Characterization of Polyurethanes from MDI, PEG 400 and Kepok Banana Hump additives with TGA, DTG and LCMS spectrometers

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Abstract. Polyurethanes from methylene diphenyl isocyanate (MDI), polyethylene glycol (PEG) 400 and banana weevil starch have been synthesized. This polymer has been characterized using thermogravimetric analysis (TGA), differential thermogravimetry (DTG), liquid chromatography-mass spectrometry (LCMS), and polyurethane physical tests which include: tensile and strain tests. Thermal properties can be measured using TGA and DTG devices, which aim to determine the weight of the sample under controlled conditions and cooling at a controlled rate as a function of time. TGA and DTG analysis results showed that KBH starch with a concentration of 15% in phase 1 polymerization reaction occurred at a temperature of 78 °C, then in phase 2 a mass change of 2.87% occurred and in phase 3 saturation occurred marked by a mass loss of 97.03%. Polyurethane physical test results showed a strain of 34.37% GL and an extension of 8.6733 nm. These results indicate that polyurethane has the potential to be applied as an ingredient in the manufacture of medical devices, that operate under heating conditions.

1. Introduction

Polyurethanes are thermoset polymer compounds formed from the condensation polymerization reaction between the polyisocyanate group and the polyhydroxy alcohol group [1]. This polymer is called polyurethane because of the relationship of urethane NH- (C = O) -O- in the compound. This polymer was first discovered by Otto von Bayer in 1937 [2,3].

Polyurethane is a unique chemical compound with good mechanical, optical and solvent resistance. In industry, polyurethane is ranked second in the world in its use [4]. In the automotive field, polyurethanes are used as vehicle components that include exterior and interior parts such as bumpers, body panels, and seats. Polyurethane can also be used as furniture, building and construction materials, insulation tanks, pipes, sports equipment, and coatings and wrappers [5,6].

The use of polymers in the health sector, in addition to making equipment operating at room temperature such as blood bags, catheters, infusion devices, heart detection devices [7,8] is also needed to make equipment that operates in hot conditions such as dental adhesives, bone implants, etc. The results of this study meet the requirements for use as medical devices that have good thermal and physical properties. Based on the description above there are very many polyurethane applications, both in industrial and household equipment, while those available on the market are polyurethanes derived from chemicals that are difficult to decompose in the environment [8].

Polyurethane synthesis from MDI, PEG and starch material showed better mechanical properties than polyurethane synthesis from trimethyl propane material. This is due to the presence of more cross-linking between polyurethanes and starches and the involvement of the -NCO and OH groups which contribute to forming three-dimensional networks that can improve mechanical properties.
In this study, we synthesized environmentally friendly polyurethane, from KBH starch materials using a one-step process method. The thermal properties test was determined by the TGA and DTG spectrometers, and the polyurethane molecular weight was demonstrated by the results of the LCMS spectrometer. In addition, the stress and strain properties of the polymer have been tested as well. Based on the characterization and results of polymer testing, the polyurethane obtained has the potential to be used as a medical device.

2. Materials
Kepok banana hump was obtained from Sengkang, South Sulawesi, Indonesia, Methylene diisocyanate (MDI) and, PEG 400, aquadest, obtained from Merck and Sigma Aldrich

3. Experimental
The polyurethane synthesis process was carried out by a one-shot method. In which, KBH starch was weighed in a 2.5979 beaker, then 10 g of PEG and 1,342 g of TiO₂ were added, then stirred with a magnetic stirrer for 3 hours, to a temperature of 100°C. After that the MDI was added then stirred together for 15 minutes. The pre-cure polyurethane was printed in a glass mold measuring 4 cm x 5 cm.

4. Results and Discussion
Polyurethane polymer analysis with a TGA spectrometer was used to evaluate the thermal stability of a polymer, the polymer decomposition reaction kinetics, and polymer identification [8]. Polymers, when heated at a certain pressure and temperature, can cause two types of reactions, namely polymerization, and depolymerization. For example, it can be seen if the heated polyurethane will decompose to form isocyanate and alcohol compounds or amines, olefins and carbon dioxide. This is due to the accompanying heat in the heating process polyurethane [10].

Figure 1. TGA / DTG Test Polyurethane with KBH starch addition in various concentrations

Figure 1, is a TGA test showing polyurethane synthesis data from MDI, PEG 400 and KBH starch with various concentrations of 20%, 15%, and 10%. The polyurethane synthesis of MDI, PEG 400 and KBH starch with a concentration of 20% results show the polymerization reaction occurring in phase 1. Polyurethane polymerization occurs at 63.6 °C where the isocyanate group reacts with
polyhydroxy alcohol forming urethane group, then in phase 2, an exothermic reaction can be observed wherein the process of polyurethane formation, heat absorption is accompanied by a change in mass, as much as 2.72%. Furthermore, in phase 3 the reaction conditions are at a saturation level which is characterized by a mass loss of 96.85%.

Polyurethane synthesis by adding 15% KBH starch can be seen in phase 1 where the polymerization reaction takes place at a temperature of 78 °C and in phase 2 an exothermic reaction occurs characterized by a mass change of 2.87%, then in phase 3, a saturation reaction occurs, marked by mass loss of 97.03%.

Addition of KBH starch as much as 10% in synthesizing polyurethanes can be seen in phase 1 where the polymerization reaction takes place at 55.4 °C and in phase 2 an exothermic reaction is indicated by a mass change of 3.18%, then in phase 3, a saturation reaction occurs, marked by a mass loss of 96.82% [11,12], the events are accompanied by a decrease in temperature shown in Figure 1.

Figure 2. Test of Polyurethane LCMS

The molecular weight of the polyurethane is shown in Figure 2, the polyurethane polymer is estimated at 1024 m/z and the % abundance is 14,584. Data from this test shows the release of ethylene oxide and isocyanate m/z 44 (m/z 952.00 - 907.79), the release of m/z 59 allows for urethane functional groups (-NCOO-). Also shown is the repeated release of the methylene m / z 14 group derived from polyethylene glycol. There is a release of neutral compound acetaldehyde m / z 30 derived from polyethylene glycol compounds. This data shows that polyurethane synthesized from MDI and PEG through the addition of KBH starch is very potential to be applied as a medical device [13,14].
Figure 3. Stress as a function of strains for polyurethane (a) amyllum and PU with KBH starch 15%. (b) Synthesized polyurethane from MDI and PEG through the addition of KBH starch produced polyurethane biopolymers. From the tensile stress test, there are many peaks.
Table 1. Polyurethane polymer test with addition starch

| No | Name       | Elastic Modulus (Kpa) | Tension Test Result (Kpa) | Break Strain (% GL) | Break Elongation (mm) |
|----|------------|-----------------------|---------------------------|---------------------|-----------------------|
| 1  | PU+KBH 15%| 904.81                | 82.181                    | 34.693              | 8.6733                |
| 2  | PU+Amylum 15% | 304.48               | 199.72                    | 60.773              | 15.193               |

The presence of many small peaks around 40-80 strains as shown in Figure 3 may be due to the dominant amorphous structure present in starch connected in polyurethane. The KBH Karesterik which has been added in the texture of about 34.869% strain GL break and elongation length 8.6733 mm and the characteristics of starch added to polyurethane around 60.77% strain GL break and elongation extension 15.193 nm are shown in Table 1.

5. Conclusion
TGA test results, DTG characterization, and polyurethane physical tests show the thermal properties of polymers that are good for use as precursors in the manufacture of medical devices. Polyurethane which has been tested for thermal properties by adding 15% KBH starch showed polymerization at a temperature of 78 °C and a mass change of 2.87% in phase 2 and occurred marked by a mass loss of 97.03% Polyurethane physical test showed strain termination 34.869 % GL and elongation of 8,6733 nm. LCMS test for determining the molecular weight of polyurethane polymers. From the characterization results, polyurethane from MDI synthesis, PEG with the addition of banana hump starch is very potential to be applied as a biodegradable medical device.

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