



Preparation and characterization of polylactic acid based polyurethane for environmental friendly packaging materials

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ABSTRACT

Conventional packaging materials are mostly produced using petroleum-based substances and its' non-biodegradability are causing landfill problems. Therefore, researches have been done to replace the non-degradable polymer substances to degradable polymers. Polylactic acid (PLA) is a type of biodegradable polymer which is brittle but has good mechanical strength, which makes it a suitable polymer to be used as packaging materials. To improve the flexibility of PLA, PLA based polyurethanes (PUs) are produced by using PLA-diol with vegetable oil polyol as the chain extender. Palm oil polyol (PO) is a type of vegetable oil polyol which are used in various productions of PUs. In this study, PO polyol is used as soft segment to improve the flexibility of PLA whereas hexamethylene diisocyanate (HDI) and toluene diisocyanate (TDI) are used as a source of isocyanate. PLA/Palm oil polyol based polyurethanes (PLAPOPUs) are synthesized using one-shot and two steps polymerization method. Fourier Transform Infra-Red (FT-IR) spectra confirmed on the formation of urethane bond and glass transition temperature was analyzed using Differential Scanning Calorimetry (DSC). The PLAPOPU prepared using HDI through one-step method has high potential to be used in environmental friendly packaging industries.

Keywords:

Polyurethane, palm oil, polylactic acid,
environmental friendly packaging

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1. Introduction

Packaging industries contribute its services to various products and there are various types of packaging materials used such as metal, glass, paper and plastics containers. Among these, containers made from plastics are not biodegradable and can cause landfill problem whereas metal, glass and paper containers can be recycled. Plastics are highly in demand for this purpose and among factors that should be considered in producing packaging materials are products characteristics, products and packaging interactions, shelf life, cost and environmental impacts [1]. From the environmental aspect, biodegradability property should be emphasized in packaging material as this material usually dumped into the landfill.

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Polylactic acid (PLA) is an aliphatic polyester which can be obtained either from polycondensation process of D- or L- lactide or by using ring opening polymerization of lactide [2]. Polylactic acid (PLA) has a good strength but its' brittleness and low thermal stability are among the disadvantages of this polymer. In order to improve the properties of PLA, PLA can be blended with various plasticizers [3], polymers [4], and fillers [5]. Other than that, PLA can be synthesized into polyurethane using one step [6] or two steps [7] polymerization methods.

Polyurethane (PU) is a polymer yielded from diisocyanate, polyol and also a chain extender. PU can be categorized into two groups, which are mainly the petroleum-based polyurethanes [8] and bio-based polyurethanes [9]. Researchers try to reduce the use of petroleum-based PU due to its' non-biodegradable behavior, unlike its counterpart, bio-based PU [2]. The properties of PU depends on the types of polyol used, usually combinations of polyols are used to produce high molecular weight PU to meet certain characteristics and requirements for certain usage [7]

Polyol derived from vegetable oil is now getting more attention from researchers as this polyol is not only biodegradable and environment friendly but it also viewed as more economical. Among the vegetable oils used in the production of PU are castor oil [10], rubber seed oil [6], and also palm oil [11]. Palm oil can be used to produce polyol by undergoing epoxidation reaction followed by addition of polyhydric alcohol to add the hydroxyl group to the polyol. Palm olein-based polyol was known to produce rigid PU [12], where it was blended with petrochemical-based polyol and reacted with diphenylmethaneisocyanate. The experiment resulted in producing medium-density rigid PU with good insulation properties compared to the standard density rigid PU foam.

In this research, we aim to produce flexible and fully biodegradable polyurethane, therefore, PLA based polyurethane synthesized using palm oil polyol as the chain extender (PLAPOPU) whereas hexamethylene diisocyanate (HDI) and toluene diisocyanate (TDI) are used as the source of isocyanate group. PLAPOPUs are also synthesized using one-shot method and two steps method. The structural and thermal properties of the polyurethane are reported.

2. Experimental Study

2.1 Material

L-lactide, stannous octoate (95%), 1, 4-butanediol (99%), toluene diisocyanate (TDI) and hexamethylene diisocyanate (HDI) were purchased from Sigma-Aldrich. Palm oil polyol (PO) was obtained from Malaysian Palm Oil Board (MPOB). Toluene (99.8%) was used as solvent in reaction, methanol and chloroform were used as it is in the purification process.

2.2 Synthesis of PLA Diol

PLA diol was prepared by a condensation polymerization. L-lactide was measured 1g (6.94×10^{-3} mol) and 1,4-butanediol (4.16×10^{-4} mol) were placed in 100 ml two necked flask with toluene as a solvent. The mixture was stirred for 10 minute under nitrogen atmosphere. Then, stannous octoate (3.46×10^{-5} mol) was added to the mixture and the reaction temperature was remained steadily at 160 oC while refluxed for 6h. The product of the reaction was purified using cold methanol and dissolved in methylene dichloride and left to evaporate and dried [7].

2.3 Synthesis of PLA/Palm based Polyurethane using One-Shot Method

PLA-Palm based polyurethane was prepared using one shot polymerization method. PLA diol (1g, 7.14×10^{-4} mol), palm oil polyol (7.14×10^{-4} mol) and stannous octoate (7.14×10^{-6} mol) were

added together in a 100 ml two necked flask with 32 ml of toluene as solvent. The reaction was carried under nitrogen atmosphere. Then HDI (1.4×10^{-3} mol) was added to the mixture and stirred for 4h at 70 oC. The resulting solution was then poured into the prepared mold and left to dry overnight [7]. To determine the compatibility of the isocyanate used in the research, PLAPOPU was also synthesized using TDI using same condition.

2.4 Synthesis of PLA/ Palm based Polyurethane (PLAPOPU) using Two Steps Polymerization Process

PLA diol (1g, 7.14×10^{-4} mol), stannous octoate (7.14×10^{-6} mol) and toluene (32ml) were inserted under nitrogen atmosphere. Then hexamethylene diisocyanate (HDI) (1.4×10^{-3} mol) was added and stirred for 2 h at 70 oC for synthesis of pre-polymer PLAHD. The HDI was added in the mole ratio of 1:1 with PLA diol. PO polyol (7.14×10^{-4} mol) was added to the PLAHD mixture. The reaction vessel was kept at 70 oC for 4 hours under nitrogen atmosphere. The polymer solution was collected and placed in diethyl ether. The precipitated product was filtered, rinsed with methanol and dried in a vacuum oven at 40 oC overnight [7].

2.5 Characterization

The chemical structure of the synthesized PLAPOPU was analyzed using Fourier Transform-Infrared spectroscopy (FT-IR) (Nicolet iS50 FT-IR) and for the thermal analysis, Differential Scanning Calorimetry (DSC) analysis was carried out using Mettler Toledo DSC. Samples were heated from -30 oC to 200 oC with constant heating rate of 10 oC min⁻¹.

3. Results and Discussion

3.1 Synthesis of PLA/Palm based Polyurethane

PLAPOPUs consist of TDI (TDI-PLAPOPU) and HDI (HDI-PLAPOPU) were prepared separately and TDI-PLAPOPU showed brittle and glassy behavior (Figure 1a) compared to the HDI-PLAPOPU which showed more flexible and rubbery behavior (Figure 1b). The brittle behavior could be due the structure of TDI itself, where TDI consists of two isocyanate groups attaching to the same phenyl that makes the backbone of the chains more rigid, besides that, higher reactivity of the compound contributed by the delocalization of negative charge on isocyanate group by aromatic structure that also causes the polymer to have higher tensile strength [13]. Whereas, HDI has a linear structure that makes it less reactive, thus, it has less rigid backbone and good flexibility. As flexibility is desired characteristic in packaging material, HDI is found more suitable to be used in the preparation of PLAPOPU and continued for further characterizations.

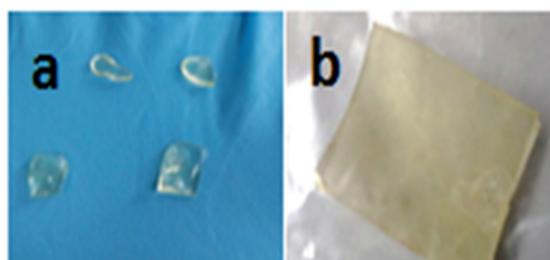


Fig. 1. PLAPOPU produced using (a) TDI and (b) HDI

PLAPOPUs were synthesized using two different methods; one-shot polymerization method and two steps polymerization method. PLAPOPU synthesized through one-shot method showed non-brittle properties with good flexibility (Figure 2a). Figure 2b showed PLAPOPU prepared by using two steps polymerization method exhibited sticky properties. Properties of polyurethane in term of strength and flexibility depends on crosslinking degree and it can be assumed that for PLAPOPU the degree of crosslinking between hard and soft segment was high because of the good strength of the polymer but enough to allow the polymer chains to be flexible [14]. As shown in Figure 3, addition of palm oil in the HDI-PLAPOPU resulted in decreasing intermolecular forces along polymer chains that enhance the chains mobility of the polymer, thus increasing its flexibility [3].

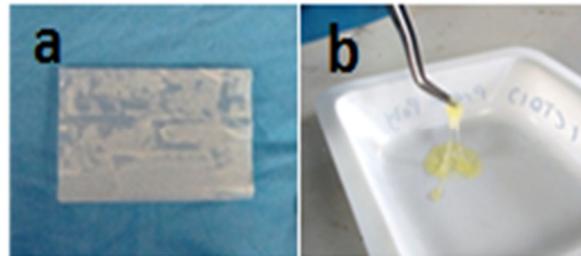


Fig. 2. PLAPOPU synthesized using (a) one-shot method and (b) two steps polymerization method

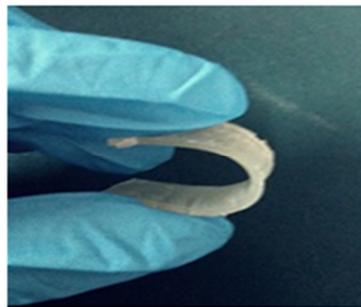


Fig. 3. HDI-PLAPOPU showed good flexibility towards bending

3.2 Fourier Transform-Infrared Spectroscopy (FT-IR)

Figure 4 showed FT-IR spectra of PLA diol and HDI-PLAPOPU. Broad peak of hydroxyl group for PLA diol can be seen at 3500 cm^{-1} which then disappeared after reacted with HDI. It exhibited a desirable peak at 3334 cm^{-1} for PU indicating an amide peak existed after the addition of HDI into the solution. This peak indicated the hydrogen bonded $-\text{NH}$ groups in urethane linkages. In addition, no peak were observed indicating isocyanate group (2270 – 2250 cm^{-1}) for PLAPOPU which proved the complete reaction of the isocyanates with polyol. Peak 1744 cm^{-1} indicated the 'free' $\text{C}=\text{O}$, while broad shoulder around 1710 cm^{-1} indicated $\text{C}=\text{O}$ that involved in hydrogen bonding in the formation of the PU [15],[16]. All the peaks were summarized in Table 1.

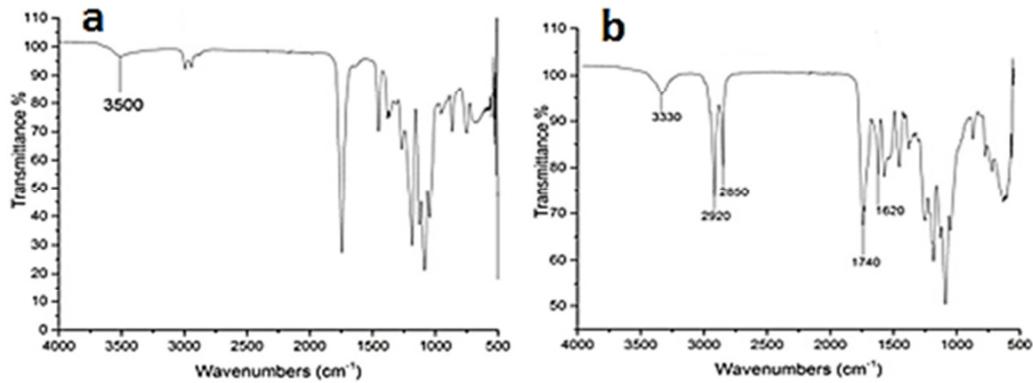


Fig. 4. FTIR analysis for (a) PLA diol and (b) HDI-PLAPOPU

Table 1
 Wavenumbers with respective characteristics peak

Wavenumbers (cm ⁻¹)	Characteristic peak
3530-3550	-OH
3330	-NH
2920	C-H symmetric bands in CH ₂ group
2850	C-H asymmetric bands in CH ₂ group
1740	Urethane -C=O

3.2 Differential Scanning Calorimetry (DSC)

Figure 4 showed thermal properties for PLAHDi and HDI-PLAPOPU. It can be seen that the glass transition temperature (T_g) of PLAHDi and HDI-PLAPOPU are around 35 oC and 60 oC, respectively. The low T_g of PLAHDi compared to the PLAPOPU could be caused by the increment of free volume in the polymer [7]. Whereas, longer chain of PLA in the PLAPOPU polymer makes the T_g of PLAPOPU closer to that pure PLA [7].

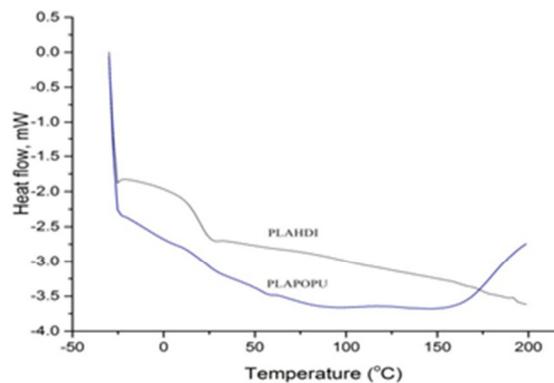


Fig. 4. DSC thermograms for PLAHDi and PLAPOPU

4. Conclusion

Flexible PLAPOPU was successfully synthesized using one shot method. HDI-PLAPOPU produced showed a good strength and improvement in flexibility. Incorporation of palm oil polyol enhances the flexibility of PU produced and reduces the brittleness of PLA. PLAPOPU produced using HDI as source of isocyanate showed a promising prospect to be used as packaging materials.

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