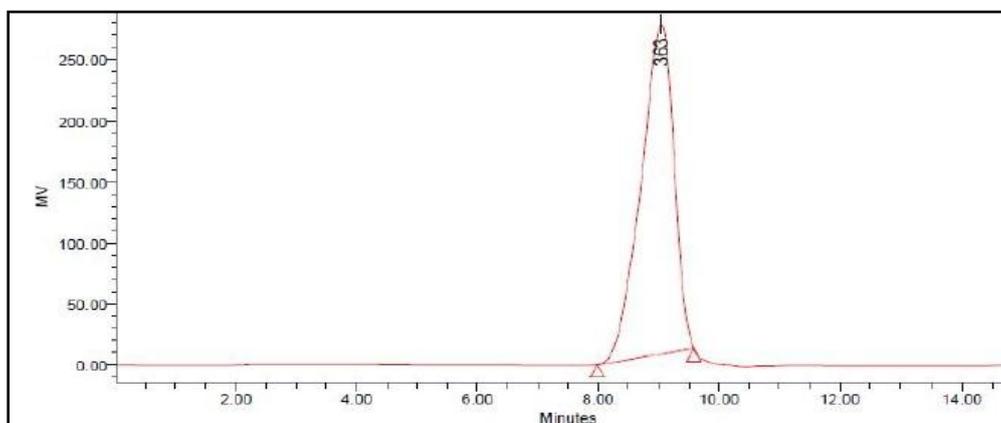


Fig. 3: Molecular weight chromatograph for PLA from kenaf biomass

Table 1 summarized the results of polydispersity index obtained from GPC analysis. Based on Table 1, the molecular weight of PLA from kenaf biomass seems to be low, which is about 534 g/mol. This may be due to its poor stability as reflected by its melting temperature, as well as the short chain PLA produced from kenaf biomass. This is consistent with Callister [16], who reported that the polymer properties, especially molecular weight, are generally affected by the melting or softening temperature. The molecular weight of polymer increased as the melting point increased, which is also influenced by the length of the polymer chains in PLA.

On the other hand, the polydispersity index of PLA from kenaf biomass indicates that the catalyst did not influence the broadness of molecular weight distribution (Figure 3). Orozco *et al.* [14] stated that if the polydispersity index is close to 2, the degree of polymerization is near to 1. For this PLA, the polydispersity index was lower than 2, thus it indicates that it has a low degree of polymerization due to the short and uneven distribution of chain length of components during the polymerization process. The short and uneven distribution of chain length of components in PLA from kenaf biomass is another factor responsible for the absence of crystallinity temperature, which directly results in poor stability of the polymer. According to Laonud *et al.* [4], the poor stability of the polymer may be due to the random main-chain scission, as well as the intramolecular transesterification to monomer and oligomeric ester.

Table 1: Molecular weight and polydispersity (PD) index for PLA from kenaf biomass

	Average molecular weight, Mn (g/mol)	Weight-average molecular weight, Mw (g/mol)	PD
PLA from kenaf biomass	444	534	1.2

Conclusions:

By means of FTIR analysis, it can be concluded that there is a possibility to produce polylactic acid from kenaf biomass that is comparable to the commercial one. Polylactic acid (PLA) from kenaf biomass possessed a glass transition temperature (T_g) around 74.83 °C and a melting temperature (T_m) in the range of 122 to 125 °C. Additionally, due to such poor thermal stability, PLA from kenaf biomass has low molecular weight and polydispersity index (PD). Further investigation of this kenaf biomass-based polylactic acid needs to be done in order to enhance its properties, especially for wide industrial usage.

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