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Research Article Design and Synthesis of Conducting Polymer Bio-Based Polyurethane Produced from Palm Kernel Oil Muhammad Abdurrahman Munir , 1 Khairiah Haji Badri , 2,3 Lee Yook Heng , 2 Ahlam Inayatullah , 4 Hamid Alkhair Badrul , 4 Emelda Emelda , 1 Eliza Dwinta , 1 Nurul Kusumawardani , 1 Ari Susiana Wulandari , 1 Veriani Aprilia , 5 and Rachmad Bagas Yahya Supriyono 1 1 Department of Pharmacy, Faculty of Health Science, Alma Ata University, Daerah Istimewa Yogyakarta 55183, Indonesia 2 Department of Chemical Sciences, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, Bangi 43600, Malaysia 3 Polymer Research Center, Universiti Kebangsaan Malaysia, Bangi 43600, Malaysia 4 Faculty of Science and Technology, Universiti Sains Islam Malaysia, Nilai 71800, Malaysia 5 Department of Nutrition Science, Alma Ata School of Health Sciences, Alma Ata University, Daerah Istimewa Yogyakarta 55183, Indonesia Correspondence should be addressed to Muhammad Abdurrahman Munir; muhammadabdurrahman2220@gmail.com Received 11 June 2021; Revised 1 October 2021; Accepted 23 March 2022; Published 7 April 2022 Academic Editor: Joanna Rydz Copyright © 2022 Muhammad Abdurrahman Munir et al.

This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. Polyurethane (PU) is a unique polymer that has versatile processing methods and mechanical properties upon the inclusion of selected additives. In this study, a freestanding bio-based polyurethane ? Im the screen-printed electrode (SPE) was prepared by the solution casting technique, using acetone as solvent.

It was a one-pot synthesis between major reactants, namely, palm kernel oil-based polyol and 4,4-methylene diisocyanate. The PU has strong adhesion on the SPE surface.

The synthesized bio-based polyurethane was characterized using thermogravimetry analysis, differential scanning calorimetry, Fourier-transform infrared spectroscopy (FTIR), surface area analysis by field emission scanning electron microscope, and cyclic voltammetry. Cyclic voltammetry was employed to study electrocatalytic properties of SPE-polyurethane towards oxidation of PU.

Remarkably, SPE-PU exhibited improved anodic peak current as compared to SPE itself using the differential pulse voltammetry method. Furthermore, the formation of urethane linkages (-NHC(O) backbone) after polymerization was analyzed using FTIR and confirmed by the absence of peak at 2241 cm^{-1} attributed to the sp-hybridized carbons atoms of C = C bonds. The glass transition temperature of the polyurethane was detected at $78.1\text{ }^{\circ}\text{C}$. 1. Introduction Conducting polymers (CPs) are polymers that can release a current [1].

The conductivity of CPs was first observed in polyacetylene, nevertheless owing to its instability, and the invention of various CPs has been studied and reported such as polyaniline (PANI), poly(o-toluidine) (PoT), polythiophene (PTH), polyfluorene (PF), and polyurethane (PU). Furthermore, natural CPs have low conductivity and are often semiconductive. Therefore, it is imperative to improve their conductivity for electrochemical sensor purposes [2–4]. The CPs can be produced from many organic materials and they have several advantages, such as having an electrical current, inexpensive materials, massive surface area, and small dimensions, and the production is straightforward.

Furthermore, according to these properties, many studies have been reported by researchers to study and report the variety of CPs applications such as sensors, biochemical applications, electrochromic devices, and solar cells [1, 5]. There is scientific documentation on the use of conductive polymers in various studies such as polyaniline [6], polypyrrole [7], and polyurethane [8–11]. Hind International Journal of Science Volume 2022, Article ID 6815187, 13 pages <https://doi.org/10.1155/2022/6815187> Polyurethane productions can be obtained by using several materials as polyols such as petroleum, coal, and crude oils.

Nevertheless, these materials have become very rare to find and the price is very expensive at the same time required a sophisticated system to produce it. The reasons such as price and time consuming to produce polyols have been considered by many researchers; furthermore, finding utilizing plants that can be used as alternative polyols should be done immediately [12]. Thus, to avoid the use of petroleum, coal, and crude oils as raw materials for a polyol, vegetable oils become a better choice to produce polyol in order to obtain a biodegradable polymer.

Vegetable oils that are generally used for polyurethane synthesis are soybean oil, corn oil, sunflower seed oil, coconut oil, nuts oil, rapeseed, olive oil, and palm oil [12, 13]. It is very straightforward for vegetable oils to react with a specific group to produce a PU such as epoxy, hydroxyl, carbonyl, and acrylate owing to the existence of (-C=C-) in vegetable oils. Thus, it provides appealing prospects to vegetable oils compared to petroleum considering the toxicity, price, and harm to the environment [14, 15].

Palm oil becomes the chosen in this study to produce PU owing to it being largely cultivated in South Asia particularly in Malaysia and Indonesia. It has several prospects compared to other vegetable oils such as the easiest materials obtained, the lowest cost of all the common vegetable oils, and recognized as the plantation that has a low environmental impact and removing CO₂ from the atmosphere as a net sequestrator [16, 17]. The application of bio-based polymer has appealed much attention until now.

Global environmental activists have forced researchers to discover another material producing polymers [18]. PUs have many advantages that have been used by many researchers, they are not merely versatile materials but also have the durability of metal and the flexibility of rubber. Furthermore, they can be promoted to replace rubber, metals, and plastics in several aspects.

Several applications of PUs have been reported and studied such as textiles, automotive, building and construction applications, and biomedical applications [19, 20]. Polyurethanes are also considered to be one of the most useful materials with many prospects, such as possessing low conductivity, low density, absorption capability, and dimensional stability. They are a great research subject due to their mechanical, physical, and chemical properties [21–24]. PU structure contains the urethane group that can be formed from the reaction between isocyanate groups (-NCO) and hydroxyl group (-OH).

Nevertheless, several groups can be found in PU structure such as urea, esters, ethers, and several aromatic groups. Furthermore, PUs can be produced from different sources as long as they contain specific materials (polyol and methylene diphenyl diisocyanate (MDI)), making them very useful for specific applications. Thus, according to the desired properties, PUs can be divided into several types such as waterborne, flexible, rigid, coating, binding, sealants, adhesives, and elastomers [25]. PUs are lighter than other materials such as metals, gold, and platinum.

The hardness of PU also relies on the number of the aromatic rings in the polymer structure [26, 27], mainly contributed by the isocyanate derivatives. PUs have also a conjugate structure where electrons can move in the main chain that causes electricity produced even the current is low. The current of conjugated linear (p) can be elaborated by the gap between the valence band and the conduction band, or called high energy level containing electrons (HOMO) and lowest energy level not containing electrons (LUMO), respectively [28, 29]. In the recent past, several conventional methods have been developed such as capillary electrophoresis, liquid, and gas chromatography coupled with several detectors.

Nevertheless, although chromatographic and spectrometric approaches are well developed for qualitative and quantitative analyses of analytes, several limitations emerged such as complicated instrumentation, expensive, tedious sample preparations, and requiring large amounts of expensive solvents that will harm the user and environment [22–24, 30–33]. Therefore, it is imperative to obtain and develop an alternative material that can be used to analyze a specific analyte.

Electrochemical methods are extremely promising methods in the determination of an analyte in samples owing to the high selectivities, sensitivities, inexpensive, requirements of small amounts of solvents, and can be operated by people who have no background in analytical chemistry. In addition, sample preparation such as separation and extraction steps are not needed owing to the selectivity of this instrument where no obvious interference on the current response is recorded [34].

Few works have been reported on the electrochemical methods for the determination of analyte using electrodes combined with several electrode modifiers such as carbon nanotube, gold, and graphene [34, 35]. Nevertheless, the materials are expensive and the production is difficult. Thus, an electrochemical approach using inexpensive and easily available materials as electrode modifiers should be developed [36, 37]. Nowadays, screen-printed electrodes (SPEs) modified with conducting polymer have been developed for various electrochemical sensing.

SPE becomes the best solution owing to the electrode having several advantages such as frugal manufacture, tiny size, being able to produce on a large scale, and can be applied for on-site detection [38]. Conducting polymers (CPs) become an alternative to modifying the screen-printed electrodes due to several advantages such as their electrical conductivity, able to capture analyte by chemical/physical adsorption, and large surface area. Thus, CPs are very appealing materials from electrochemical perspectives [39].

Such advantages of SPE encourage us to construct a new electrode for electrochemical sensing, and no research reported on the direct electrochemical oxidation of histamine using a screen-printed electrode modified by bio-based polyurethane. Therefore, this research is the first to develop a new electrode using (screen printed polyurethane electrode) SPPE without any conducting materials. The purpose of this work was to synthesize, characterize, and study the electrobehavior of polyurethane using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) attached to the screen-printed electrode.

To the best of our knowledge, this is the first attempt to use a modified International Journal of Polymer Science polyurethane electrode. The electrochemistry of polyurethane mounted onto SPE is discussed in detail. PUs are possible to become an advanced frontier material that has been chemically modified the specific electrodes for bio/chemical sensing application. 2. Experimental 2.1. Chemicals 2.1.1. Synthesis of Bio-Based Polyurethane Film. Palm kernel oil- (PKO-p-) based polyol was supplied by the UKM Technology Sdn Bhd through MPOB/UKM station plant, Pekan Bangi Lama, Selangor, and prepared using Badri et al. [40] method.

4,4-diphenylmethane diisocyanate (MDI) was acquired from Cosmopolyurethane (M) Sdn. Bhd., Klang, Malaysia. Solvents and analytical reagents were benzene ($\geq 99.8\%$), toluene ($\geq 99.8\%$), hexane ($\geq 99\%$), acetone ($\geq 99\%$), dimethylsulfoxide (DMSO) ($\geq 99.9\%$), dimethylformamide (DMF) ($\geq 99.8\%$), tetrahydrofuran (THF) ($\geq 99.8\%$), and polyethylene glycol (PEG) with a molecular weight of 400 Da obtained from Sigma Aldrich Sdn Bhd, Shah Alam. 2.2. Apparatus.

Tensile testing was performed using a universal testing machine model Instron 5566 following ASTM D638 (Standard Test Method for Tensile Properties of Plastics). The tensile properties of the polyurethane film were measured at a velocity of 10 mm/min with a cell load of 5 kN. The thermal properties were performed using thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC) analysis. TGA was performed using a thermal analyzer of the Perkin Elmer Pyris model with a heating rate of $10^\circ\text{C}/\text{min}$ at a temperature range of 30 to 800°C under a nitrogen gas atmosphere.

The DSC analysis was performed using a thermal analyzer of the Perkin Elmer Pyris model with a heating rate of $10^\circ\text{C}/\text{minute}$ at a temperature range of -100 to 200°C under a nitrogen gas atmosphere. Approximately, 5–10 mg of PU was weighed. The sample was heated from 25 to 150°C for one minute, then cooled immediately from 150 to 100°C for another one minute and finally, reheated to 200°C at a rate of 10°

C/ min. At this point, the polyurethane encounters changing from elastic properties to brittle due to changes in the movement of the polymer chains.

Therefore, the temperature in the middle of the inclined regions is taken as the glass transition temperature (T_g). The melting temperature (T_m) is identified as the maximum endothermic peak by taking the area below the peak as the enthalpy point (ΔH_m). The morphological analysis of PU-Im was performed by field emission scanning electron microscope (FESEM) model Gemini SEM microscope model 500-70-22.

Before the analysis was carried out, the polyurethane-Im was coated with a thin layer of gold to increase the conductivity of the Im. The coating method was carried out using a sputter-coater. The observations were conducted at a magnification of 200x and 5000x with 10.00 kV (electron high tension (EHT)). The crosslinking of PU was determined using the Soxhlet extraction method. About 0.60 g of PU sample was weighed and put in an extractor tube containing 250 mL of toluene, used as a solvent. This flow of toluene was let running for 24 h. Mass of the PU was weighed before and after the reflux process was carried out.

Then, the sample was dried in the conventional oven at 100 °C for 24 h in order to get a constant mass. The percentage of crosslinking content known SPE modified with polyurethane-Im as working electrode Auxiliary electrode Reference electrode Figure 1: Potentiostat instrument to study the conductivity of SPE modified with polyurethane-Im using voltammetric approach: CV and DPV. 3 International Journal of Polymer Science as the gel content can be calculated using Equation (1).

Gel content % $\delta P = \frac{W_o - W}{W} \times 100\%$, $\delta 1 P$ where W_o is the mass of PU before the reflux process (g) and W is the mass of PU after the reflux process (g). FTIR spectroscopic analysis was performed using a Perkin-Elmer Spectrum BX instrument using the diamond attenuation total reflectance (ATR) method to confirm the polyurethane, PKO-p, and MDI functional group. FTIR spectroscopic analysis was performed at a wavenumber of 4000 to 600 cm^{-1} to identify the peaks of the major functional groups in the formation of the polymer such as amide group (-NH), urethane carbonyl group (-C=O), isocyanate group (-O=C=N-), and carbamate group (-CN). 2.3. Synthesis of Polyurethane. Firstly, the polyol prepolymer solution was produced by combining palm kernel oil-based polyol and poly(ethylene glycol) (PEG) 400 (100 : 40 g/g), and acetone 30% was used as a solution.

The compound was homogenized using a centrifuge (100 rpm) for 5 min. Whereas diisocyanate prepolymer was obtained by mixing 4,4'-diphenylmethane diisocyanate (100 g) to acetone 30%, afterward the mixture was mixed using a centrifuge for 1 min

to obtain a homogenized solution. Afterward, diisocyanate solution (10 g) was poured into a container that contains polyol prepolymer solution (10 g) slowly to avoid an exothermic reaction occurring. The mixture was mixed for 30 sec until a homogenized solution was acquired.

Lastly, the polyurethane solution was poured on the electrode surface by using the casting method and dried at ambient temperature for 12 h. 2.4. Modification of Electrode. Voltammetric tests were performed using Metrohm Autolab Software (Figure 1) analyzer using cyclic voltammetry method or known as amperometric mode and differential pulse voltammetry. All electrochemical experiments were carried out using screen-printed electrode (diameter 3 mm) modified using polyurethane film as working electrode, platinum wire as the auxiliary electrode, and Ag/AgCl electrode as a reference electrode.

All experiments were conducted at a temperature of $20 \pm 2^\circ \text{C}$. The PU was cast onto the screen-printed electrode (SPE) and analyzed using a single voltammetric cycle between -1200 and +1500 mV (vs Ag/AgCl) of ten cycles at a scanning rate of 100 mV/s in 5 mL of KCl in order to study the activity of SPE and polyurethane film. Approximately, 0.1, 0.3, and 0.5 mg of polyurethane were dropped separately onto the SPE surface, and dried at room temperature.

The modified palm-based polyurethane electrodes were then rinsed with deionized water to remove physically adsorbed impurities and residues of unreacted material on the electrode surface. All electrochemical materials and calibration measurements were carried out in a 5 mL glass beaker with a configuration of three electrodes inside it. Platinum wire and silver/silver chloride (Ag/AgCl) electrodes were used as auxiliary and reference electrodes, while a screen-printed electrode that had been modified with polyurethane was applied as a working electrode. 3.

Results and Discussion The synthesis of PU films was carried out using a prepolymerization method which involves the formation of urethane polymer at an early stage. The reaction took place between diisocyanate (MDI) and palm kernel oil-based polyol. Table 1 presents the PKO-p properties used in this study. The structural chain was extended with the aid of poly(ethylene glycol) to form flexible and elastic polyurethane film.

In order to produce the urethane prepolymer, the isocyanate group (-NCO) attacks with the hydroxyl group (-OH) of polyol (PKO-p) while the other hydroxyl group of the polyol is attacked by the other isocyanate group [41] as shown in Figure 2. 3.1. FTIR Analysis. Figure 3 shows the FTIR spectra for polyurethane, exhibiting the important

functional group peaks. According to a study researched by [41], PKO-p reacts with MDI to form urethane prepolymer. The NCO group on MDI reacts with the OH group on polyol whether PKO-p or PEG. It can be seen there are no important peaks of MDI in the FTIR spectra.

This is further verified by the absence of an absorption bands at the 2400 cm^{-1} belonging to MDI (-NCO groups). This could also confirm that the -NCO group on MDI had completely reacted with PKO-p to form the urethane -NHC(O) backbone. The presence of amides (-NH), carbonyl urethane group (-C=O), carbamate group (C-NH), and -C-O-C confirmed the formation of urethane chains. In this study, the peak of carbonyl urethane (-C=O) detected at 1727 cm^{-1} indicated that the carbonyl urethane group was bonded without hydrogen owing to the hydrogen reacts with the carbonyl urethane group.

The reaction of polyurethane has been studied by Hamuzana and Badri [42] where the urethane carbonyl group was detected at 1730–1735 cm^{-1} while the MDI carbonyl was detected at 2400 cm^{-1} . The absence of absorption bands at 2250–2270 cm^{-1} associated with N=C=O bond stretching indicates the absence of NCO groups. It shows that the polymerization reaction occurs entirely between NCO groups in MDI with hydroxyl groups on polyol and PEG [43].

The absence of peaks at 1690 cm^{-1} representing urea (C=O) in this study indicated there is no urea formation as a byproduct [44] of the polymerization reaction that possibly occurs due to the excessive water. For the amine (-NH) group, hydrogen bond to -NH and oxygen to form ether, and Table 1: The specification of PKO-p (Badri et al. [40]). Property Values Viscosity at 25 °C (cps) 1313.3 Specific gravity (g/mL) 1.114 Moisture content (%) 0.09 pH value 10–11 The hydroxyl number mg KOH/g 450–470 4 International Journal of Polymer Science hydrogen bond to NH and oxygen to form carbonyl on urethane can be detected at the peak of 3301 cm^{-1} and in the wavenumber at range 3326–3428 cm^{-1} . This has also been studied and detected by Mutsuhisa et al. [45] and Lampman et al. [46].

In this research, the proton acceptor is carbonyl (-C=O) while the proton donor is an amine (-NH) to form a hydrogen bond. The MDI chemical structure has the electrostatic capability that produces dipoles from several atoms such as hydrogen, oxygen, and nitrogen atoms. The characteristic of isocyanates causing them are highly reactive [47]. MDI was one of the isocyanates used in this study, has an aromatic group, and is more reactive compared to aliphatic group isocyanates such as hexamethylene diisocyanate (HDI) or isophorone diisocyanate (IPDI).

Isocyanates have two groups of isocyanates on each molecule. Diphenylmethane diisocyanate is an exception owing to its structure consisting of two, three, four, or more isocyanate groups [48]. The use of PEG 400 in this study as a chain extender for polyurethane increases the chain mobility of polyurethane at an optimal amount. The properties of polyurethane are contributed by hard and soft copolymer segments of both polyol monomers and MDI.

This makes the hard segment of urethane serves as a crosslinking site between the soft segments of the polyol [47]. The mechanism of the prepolymerization in urethane chains formation is a nucleophilic substitution reaction as studied by Yong et al. [49]. However, this study found amines as nucleophiles. Amine attacks carbonyl on isocyanate in MDI in order to form two resonance structures of intermediate complexes A and B (Figure 4).

Intermediate complex B has a greater tendency to react with polyols due to stronger carbonyl (C=O) bonds than C=N bonds on intermediate complexes A. Thus, intermediate complex B is more stable than intermediate complex A, as suggested by previous researchers conducted by Wong and Badri [41]. Moreover, oxygen is more electronegative than nitrogen causing cations (H⁺) to tend to attack -CN bonds compared to -CO.

The combination between long polymer chain and low crosslinking content gives the polymer elastic properties whereas short-chain and high crosslinking produce hard and rigid polymers. Crosslinking in polymers consists of three-dimensional networks with high molecular weight. In some aspects, polyurethane can be a macromolecule, a giant molecule [50]. However, complexes A and B intermediate were produced after the nucleophile of PEG attacking the isocyanate group in the MDI.

However, PEG contains oxygen atoms that are more electronegative than nitrogen atoms inside the PKO-p chemical structure causing the reaction of nucleophilic substitution that occurs in PKO-p. Furthermore, amine has a higher probability of reacting compared to hydroxyl [51]. Amine with high alkalinity reacts with carbonyl on MDI as proposed by Wong and Badri [41]. The production of intermediate complexes destabilizes the alkyl ions; nevertheless, the long carbon chains of PKO-p ensure the stability of alkyl ions.

The addition of PEG in this study is imperative, not merely to increase the chain length of PU but also to avoid the production of urea as a byproduct after the NCO group reacts with H₂O from the environment. If the NCO group reacts with the excess water in the environment, the formation of urea and carbon dioxide gas will also occur

excessively (Figure 5). This reaction can cause a polyurethane foam, not polyurethane
 as we studied the reaction. $\text{HO R}_1 \text{OH} + \text{OCN R}' \text{NCO OCN R}' \text{NCHOO} \text{R}_1 \text{OCNOR}'$
 $\text{NCOH} + \text{PEG 400}$ and Acetone $\text{CNOR}' \text{H NCHOO} \text{R}_1 \text{OCNH R}' \text{NHCO diol O n}$
 Polyurethane O O Urethane prepolymer with isocyanate end group Diisocyanate +
 Acetone Polyol ?? Figure 2: PU production via the prepolymerization method [41].

5 International Journal of Polymer Science 86 88 90 92 94 96 98 100 102 2950 3150
 3350 3550 (%) T cm^{-1} _e absorption bands of -NH (a) 45 55 65 75 85 95 105 2800 2850
 2900 2950 3000 _e peaks of alkene groups cm^{-1} (%) T (b) 0 20 40 60 80 100 120 1750
 1950 2150 2350 _e absorption bands of -NCO groups (%) T cm^{-1} (c) 60 70 80 90 100
 110 1635 1685 1735 1785 _e peaks of -C = O cm^{-1} (%) T (d) 63 68 73 78 83 88 93 98
 1280 1300 1320 1340 _e peaks of -C-N-H cm^{-1} (%) T (e) 45 55 65 75 85 95 105 900
 1000 1100 _e peaks of -C-O-O- (%) T cm^{-1} PU MDI PKOp (f) Figure 3: FTIR spectra of
 several important peaks between polyurethane, PKO-p, and MDI.

6 International Journal of Polymer Science Furthermore, the application of PEG can in-
 fluence the conductivity of PU where by Porcarella et al. [52] have
 reported the application of PEG using several molecular weights. PEG 1500 decreased
 the conductivity of PU in consequence of the semicrystalline phase of PEG 1500 that
 acted as a poor ion-conducting phase for PU. It is also well known that PEG with a
 molecular weight of more than 1000 $\text{g} \cdot \text{mol}^{-1}$ tends to crystallize with deleterious effects
 on room temperature ionic conductivity [52]. 3.2. Morphological
 Analysis.

The field emission scanning electron microscope micrograph in Figure 6 shows the for-
 mation of a uniform polymer film contributed by the polymerization method appli-
 ed. The magnification used for this surface analysis ranged from 200 to 5000x. The
 polymerization method can also avoid the failure of the reaction in PU polymerization.
 Furthermore, no trace of separation was detected by FESEM. This has also been justifi-
 ed by the wavelengths obtained by the FTIR spectra above. 3.3. The Crosslinking Analysis.
 Soxhlet analysis was applied to determine the degree of crosslinking between the
 hard segments and the soft segments in the polyurethane.

The urethane group on the hard segment along the polyurethane chain is polar
 [53]. Therefore, during the testing, it was very difficult to dissolve in
 toluene, as the testing reagent. The degree of crosslinking is determined by the
 percentage of the gel content. The analysis result obtained from the soxhlet testing
 indicated a 99.3% gel content. This is significant in getting a stable polymer at a higher
 working temperature [54, 55]. Gel content % $\delta P = 0 : 6 - 0 : 301 \delta P \text{ g } 0 :$
 $301 \text{g} \times 100 \% = 99 : 33 \% : \delta P$ 3.4. The Thermal Analysis.

Thermogravimetric analysis can be used to observe the material mass based on temperature shift. It can also examine and estimate the thermal stability and material properties such as the alteration weight owing to absorption or desorption, decomposition, reduction, and oxidation. The material composition of polymer is specified by analyzing the temperatures and the height soft the individual mass steps [56].

Figure 7 shows the TGA and derivative thermogravimetry (DTG) thermograms of polyurethane. The percentage weight loss (%) is listed in Table 2. Generally, only a small amount of weight was observed. It is shown in Figure 7 in the region of 45–180 °C. This is due to the presence of condensation on moisture and solvent residues. T_{max}: the temperature of polyurethane started to degrade; T_{d1}: thermal degradation first; T_{d2}: thermal degradation second; T_{d3}: thermal degradation third.

The bio-based polyurethane is thermally stable up to 240 °C before it has undergone a thermal degradation [57]. The first stage of thermal degradation (T_{d1}) on polyurethane films was shown in the region of 200–290 °C as shown in Figure 7. The T_{d1} is associated with degradation of the hard segments of the urethane bond, forming alcohol or degradation of the polyols chains and releasing isocyanates [58], primary and secondary amines, as well as carbon dioxide [59, 60]. Meanwhile, these second thermal degradation stage (T_{d2}) of polyurethane films experienced a weight loss of 39.29%.

This endotherm of T_{d2} is related to the dimerization of isocyanates to form carbodiimides and release CO₂. The formed carbodiimide reacts with alcohol to form urea. The H₂CNCO NCO NHCH₂CH₂C_nH_{2n+1}OH HOH₂CH₂CH₂CNCO NCO NHCH₂CH₂C_nH_{2n+1}OH HOH₂CH₂CH₂ Intermediate complex A Intermediate complex B + -- + Figure 4: The formation of intermediate complexes. NCO + H₂O Step 1 RNHCOH Step 2 Degradation RO RNH₂ + CO₂ Figure 5: The reaction between the NCO group and water producing carbon dioxide. Figure 6: The micrograph of polyurethane film was analyzed by FESEM at (a) 200x and (b) 5000x magnifications.

7 International Journal of Polymer Science third stage of thermal degradation (T_{d3}) is related to the degradation of urea [58] and the soft segment on polyurethane. Generally, DSC analysis exhibited thermal transitions as well as the initial crystallization and melting temperatures of the polyurethane [61]. Its service to analyze changes in thermal behavior due to changes occurring in the chemical chain structure based on the T_g of the sample obtained from the DSC thermogram (Figure 8).

DSC analysis on polyurethane was performed in the temperature at the range 100 °C to 200 °C of using nitrogen gas as a blanket as proposed by Furtwengler et al. [62]. The glass transition temperature on polyurethane was above room temperature, at 78.1 °C indicated the state of glass on polyurethane. The presence of MDI contributes to the formation of hard segments in polyurethanes. Porcarelli et al. [52] stated that possessing a low T_g may contribute to PU conductivity.

During polymerization, this hard segment restricts the mobility of the polymer chain [63] owing to the steric effect on the benzene ring in the hard segment. The endothermic peak of acetone used as the solvent in this study was supposedly at 56 °C. However, the acetone peak was not detected in the DSC and TGA instruments, which can be concluded the acetone was completely evaporated during the polyurethane synthesis. The presence of acetone in the synthesis was to lower the reaction kinetics.

3.5. The Solubility and Mechanical Properties of the Polyurethane Film. The chemical resistivity of a polymer will be the determinant in performing as a conductor. Thus, its solubility in various solvents was determined by dissolving the polymer in selected solvents such as hexane, benzene, acetone, THF, DMF, and DMSO. On the other hand, the mechanical properties of polyurethane were determined based on the standard testing following ASTM D638. The results from the polyurethane solubility and tensile test are shown in Table 3.

Polyurethanes were insoluble with acetone, hexane, and benzene and are only slightly soluble in THF, DMF, and DMSO solutions. While the tensile strength of a PU film indicated how much elongation load the film was capable of withstanding the material before breaking. The tensile stress, strain, and modulus of polyurethane film also indicated that polyurethane has good mechanical properties that are capable of being a supporting substrate for the next stage of the study.

In the production of polyurethane, the properties of polyurethane are easily influenced by the content of MDI and polyol used. The length of the chain and its flexibility are contributed by the polyol which makes it elastic. High crosslinking content can also produce hard and rigid polymers. MDI is a major component in the formation of hard segments in polyurethane. It is this hard segment that determines the rigidity of the PU. Therefore, high isocyanate content results in higher rigidity on PU (Petrovic et al. 2002). Thus, the polymer has a higher resistance to deformation and more stress can be applied to the PU. 3.6.

The Conductivity of the Polyurethane as a Polymeric Film on SPE. Polyurethane film was deposited onto the screen-printed electrode by casting method as shown in Figure 1. After that, the modified electrode was analyzed using cyclic voltammetry and differential pulse voltammetry in order to study the behavior of the modified electrode. The modified electrode was tested in a 0.1 mmol · L⁻¹ KCl solution containing 5 mmol · L⁻¹ (K₃Fe(CN)₆). The use of potassium ferricyanide is intended to increase the sensitivity of the KCl solution. The conductivity of the modified electrode was studied.

The electrode was analyzed by cyclic voltammetry method with a potential range of -1.00 to +1.00 with a scan rate of 0.05 V · s⁻¹. The voltammograms at the electrode have shown a specific redox reaction. Furthermore, the conductivity of the modified electrode is lower due to the use of polyurethane. This occurs due to PU being a natural polymer produced from the polyol of palm kernel oil-based. Figure 7: DTG thermogram of polyurethane film.

Table 2: Weight loss percentage (wt%) and thermal degradation (Td) of polyurethane film. % weight loss (wt%) and thermal degradation (Td) Total of weight loss (%) Residue after 550 °C (%) T max, °C Td 1, 200 – 290 °C Td 2, 350 – 500 °C Td 3, 500 – 550 °C 240 8.04 39.29 34.37 81.7 18.3 8 International Journal of Polymer Science polyol. The electrochemical signal at the electrode is low if there is a decrease in electrochemical conductivity [64]. It can be concluded that polyurethane is a biopolymer with a low current value.

The current of the modified electrode was found at 5.3×10^{-5} A or 53 μA. Nevertheless, the current of PU in this study showed better results compared to Bahrami et al. (2019) that reported the current of PU as 1.26×10^{-6} A, whereas Li et al. [65] reported the PU current in their study was even very low, namely, 10⁻¹⁴ A. The PU can obtain a current owing to the benzene ring in the hard segment (MDI) could exhibit the current by inducing electron delocalization along the polyurethane chain [66]. The PU can also release a current caused by PEG.

The application of PEG as polyol has been studied by Porcarelli et al. [52] that reported that the current of PU based on PEG – polyol was 9.2×10^{-8} A. According to Figure 9, it can be concluded that the anodic peak present in the modified electrode was at +0.5 V, and it also represented the anodic peak of the SPE-PU. The first oxidation signal on both electrodes ranged from -0.2 to +1.0 V, which revealed a particular oxidative peak at a potential of +0.5 V. Figure 10 also presents the DPV

voltam mogram of the modi ? ed electrode. DPV is a measurement based on the dif- ferenc e in potentia l pulses that produce an electric current.

Scan ning the capability pulses to the working electrode will produce di ? erent currents. Optimal peak curr ents will be produced to the reduction capacity of the redox material . The peak current produced is proporti onal to the concentra- tion of the redox substance and can be detected up to a con- ce ntration below 10^{-8} M. DPV was conducted to obtain the current v alu e th a t i s m o r e a c c u r a t e t h a n CV [6 7] . This study used a redox pair ($K_3Fe(CN)_6$) as a test device (probe).

The currents generated by SPE-PU and prove d by CV and DPV have shown conductivity on polyu rethane ? lms. This suggests that polyu rethane ? lms can conduct elect ron transfer. The electrochemica l are a on the modi ? ed elect rode can be calculat ed using the formula from Randles - Sevcik [6 8] , wher e the electro che m ica l area for SPE - PU is considered to be A , using Equation (3) : C ur r ent of SP E - PU , $I_p = 2.65 \times 10^5 AC n^{3/2} v^{1/2} D^{1/2}$, đ3 P where n – 1 is the amount of electron transfer involve d, while C is the solve nt concentratio n used ($mmol \cdot L^{-1}$) and th e val u e of D is the di ? usion constant of $5 mmol \cdot L^{-1}$ at ($K_3Fe(CN)_6$) dissolved using $0.1 mmol \cdot L^{-1}$ KCl. The esti- mated surface area of the elect rode (Figure 1) was 0.2

cm^2 , wher e the length and width of the electrode used duri ng th e study was $0.44 cm \times 0.44 cm$, while the surface area of th e SPE-PU was $0.25 cm^2$ with the length and width of the elect rode estimat ed at $0.5 cm \times 0.5 cm$, causing the SPE-PU has a large r surface. The corresponding surface concentra- tion (t) (mol/cm^2) i s m e a s u r e d u s i n g E q u a t i o n (4) . $I_p = n^2 F^2 A t v$, đ4 P where I_p is the peak curr ent (A), while A is the surface are a of the electrode (cm^2), the value of v is the applied scan rate (mV/s) and F is the Faraday constant (96,584 C/mol), R is the const ant ideal gas (8.314 J/mol K), and T is the temper- ature used during the exper iment being condu cted (298 K) –4.5 –4 –3.5 –3 –2.5 –2 –1.5 –1 –0.5 0 0.5 20 40 60 80 100 120 140 160 T (mW) Temperature (°C) Onset Figure 8: DSC thermogram of polyurethane ? lm.

Table 3: The solubility and mechanical properties of the polyurethane ? lm. Parameters Polyurethane ? lm Solubility Benzene Insoluble Hexane Insoluble Acetone Insoluble THF Less soluble DMF Less soluble DMSO Less soluble Stress (MPa) 8.53 Elongation percentage (%) 43.34 Strain modulus (100) (MPa) 222.10 9 International Journal of Polymer Science [6 9] . Th e a p p l i c a t i o n o f P K O - p t o p r o d u c e a c o n d u c t i n g polymer will be a great prospect as this material can be employed in the anal ytical indust ry in order to modify elec- trodes for electrochemic al purposes.

Furthermore, a number of palm oils are abundant in Malaysia and Indonesia such as palm stearin and refined-bleached-deodorized (RBD) palm oil. They have several benefits such as being sustainable, cheap, and environmentally biodegradable. These palms are the potential to produce bio-materials that can be used to replace other polymers that are chemical based [17]. Several studies have been reported the application of PU to produce elastic conductive fibres and films owing to it being highly elastic, scratch-resistant, and adhesive [70]; thus, it is easy for PU to adhere to the screen-printed electrode to modify the electrode. PU is also being used as a composite material to make elastic conducting composite films [71].

Conclusion Polyurethane film was prepared by prepolymerization between palm kernel oil-based polyol (PKO-p) with MDI. The presence of PEG 400 as the chain extender formed free-standing flexible film. Acetone was used as the solvent to lower the reaction kinetics since the prepolymerization was carried out at room temperature. The formation of urethane links (-NHC(O) backbone) after polymerization was confirmed by the absence of absorption bands at 2241 cm^{-1} associated with the N=C=O bond stretching and the presence of N-H peak at 3300 cm^{-1} , carbonyl (C=O) at 1710 cm^{-1} , carbamate (C-N) at 1600 cm^{-1} , ether (C-O-C) at 1065 cm^{-1} , benzene ring (C=C) at 1535 cm^{-1} in the bio-based polyurethane chain structure.

Soxhlet analysis for the determination of crosslinking on polyurethane films has yielded a high percentage of 99.33%. This is contributed by the hard segments formed from the reaction between isocyanates and hydroxyl groups causing elongation of polymer chains. FESEM analysis exhibited an absence of phase separation and smooth surface. Meanwhile, the current of the modified electrode was found at 5.2×10^{-5} A. This bio-based polyurethane film can be used as a conducting biopolymer, and it is very useful for other studies such as electrochemical sensor purposes.

Furthermore, advanced technologies are promising, and the future of bio-based polyol looks very bright. Data Availability All data experiments can be found in the manuscript.

Figure 9: The voltammogram of SPE-PU modified electrode after analyzed using cyclic voltammetry technique.

Figure 10: The voltammogram of SPE-PU modified electrode after analyzed using differential pulse voltammetry technique.

10 International Journal of Polymer Science Conflicts of Interest The authors declare no conflict of interest.

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