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> Abstract

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Revision requested

Message for Author

The topic of this manuscript is suitable for Int. J. Polym. Sci. but it must be revised before it can be sent for peer-review. The grammar and typing are very poor, and there are many incorrectly-used words. Reviewers would not properly understand the authors' meaning in many parts of the text. The authors should also emphasize the novel aspects of their research, since there is an abundance of published work on PUs made from vegetable oil derivatives.

Design and Synthesis of Conducting Polymer Based on Polyurethane produced from Palm Kernel Oil

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Abstract

Polyurethane (PU) is a unique polymer that has versatile processing method and mechanical properties upon inclusion of selected additives. In this study, a freestanding bio-polyurethane film on screen – printed electrode (SPE) was prepared by solution casting technique, using acetone as solvent. It was a one-pot synthesis between major reactants namely, palm kernel oil-based polyol (PKOp) and 4,4-methylene diisocyanate. The PU undergone strong adhesion on SPE. The formation of urethane linkages (NHCO backbone) after polymerization was confirmed by the absence of N=C=O peak at 2241 cm^{-1}. The glass transition temperature (T_g) of the polyurethane was detected at 78.1^oC. The conductivity of PU was determined using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The current of electrode was at 5.2 x 10^{-5} A.

Keywords: Polyurethane, polymerization, screen – printed electrode, voltammetry

1. Introduction

Polymers are molecules composed of many repeated sub-units referred to as monomers (Sengodu & Deshmukh 2015). Conducting polymers (CPs) are polymers that exhibit electrical behaviour (Alqarni et al. 2020). The conductivity of CPs was first observed in polyacetylene,

nevertheless owing to its instability led to the discovery of other forms of CPs such as polyaniline (PANI), poly(o-toluidine) (PoT), polythiphene (PTh), polyfluorene (PF) and polyurethane (PU). Furthermore, natural CPs have low conductivity and are often semi-conductive. Therefore, it is essential to increase their conductivity mainly for use in electrochemical sensor programs (Dzulkipli et al. 2021; Wang et al. 2018). Conducting polymers (CPs) represent a sizeable range of useful organic substances. Their unique electrical, chemical and physical properties; reasonable price; simple preparation; small dimensions and large surface area have enabled researchers to discover a wide variety of uses such as sensors, biochemical applications, solar cells and electrochromic devices (Alqarni et al. 2020). There are many scientific documentations on the use of conductive polymers in various studies such as polyaniline (Pan & Yu 2016), polypyrrole (Ladan et al. 2017) and polyurethane (Tran et al. 2020; Vieira et al. 2020; Guo et al. 2020; Fei et al. 2020).

The application of petroleum as polyol in order to produce polyurethane has been applied. The coal and crude oil used as raw materials to produce it. Nevertheless, these materials become very rare to find and the price is very expensive at the same time required sophisticated system to produce it. These reasons have been considered and finding utilizing plants that can be used as alternative polyols should be done immediately (Badri 2012). Furthermore, in order to avoid the application of petroleum as raw material for polyol, vegetable oils become a better choice as polyol in order to obtain a biodegradable polyol. Vegetable oils that generally used for synthesis polyurethane are soybean oil, corn oil, sunflower seed oil, coconut oil, nuts oil, rape seed, olive oil and palm oil (Badri 2012; Borowicz et al. 2019).

Biopolymer, a natural biodegradable polymer has attracted much attention in recent years. Global environmental awareness and fossil fuel depletion urged researchers to work in the biopolymer field (Priya et al. 2018). Polyurethane is one of the most common, versatile and researched materials in the world. These materials combine the durability and toughness of

metals with the elasticity of rubber, making them suitable to replace metals, plastics and rubber in several engineered products. They have been widely applied in biomedical applications, building and construction applications, automotive, textiles and in several other industries due to their superior properties in terms of hardness, elongation, strength and modulus (Zia et al. 2014; Romaskevic et al. 2006).

The urethane group is the major repeating unit in Pus and is produced from the reaction between alcohol (-OH) and isocyanate (NCO); albeit polyurethanes also contain other groups such as ethers, esters, urea and some aromatic compounds. Due to the wide variety of sources from which Pus can be synthesized, thus a wide range of specific applications can be generated. They are grouped into several different classes based on the desired properties: rigid, flexible, thermoplastic, waterborne, binders, coating, adhesives, sealants and elastomers (Akindoyo et al. 2016).

Although, PU has low conductivity but it is lighter than other materials such as metals. The hardness of PU also relies on the aromatic rings number in the polymer structure (Janpoung et al, 2020; Su'ait et al. 2014), majorly contributed by the isocyanate derivatives. PU has also a conjugate structure where electrons can move in the main chain that causing electricity produced even the conductivity is low. The electrical conductivity of conjugated linear (π) can be explained by the distance between the highest energy level containing electrons (HOMO) called valence band and the lowest energy level not containing electrons (LUMO) called the conduction band (Wang et al. 2017; Kotal et al. 2011).

The purpose of this work was to study the conductivity of polyurethane using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) attached onto screen printed electrode (SPE). To the best of our knowledge, this is the first attempt to use a modified polyurethane electrode. The electrochemistry of polyurethane mounted onto screen-printed

electrode (SPE) is discussed in detail. Polyurethane is possible to become an advanced frontier material in chemically modified electrodes for bio sensing application.

2. Experimental

2.1 Chemicals

Synthesis of polyurethana film: Palm kernel oil (PKOp) supplied by UKM Technology Sdn Bhd through MPOB/UKM station plant, Pekan Bangi Lama, Selangor and prepared using Badri et al. (2000) method. 4, 4-diphenylmethane diisocyanate (MDI) was acquired from Cosmopolyurethane (M) Sdn. Bhd., Klang, Malaysia. Solvents and analytical reagents were benzene (≥ 99.8%), toluene (≥ 99.8%), hexane (≥ 99%), acetone (≥ 99%), tetrahydrofuran (THF), dimethylformamide (DMF) (≥ 99.8%), dimethylsulfoxide (DMSO) (≥ 99.9%) and polyethylene glycol (PED) 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 638 (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 Perkin Elmer Pyris model with heating rate of 10 °C/minute at a temperature range of 30 to 800 °C under a nitrogen gas atmosphere. The DSC analysis was performed using a thermal analyzer of Perkin Elmer Pyris model with heating rate of 10 °C /minute at a temperature range of -100 to 200 °C under a nitrogen gas atmosphere. Approximately, 5-10 mg of PU was weighed. Sample was heated from 25 to 150 °C for one minute, then cooled

immediately from 150 -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 changes 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 film 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 film was coated with a thin layer of gold to increase the conductivity of the film. The coating method was carried out using a sputter - coater. The observations were conducted at magnification of 200× and 5000 × with 10.00 kV (Electron high tension - EHT).

The crosslinking of PU was determined using 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 to run for 24 hours. 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 hours in order to get a constant mass. The percentage of crosslinking content known as the gel contet, can be calculated using Equation (1).

$$\text{Gel content } (\%) = \frac{W_o - W}{W} \text{ x } 100\ \% \qquad (1)$$

W_o is mass of PU before the reflux process (g) and W is 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 (DATR) method to confirm the

polyurethane, PKOp and MDI functional group. FTIR spectroscopic analysis was performed at a wave number of 4000 to 600 cm^{-1} to identify the peaks of the major functional groups in the formation of polymer such as amide group (-NH), urethane carbonyl group (-C = O) and carbamate group (-CN).

2.3 Modification of Electrode

Voltammetric tests were performed using Metrohm Autolab Software (**Figure 1**) analyzer using cyclic voltammetry (CV) method or known as amperometric mode and differential pulse voltametry (DPV). All electrochemical experiments were carried out using screen printed electrode (diameter 3 mm) modified using polyurethane film as working electrode, platinum wire as auxiliary electrode and AG/AgCl electrode as reference electrode. All experiments were conducted at temperature of 20 ± 2^{o}C.

PU casted onto the screen – printed electrode (SPE + PU) was analyzed using a single voltametric 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 & 0.5) mg of palm – based prepolyurethane was dropped separately onto the surface of the SPE 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 AG/AgCl electrodes were used as auxiliary and reference electrodes, while screen printed electrode that had been modified with polyurethane was applied as a working electrode.

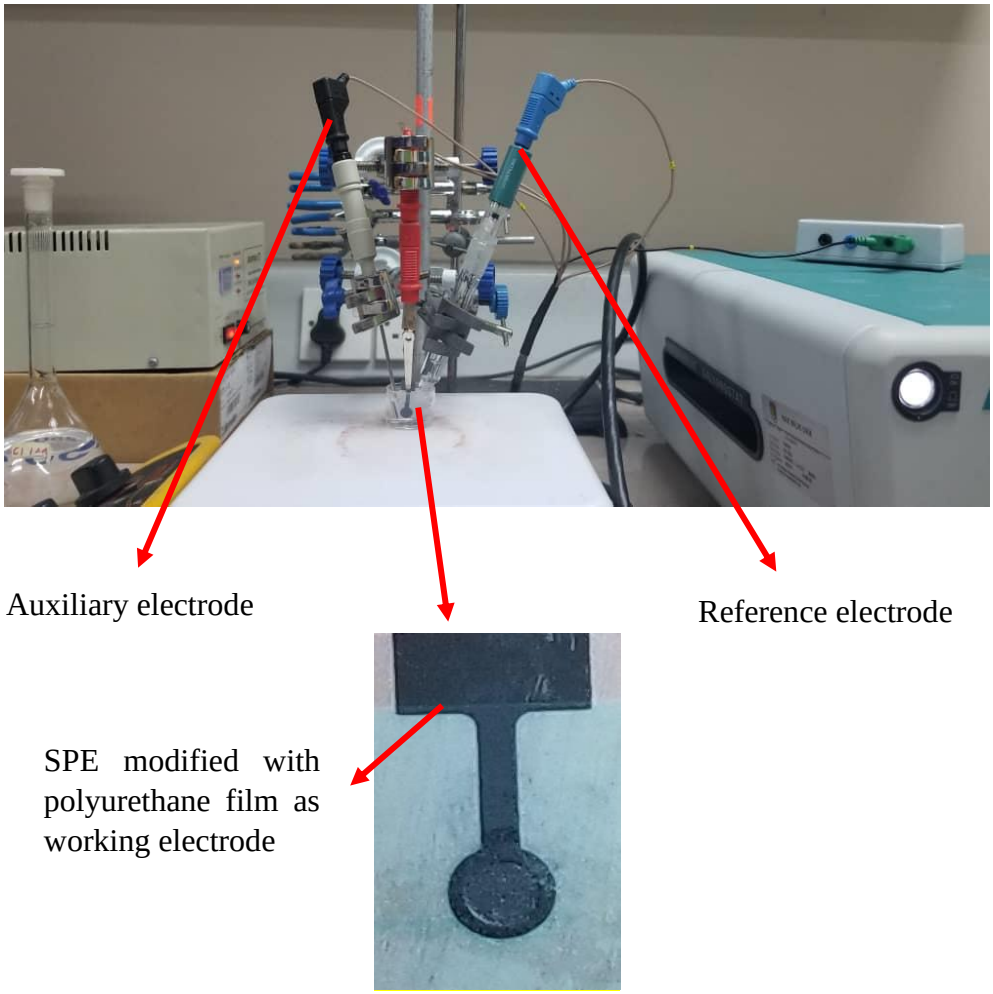


Figure 1. Potentiostat instrument to study the conductivity of SPE modified with polyurethane film using cyclic voltametry (CV) and differential pulse voltammetry (DPV)

3. Results and Discussion

The synthesis of PU films was carried out using pre - polymerization method which involves the formation of urethane polymer at an early stage. The reaction took place between palm kernel oil – based polyol (PKOp) and diisocyanate (MDI). The structural chain was extended with the aid of polyethylene glycol (PED) to form flexible and elastic polyurethane film. In order to form the urethane prepolymer, one of the isocyanate groups (NCO) reacts with one hydroxyl group (OH) of polyol while the other isocyanate group attacks another hydroxyl group in the polyol (Wong & Badri 2012) as shown in **Figure 2**.

a. FTIR analysis

Figure 3 shows the FTIR spectrum for polyurethane, exhibiting the important functional group peaks. According to study researched by Wong & Badri 2012, PKO-p reacts with MDI to form urethane prepolymers. The NCO group on MDI reacts with OH group on polyol whether PKOp or PEG. It can bee seen there are no important peaks of MDI in the FTIR spectrums. This is further verified by the absence of peak at the 2400 cm^{-1} belongs 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 reacted with the carbonyl urethane group.

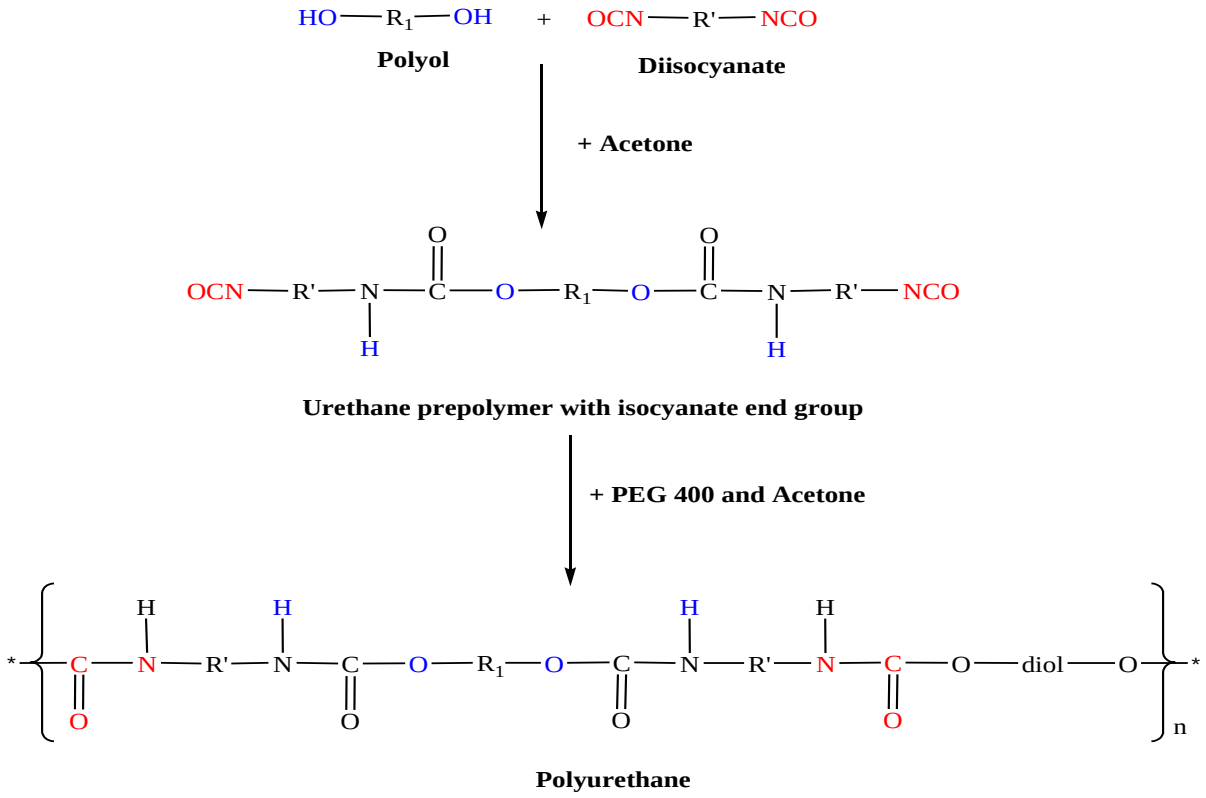
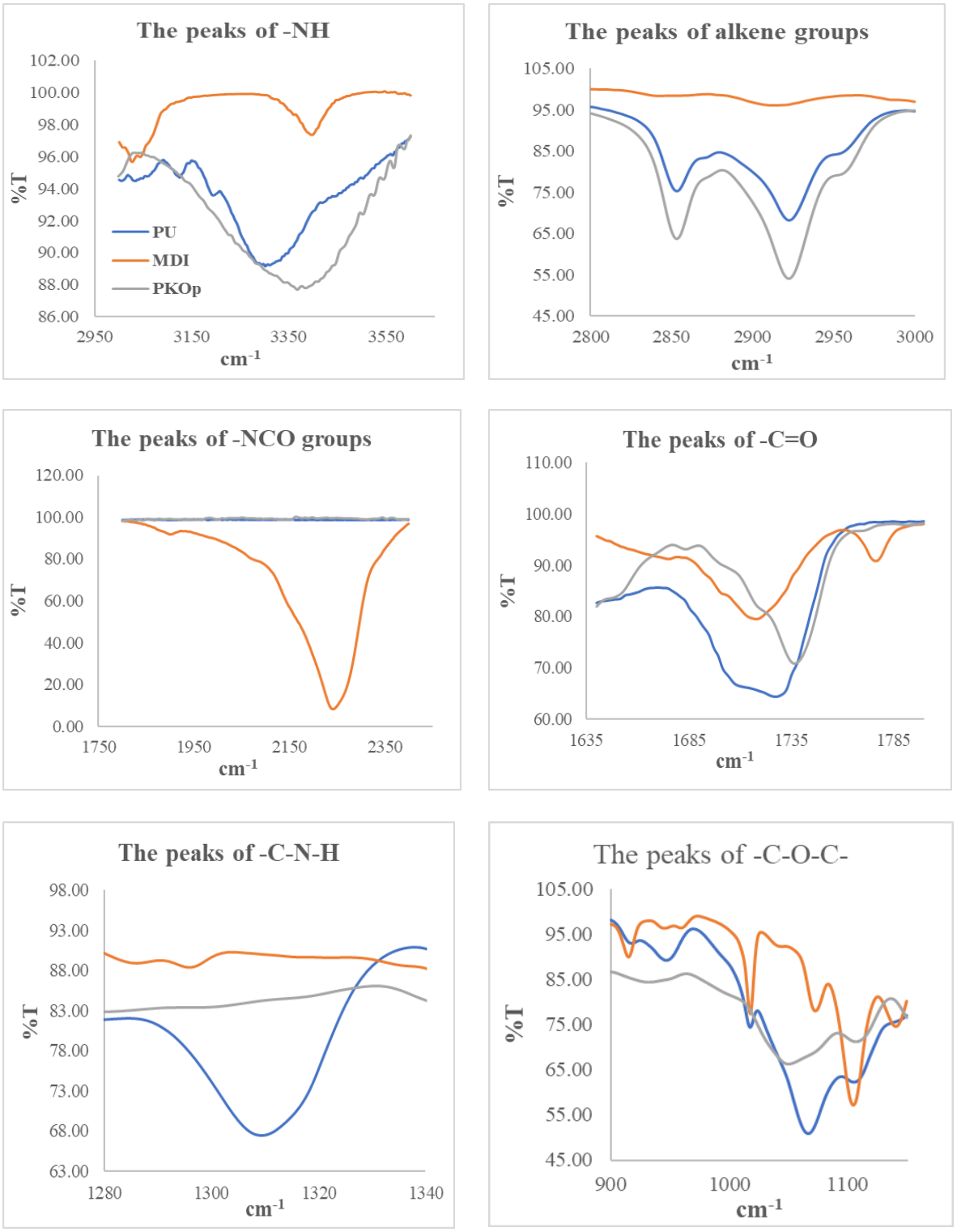


Figure 2. The chemical route of producing polyurethane via pre-polymerization method (Wong & Badri 2012).

The reaction of polyurethane has been studied by Hamuzan & Badri (2016) 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 peaks at 2250 – 2270 cm^{-1} indicates the absence of NCO groups. It shows that the polymerization reaction occurs entirely between NCO groups in MDI with hydroxyl groups on polyols and PEG (Mishra et al. 2012). The absence of peaks at 1690 cm^{-1} representing urea (C = O) in this study indicated, there is no urea formation as a byproduct (Clemitson 2008) of the polymerization reaction that possibly occur due to the excessive water. For the amine (NH) group, hydrogen-bond to NH and oxygen to form ether and hydrogen bond to NH and oxygen to form carbonyl on urethane can be detected at the peak of 3301 cm^{-1} and in the wave number at range 3326 – 3428 cm^{-1}. This has also been studied and detected by Lampman et. al. (2010) and Mutsuhisa et al. (2007). In this study, the hydrogen bond formed by C = O acts as a proton acceptor whereas NH acts as a proton donor. The urethane group in the hard segment (MDI) has electrostatic forces on the oxygen, hydrogen and nitrogen atoms and these charged atoms form dipoles that attract other opposite atoms. These properties make isocyanates are highly reactive and having different properties (Leykin et al. 2016).

MDI was one of the isocyanate used in this study, has an aromatic group and more reactive compared to aliphatic group isocyanates such as hexamethylene diisocyanate (HDI) or isoporona diisocyanate (IPDI). Isocyanates have two groups of isocyanates on each molecule. Diphenylmethane diisocynate is an exception owing to its structure consists of two, three, four or more isocyanate groups (Nohra et al. 2013). The use of PEG 400 in this study as a chain extender for polyurehane 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 (Leykin et al. 2016).



201 **Figure 3.** FTIR spectrums of several important peaks between polyurethane, PKO-p and MDI

202

203 The mechanism of the pre – polymerization in urethane chains formation is a

204 nucleophilic substitution reaction as studied by Yong et al. (2009). 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. 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 who have conducted by Wong and Badri (2012). Moreover, nitrogen was more electropositive than oxygen, therefore, -CN bonds were more attracted to cations (H+) than -CO. The combination between long polymer chain and low cross linking content gives the polymer an elastic properties whereas short chain and high cross linking producing hard and rigid polymers. Cross linking in polymers consist of three - dimensional networks with high molecular weight. In some aspects, polyurethane can be a macromolecule, a giant molecule. Polyurethanes are usually thermoset polymers (Petrovic 2008).

Moreover, reaction between MDI and PEG as a chain extender where oxygen on the nucleophile PEG attacks the NCO group in the MDI to form two intermediate complexes A and B can occur. Nevertheless, nucleophilic substitution reactions have a greater tendency to occur in PKOp compared to PEG because the presence of nitrogen atoms is more electropositive than oxygen atoms in PEG. Amine has a higher probability of to react compared to hydroxyl (Herrington & Hock 1997). Amine with high alkalinity reacts with carbon atoms on MDI as proposed by Wong and Badri (2012). PKOp contains long carbon chains that can easily stabilize alkyl ions when intermediate complexes are formed. Therefore, polyol is more reactive than PEG to react with MDI. However, the addition of PEG will increase the length of the polyurethane chain and prevent side effects such as the formation of urea by -products of the NCO group reaction in urethane pre - polymer and water molecules 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 4**). This reaction can cause a polyurethane foam not polyurethane film as we studied the film.

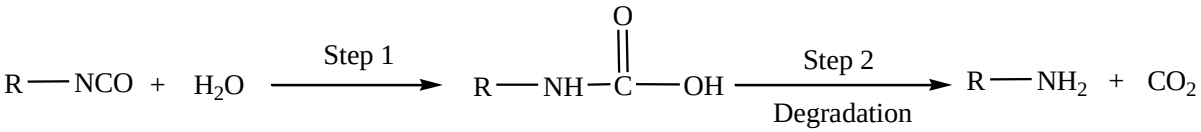


Figure 4. The reaction between NCO group and water producing carbon dioxide

b. Morphological analysis

The Field Emission Scanning Electron Microscope (FESEM) micrograph in **Figure 5** shows the formation of a uniform polymer film contributed by the polymerization method applied. The magnification used for this surface analysis ranged from 200 to 5000 ×. 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 justified by the wavelengths obtained by the FTIR spectrums above.

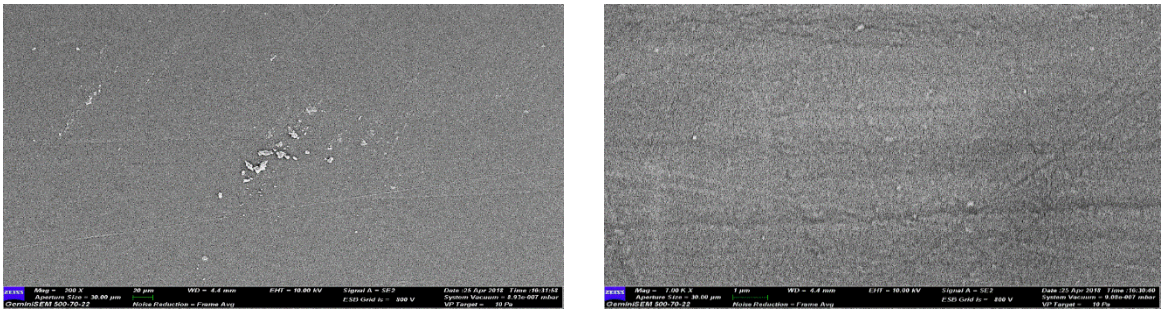


Figure 5. The micrograph of polyurethane films analysed by FESEM at (a) 200 × and (b) 5000× magnifications.

c. 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 (Cuve & Pascault 1991). Therefore, during the testing, it was very difficult to dissolve in toluene, as the testing reagent. The degree of the crosslinking

is determined by the percentage of the gel content. The analysis result obtained from the Soxhlet testing indicating a 99.3 % gel content. This is significant in getting a stable polymer at higher working temperature (Rogulska et al. 2007).

$$\text{Gel content (\%)} = \frac{(0.6 - 0.301)\ \text{g}}{0.301\ \text{g}} \times 100\% = 99.33\%$$

d. The thermal analysis

Figure 6 shows the TGA and DTG thermograms of polyurethane. The percentage weight loss (%) is listed in **Table 1**. Generally, only a small amount of weight was observed. It is shown in **Figure 6** in the region of 45 – 180°C. This is due to the presence of condensation on moisture and solvent residues.

Table1 Weight loss percentage of (wt%) polyurethane film

Sample	% Weight loss (wt%)				Total of weight loss (%)	Residue after 550°C (%)
	$T_{max,}$ °C	T_{d1}, 200 – 290°C	T_{d2}, 350 – 500°C	T_{d3}, 500 – 550°C		
Polyurethane	240	8.04	39.29	34.37	81.7	18.3

The bio polyurethane is thermally stable up to 240 °C before it undergone thermal degradation. The first stage of thermal degradation (T_{d1}) on polyurethane films was shown in the region of 200 – 290°C as shown in **Figure 6**. The T_{d1} is associated with degradation of the hard segments of the urethane bond, forming alcohol or degradation of the polyol chains and releasing of isocyanates (Berta et al. 2006), primary and secondary amines as well as carbon dioxide (Corcuera et al. 2011; Pan & Webster 2012). Meanwhile, the second thermal degradation stage (T_{d2}) of polyurethane films experienced a weight loss of 39.29 %. This endotherm of T_{d2} is related to dimmerization of isocyanates to form carbodiimides and release CO_2. The formed

carbodiimide reacts with alcohol to form urea. For the third stage of thermal degradation (T_{d3}) is related to the degradation on urea (Berta et al. 2006) and the soft segment on polyurethane.

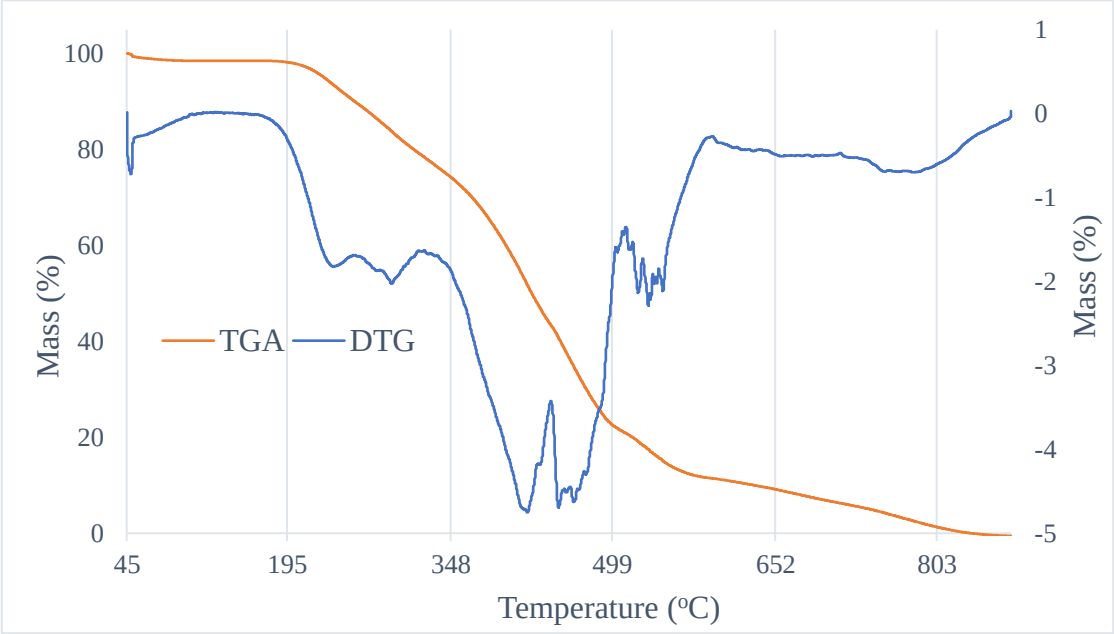


Figure 6. DTG and TGA thermogram of polyurethane film

Generally, DSC analysis exhibited thermal transitions as well as the initial crystallisation and melting temperatures of the polyurethane (Khairuddin et al. 2018). It serves to analyse changes in thermal behaviour due to changes occurring in the chemical chain structure based on the glass transition temperature (T_g) of the sample obtained from the DSC thermogram (**Figure 7**). DSC analysis on polyurethane films was performed in the temperature at range 100 °C to 200 °C using nitrogen gas as blanket as proposed by Furtwengler et al. (2017). The glass transition temperature (T_g) 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. During polymerization, this hard segment restricts the mobility of the polymer chain (Ren et al. 2013) owing to steric effect on benzene ring in hard segment. The endothermic peak of acetone used as the solvent in this study was supposedly be at 56°C. However, it was detected in the DSC thermogram nor the TGA thermogram, which indicates that acetone was removed from the polyurethane during the

synthesis process, owing to its volatility nature. The presence of acetone in the synthesis was to lower the reaction kinetics.

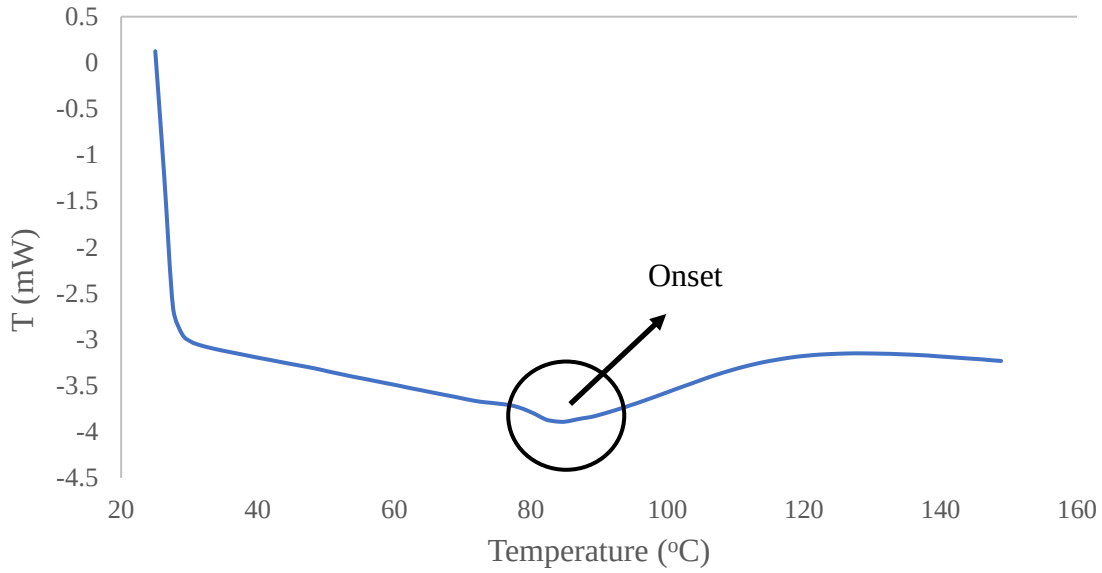


Figure 7. DSC thermogram of polyurethana film

e. The solubility and mechanical properties of the polyurethane film

The chemical resistivity of a polymer will be the determinant in performing as conductor. Thus, its solubility in various solvents was determined by dissolving the polymer in selected solvents such as hexane, benzene, acetone, tetrahydrofuran (THF), dimethylformamide (DMF) and dimethylformamide (DMSO). On the other hand, the mechanical properties of polyurethane were determined based on the standard testing following ASTM D 638 (Standard Test Method for Tensile Properties of Plastics) . The results from the polyurethane film solubility and tensile test are shown in **Table 2**. Polyurethane films were insoluble with benzene, hexane and acetone and are only slightly soluble in tetrahydrofuran (THF), dimethylformamide (DMF) and dimethylformamide (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 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.

Table 2 The solubility and mechanical properties of the polyurethane film

Parameters		Polyurethane film
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

f. Conductivity of the polyurethane as polymeric film on SPE

Polyurethane film deposited onto the screen printed electrode by casting method as shown in **Figure 1**. After that, the modified electrode was analysed using cyclic voltammetry (CV) and

differential pulse voltammetry (DPV) in order to study the behaviour of modified electrode. The modified electrode was tested in a 0.1 mmol/L KCl solution containing 5 mmol/L ($K_3Fe(CN)_6$). 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 voltametry method with a potential range of -1.00 to +1.00 with a scan rate of 0.05 V/s. The voltamogram at electrode have shown a specific redox reactions. Furthermore, the conductivity of the modified electrode is lower due to the use of polyurethane. This occurs due to PU is a natural polymer produced from the polyol of palm kernel oil. The electrochemical signal at the electrode is low if there is a decrease in electrochemical conductivity (El - Raheem et al. 2020). It can be conluded that polyurethane is a bio – polymer with a low conductivity value. The current of modified electrode was found at 5.3 x 10^{-5} A or 53 µA.

Accoridng to **Figure 8**, it can be concluded that the anodic peak present in the modifed electrode was at +0.5 V, it also represented the oxidation process of the modified electode. The first oxidation scan on both electrodes ranged from -0.2 to +1.0 V, which showed a significant anodic peak at a potential of +0.5 V.

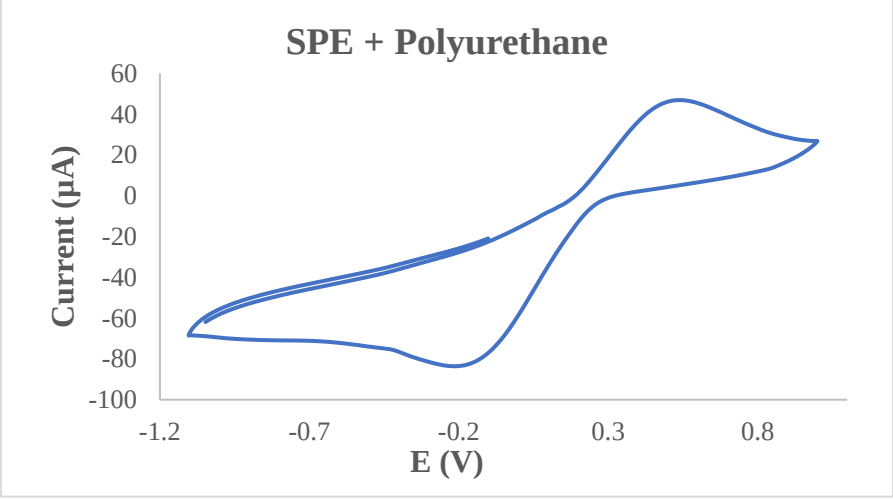


Figure 8. The voltamogram of SPE – PU modified electrode after analysed using cyclic voltammetry (CV) technique

Figure 9 also presents the DPV voltammogram of modified electrode. DPV is a measurement based on the difference in potential pulses that produce an electric current. Scanning the capability pulses to the working electrode will produce different currents. Optimal peak currents will be produced to the reduction capacity of the redox material. The peak current produced is proportional to the concentration of the redox substance and can be detected up to concentration below 10^{-8} M. DPV conducted to obtain the current value that more accurate than CV (Lee et al. 2018).

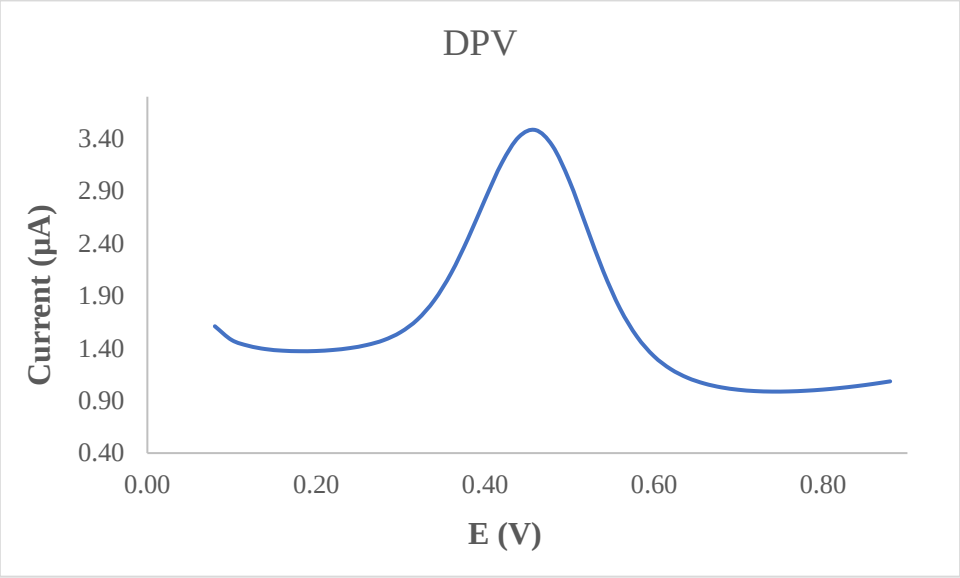


Figure 9. The voltammogram of SPE – PU modified electrode after analyzed using differential pulse voltammetry (DPV) technique

This study used a redox pair ($K_3Fe(CN)_6$) as a test device (probe). The currents generated by SPE-PU and proved by CV and DPV have shown conductivity on polyurethane films. This suggests that polyurethane films can conduct electron transfer. The electrochemical area on the modified electrode can be calculated using the formula from Randles-Sevcik (Butwong et al. 2019), where the electrochemical area for SPE-PU is considered to be A, using Equation 2:

$$\textbf{Current of SPE-PU , } I_p = 2.65 \times 10^5\, n^{3/2}\, A v^{1/2}\, C D^{1/2} \qquad (2)$$

Where, n – 1 is the amount of electron transfer involved, while C is the solvent concentration used (mmol/L) and the value of D is the diffusion constant of 5 mmol/L at ($K_3Fe(CN)_6$) dissolved using 0.1 mmol/L KCl. The estimated surface area of the electrode (**Figure 1**) was 0.2 cm^2 where the length and width of the electrode used during the study was 0.44 cm × 0.44 cm while the surface area of the modified electrode was 0.25 cm^2 with the length and width of the electrode estimated at 0.5 cm × 0.5 cm, and causing the modified electrode has a larger surface. The corresponding surface concentration (τ) (mol/cm^2) is calculated using Equation 3.

$$\mathbf{I_p = (n^2 F^2 / 4RT) A\tau v} \qquad (3)$$

I_p is the peak current (A), while A is the surface area 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 constant ideal gas (8.314 J/mol K) and T is the temperature used during the experiment being conducted (298 K) (Koita et al. 2014).

4. Conclusion

Polyurethane film was prepared by pre-polymerization between palm kernel oil-based polyol (PKO-p) with MDI. The presence of PEG 400 as the chain extender formed freestanding flexible film. Acetone was used as the solvent to lower the reaction kinetics since the pre-polymerization was carried out at room temperature. The formation of urethane links (NHCO – backbone) after polymerization was confirmed by the absence of N=C=O peak at 2241 cm^{-1} 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 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 absence of phase separation and

smooth surface. Meanwhile, the current of modified electrode was found at 5.2×10^{-5} A. This bio polyurethane film can be used as a conducting bio – polymer and it is very useful for other studies such as electrochemical sensor purpose.

5. Patents

There are no patents resulting from the work reported in this manuscript.

6. Author contributions

Munir. M.A. and Badri. K.H. performed the measurements, Badri. K.H. and Heng. L.Y. were involved in planning and supervised the work, Munir. M.A and Badri. K.H. processed the experimental data, performed the analysis, drafted the manuscript, designed the figures, and performed the calculations. Munir. M.A. and Badri. K.H. prepared and characterized the samples through FTIR spectroscopy, TGA and DSC analyses as well as the conductivity. Munir. M.A. and Badri. K.H. conducted the interpretation of results and write up of the manuscript. All authors discussed the results and commented on the manuscript.

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9. Conflict of Interest

The authors declare no conflict of interest.

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Design and Synthesis of Conducting Polymer Based on Polyurethane produced from Palm Kernel Oil

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This manuscript is interesting and has sufficient merits to be considered further for publication after due amendments to address the reviewers' comments. The English is quite understandable, but it requires revision to improve the clarity sufficiently for publication.

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Design and Synthesis of Conducting Polymer Based on Polyurethane produced from Palm Kernel Oil

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Abstract

Polyurethane (PU) is a unique polymer that has versatile processing method and mechanical properties upon inclusion of selected additives. In this study, a freestanding bio-polyurethane film on screen – printed electrode (SPE) was prepared by solution casting technique, using acetone as solvent. It was a one-pot synthesis between major reactants namely, palm kernel oil-based polyol (PKOp) and 4,4-methylene diisocyanate. The PU undergone strong adhesion on SPE. The formation of urethane linkages (NHCO backbone) after polymerization was confirmed by the absence of N=C=O peak at 2241 cm^{-1}. The glass transition temperature (T_g) of the polyurethane was detected at 78.1°C. The conductivity of PU was determined using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The current of electrode was at 5.2 x 10^{-5} A.

Keywords: Polyurethane, polymerization, screen – printed electrode, voltammetry

1. Introduction

Polymers are molecules composed of many repeated sub-units referred to as monomers (Sengodu & Deshmukh 2015). Conducting polymers (CPs) are polymers that exhibit electrical behaviour (Alqarni et al. 2020). The conductivity of CPs was first observed in polyacetylene, nevertheless owing to its instability led to the discovery of other forms of CPs such as polyaniline (PANI), poly (o-toluidine) (PoT), polythiophene (PTh), polyfluorene (PF) and polyurethane (PU). Furthermore, natural CPs have low conductivity and are often semi-conductive. Therefore, it is essential to increase their conductivity mainly for use in electrochemical sensor programs (Dzulkipli et al. 2021; Wang et al. 2018). Conducting polymers (CPs) represent a sizeable range of useful organic substances. Their unique electrical, chemical and physical properties; reasonable price; simple preparation; small dimensions and large surface area have enabled researchers to discover a wide variety of uses such as sensors, biochemical applications, solar cells and electrochromic devices (Alqarni et al. 2020; Ghosh et al. 2018). There are scientific documentations on the use of conductive polymers in various studies such as polyaniline (Pan & Yu 2016), polypyrrole (Ladan et al. 2017) and polyurethane (Tran et al. 2020; Vieira et al. 2020; Guo et al. 2020; Fei et al. 2020). The application of petroleum as polyol in order to produce polyurethane has been applied. The coal and crude oil used as raw materials to produce it. Nevertheless, these materials become very rare to find and the price is very expensive at the same time required sophisticated system to produce it. These reasons have been considered and finding utilizing plants that can be used as alternative polyols should be done immediately (Badri 2012). Furthermore, in order to avoid the application of petroleum as raw material for polyol, vegetable oils become a better choice as polyol in order to obtain a biodegradable polyol. Vegetable oils that generally used for synthesis polyurethane are soybean oil, corn oil,

sunflower seed oil, coconut oil, nuts oil, rape seed, olive oil and palm oil (Badri 2012; Borowicz et al. 2019).

It is very straightforward for vegetable oils to react with specific group in order to form PU such as epoxy, hydroxyl, carboxyl and acrylate owing to the existence of (-C=C-) in vegetable oils. Thus, it has provided appealing profits to vegetables oils compared to petroleum considered the toxicity, price and harm the environment (Mustapha et al. 2019; Mohd Noor et al. 2020). Palm oil becomes the chosen in this study to produce PU owing to it is largely cultivated in South Asia particularly in Malaysia and Indonesia. It has several profits compared to other vegetables oils such as the easiest materials obtained, the lowest cost of all the common vegetable oils and recognized as the plantation that has low environmental impact and removing CO_2 from atmosphere as netsequester (Tajau et al. 2021; Septevani et al. 2015).

Biopolymer, a natural biodegradable polymer has attracted much attention in recent years. Global environmental awareness and fossil fuel depletion urged researchers to work in the biopolymer field (Priya et al. 2018). Polyurethane is one of the most common, versatile and researched materials in the world. These materials combine the durability and toughness of metals with the elasticity of rubber, making them suitable to replace metals, plastics and rubber in several engineered products. They have been widely applied in biomedical applications, building and construction applications, automotive, textiles and in several other industries due to their superior properties in terms of hardness, elongation, strength and modulus (Zia et al. 2014; Romaskevic et al. 2006). Polyurethanes also considered to be one of the most useful materials with many profits such as, possess low conductivity, low density, absorption capability and dimensional stability. They are clearly a great research subject owing to their mechanical, physical and chemical properties (Badan & Majka 2017).

The urethane group is the major repeating unit in PUs and is produced from the reaction between alcohol (-OH) and isocyanate (NCO); albeit polyurethanes also contain other groups such as ethers, esters, urea and some aromatic compounds. Due to the wide variety of sources from which Pus can be synthesized, thus a wide range of specific applications can be generated. They are grouped into several different classes based on the desired properties: rigid, flexible, thermoplastic, waterborne, binders, coating, adhesives, sealants and elastomers (Akindoyo et al. 2016).

Although, PU has low conductivity but it is lighter than other materials such as metals. The hardness of PU also relies on the aromatic rings number in the polymer structure (Janpoung et al, 2020; Su'ait et al. 2014), majorly contributed by the isocyanate derivatives. PU has also a conjugate structure where electrons can move in the main chain that causing electricity produced even the conductivity is low. The electrical conductivity of conjugated linear (π) can be explained by the distance between the highest energy level containing electrons (HOMO) called valence band and the lowest energy level not containing electrons (LUMO) called the conduction band (Wang et al. 2017; Kotal et al. 2011).

Nowadays, screen – printed electrodes (SPEs) modified with conducting polymer have been developed for various electrochemical sensing. SPE becomes the best solution owing to its frugal manufacture, tiny size, able to produce in large – scale and can be applied for on – site detection (Nakthong et al. 2020). Conducting polymers (CPs) become an alternative to modify the screen – printed electrodes due to their electrical conductivity, able to capture analyte by chemical/physical adsorption, large surface area and making CPs are very appealing material from electrochemical perspectives (Baig et al. 2019). Such advantages of SPE encourage us to construct a new electrode for electrochemical sensing, and no research reported on direct electrochemical oxidation of histamine using screen printed electrode

modified by 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 synthesis, characterize and study the conductivity of polyurethane using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) attached onto screen printed electrode (SPE). To the best of our knowledge, this is the first attempt to use a modified polyurethane electrode. The electrochemistry of polyurethane mounted onto screen-printed electrode (SPE) is discussed in detail. Polyurethane is possible to become an advanced frontier material in chemically modified electrodes for bio sensing application.

2. Experimental

2.1 Chemicals

Synthesis of polyurethana film: Palm kernel oil (PKOp) supplied by UKM Technology Sdn Bhd through MPOB/UKM station plant, Pekan Bangi Lama, Selangor and prepared using Badri et al. (2000) method. 4, 4-diphenylmethane diisocyanate (MDI) was acquired from Cosmopolyurethane (M) Sdn. Bhd., Klang, Malaysia. Solvents and analytical reagents were benzene (≥ 99.8%), toluene (≥ 99.8%), hexane (≥ 99%), acetone (≥ 99%), tetrahydrofuran (THF), dimethylformamide (DMF) (≥ 99.8%), dimethylsulfoxide (DMSO) (≥ 99.9%) and polyethylene glycol (PED) 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 638 (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 Perkin Elmer Pyris model with heating rate of 10 °C/minute at a temperature range of 30 to 800 °C under a nitrogen gas atmosphere. The DSC analysis was performed using a thermal analyzer of Perkin Elmer Pyris model with heating rate of 10 °C /minute at a temperature range of -100 to 200 °C under a nitrogen gas atmosphere. Approximately, 5-10 mg of PU was weighed. Sample was heated from 25 to 150 °C for one minute, then cooled immediately from 150 -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 changes 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 film 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 film was coated with a thin layer of gold to increase the conductivity of the film. The coating method was carried out using a sputter - coater. The observations were conducted at magnification of 200× and 5000 × with 10.00 kV (Electron high tension - EHT).

The crosslinking of PU was determined using 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 to run for 24 hours. 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 hours in order to get a constant mass. The percentage of crosslinking content known as the gel contet, can be calculated using Equation (1).

$$\text{Gel content } (\%) = \frac{W_o - W}{W} \text{ x } 100\ \% \qquad (1)$$

W_o is mass of PU before the reflux process (g) and W is 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 (DATR) method to confirm the polyurethane, PKOp and MDI functional group. FTIR spectroscopic analysis was performed at a wave number of 4000 to 600 cm^{-1} to identify the peaks of the major functional groups in the formation of polymer such as amide group (-NH), urethane carbonyl group (-C = O) and carbamate group (-CN).

2.3 Modification of Electrode

Voltammetric tests were performed using Metrohm Autolab Software (**Figure 1**) analyzer using cyclic voltammetry (CV) method or known as amperometric mode and differential pulse voltametry (DPV). All electrochemical experiments were carried out using screen printed electrode (diameter 3 mm) modified using polyurethane film as working electrode, platinum wire as auxiliary electrode and Ag/AgCl electrode as reference electrode. All experiments were conducted at temperature of 20 ± 2^oC.

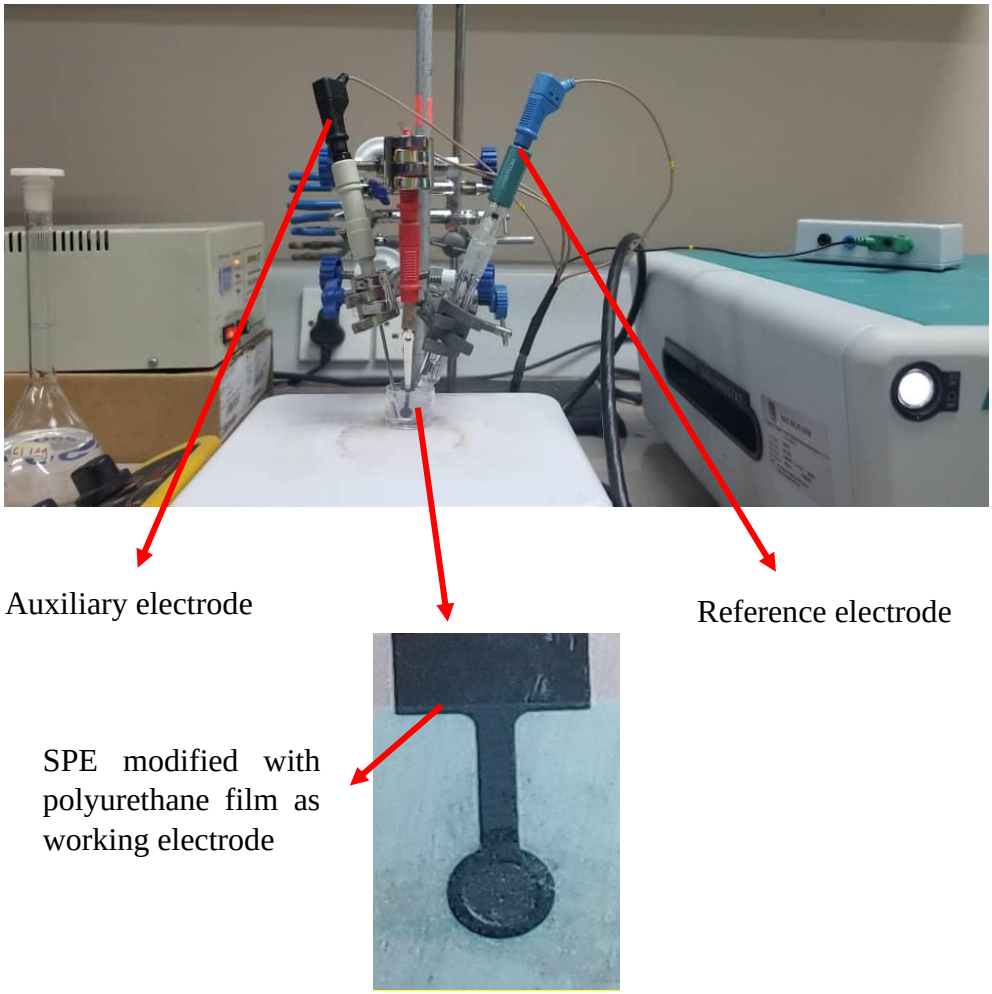


Figure 1. Potentiostat instrument to study the conductivity of SPE modified with polyurethane film using cyclic voltametry (CV) and differential pulse voltammetry (DPV)

PU casted onto the screen – printed electrode (SPE + PU) was 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 & 0.5) mg of palm – based prepolyurethane was dropped separately onto the surface of the SPE 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 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 pre - polymerization method which involves the formation of urethane polymer at an early stage. The reaction took place between palm kernel oil – based polyol (PKOp) and diisocyanate (MDI). **Table 1** presents the PKO-p properties used in this study. The structural chain was extended with the aid of polyethylene glycol (PEG) to form flexible and elastic polyurethane film. In order to form the urethane prepolymer, one of the isocyanate groups (NCO) reacts with one hydroxyl group (OH) of polyol while the other isocyanate group attacks another hydroxyl group in the polyol (Wong & Badri 2012) as shown in **Figure 2**.

Table 1 Characteristics of PKO-p (Badri et al. (2000)).

Property	**Values**
Viscosity at 25^{o}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

a. FTIR analysis

Figure 3 shows the FTIR spectrum for polyurethane, exhibiting the important functional group peaks. According to study researched by Wong & Badri 2012, PKO-p reacts with MDI to form urethane prepolymers. The NCO group on MDI reacts with OH group on polyol

whether PKOp or PEG. It can bee seen there are no important peaks of MDI in the FTIR spectrums. This is further verified by the absence of peak at the 2400 cm^{-1} belongs 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 reacted with the carbonyl urethane group.

The reaction of polyurethane has been studied by Hamuzan & Badri (2016) 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 peaks at 2250 – 2270 cm^{-1} indicates the absence of NCO groups. It shows that the polymerization reaction occurs entirely between NCO groups in MDI with hydroxyl groups on polyols and PEG (Mishra et al. 2012). The absence of peaks at 1690 cm^{-1} representing urea (C = O) in this study indicated, there is no urea formation as a byproduct (Clemitson 2008) of the polymerization reaction that possibly occur due to the excessive water. For the amine (NH) group, hydrogen-bond to NH and oxygen to form ether and hydrogen bond to NH and oxygen to form carbonyl on urethane can be detected at the peak of 3301 cm^{-1} and in the wave number at range 3326 – 3428 cm^{-1}. This has also been studied and detected by Lampman et. al. (2010) and Mutsuhisa et al. (2007). In this study, the hydrogen bond formed by C = O acts as a proton acceptor whereas NH acts as a proton donor. The urethane group in the hard segment (MDI) has electrostatic forces on the oxygen, hydrogen and nitrogen atoms and these charged atoms form dipoles that attract other opposite atoms. These properties make isocyanates are highly reactive and having different properties (Leykin et al. 2016).

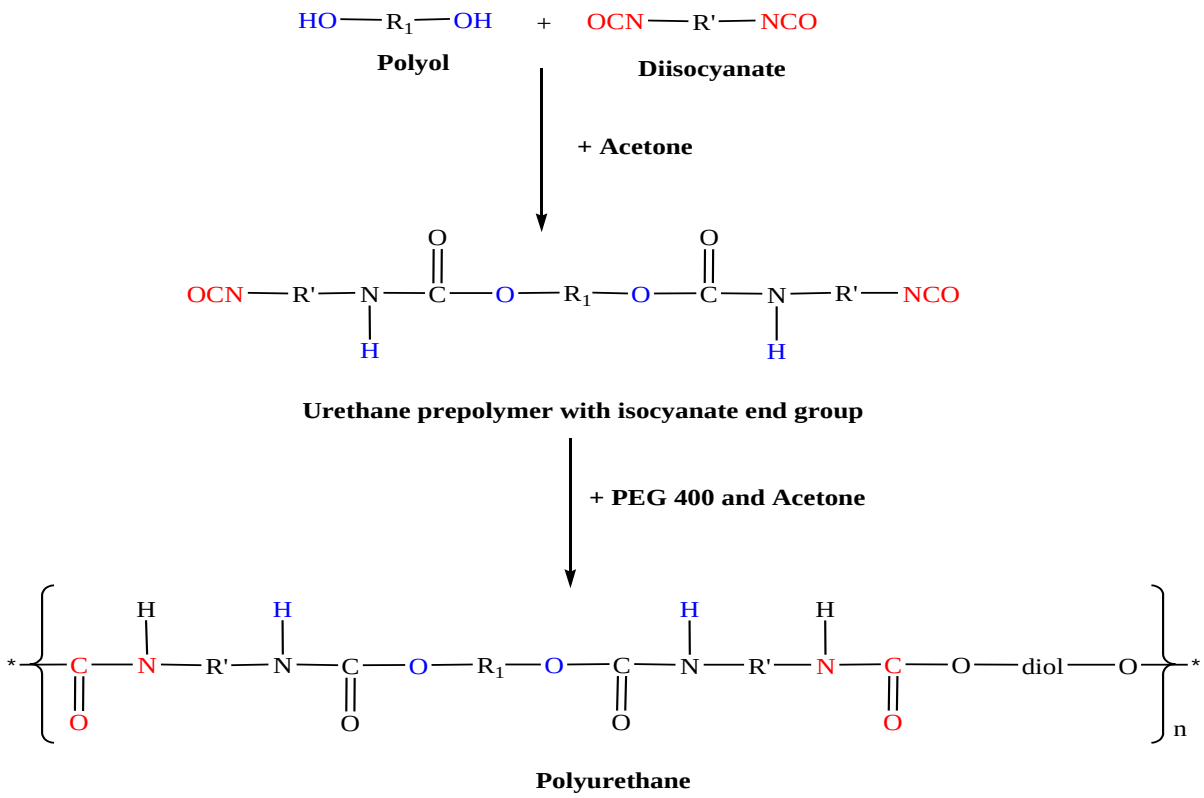


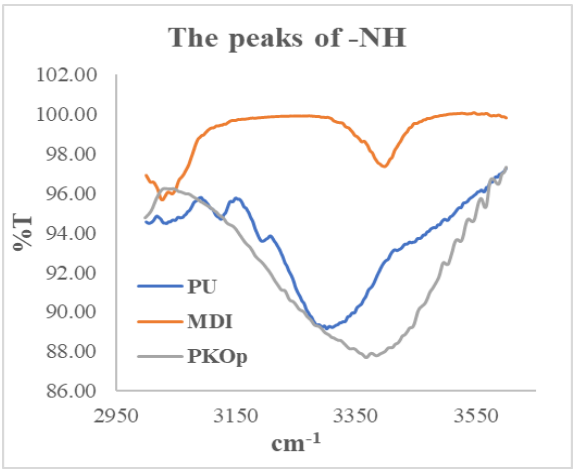
Figure 2. The chemical route of producing polyurethane via pre-polymerization method (Wong & Badri 2012).

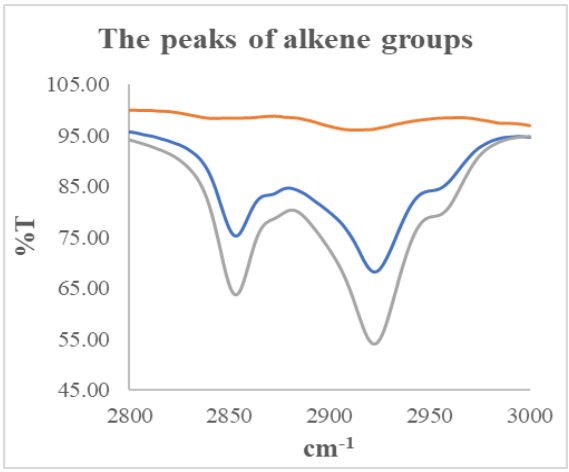
MDI was one of the isocyanate used in this study, has an aromatic group and more reactive compared to aliphatic group isocyanates such as hexamethylene diisocyanate (HDI) or isophorone diisocyanate (IPDI). Isocyanates have two groups of isocyanates on each molecule. Diphenylmethane diisocynate is an exception owing to its structure consists of two, three, four or more isocyanate groups (Nohra et al. 2013). The use of PEG 400 in this study as a chain extender for polyurehane 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 (Leykin et al. 2016).

The mechanism of the pre – polymerization in urethane chains formation is a nucleophilic substitution reaction as studied by Yong et al. (2009). 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. 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 who have conducted by Wong and Badri (2012).

Moreover, nitrogen was more electropositive than oxygen, therefore, -CN bonds were more attracted to cations (H+) than -CO. The combination between long polymer chain and low cross linking content gives the polymer an elastic properties whereas short chain and high cross linking producing hard and rigid polymers. Cross linking in polymers consist of three - dimensional networks with high molecular weight. In some aspects, polyurethane can be a macromolecule, a giant molecule (Petrovic 2008).





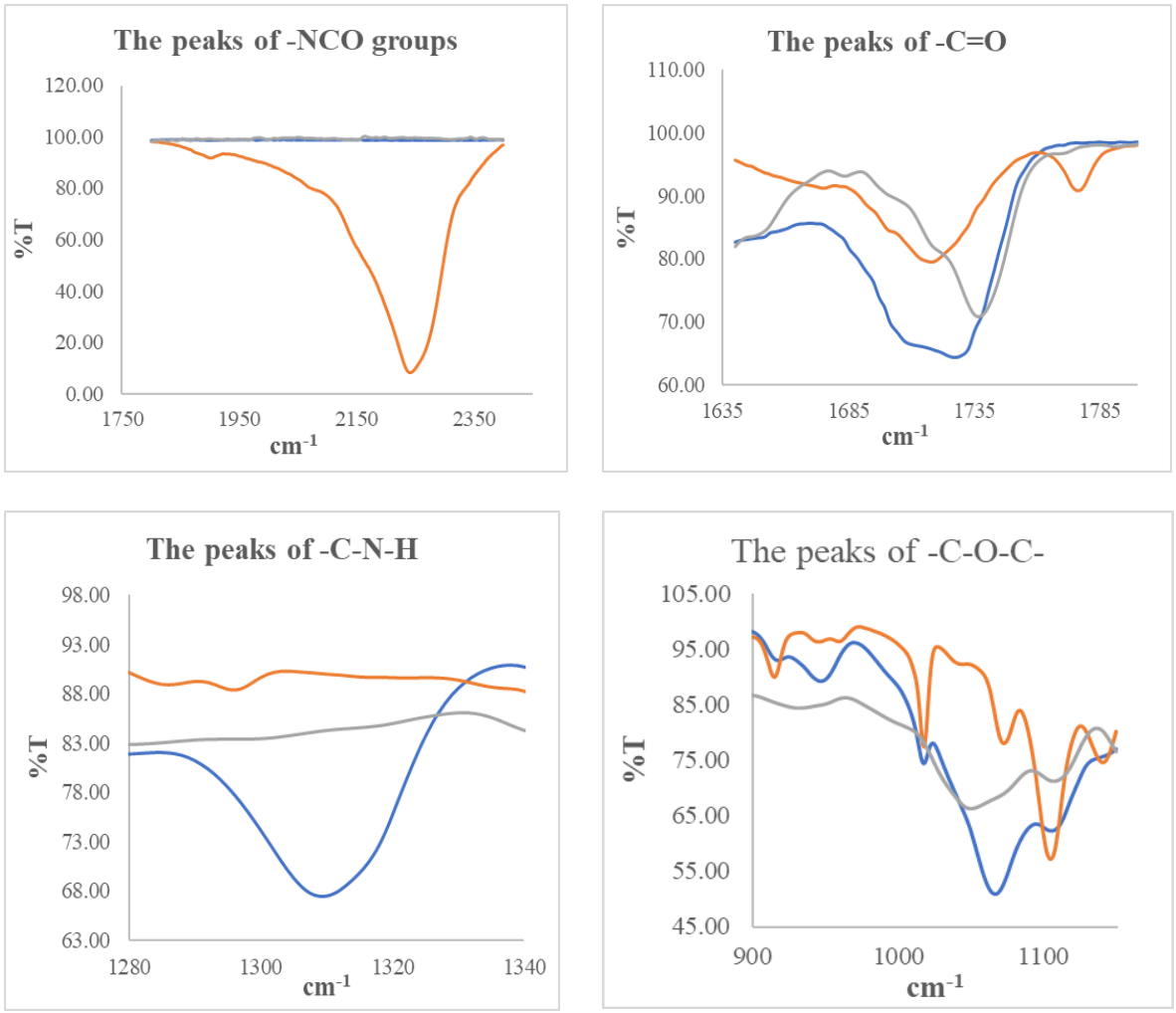


Figure 3. FTIR spectrums of several important peaks between polyurethane, PKO-p and MDI

However, reaction between MDI and PEG as a chain extender where oxygen on the nucleophile PEG attacks the NCO group in the MDI to form two intermediate complexes A and B can occur. Nevertheless, nucleophilic substitution reactions have a greater tendency to occur in PKOp compared to PEG because the presence of nitrogen atoms is more electropositive than oxygen atoms in PEG. Amine has a higher probability of to react compared to hydroxyl (Herrington & Hock 1997). Amine with high alkalinity reacts with carbon atoms on MDI as proposed by Wong and Badri (2012). PKOp contains long carbon chains that can easily stabilize alkyl ions when intermediate complexes are formed.

Therefore, polyol is more reactive than PEG to react with MDI. However, the addition of PEG will increase the length of the polyurethane chain and prevent side effects such as the formation of urea by -products of the NCO group reaction in urethane pre - polymer and water molecules 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 4**). This reaction can cause a polyurethane foam not polyurethane film as we studied the film.

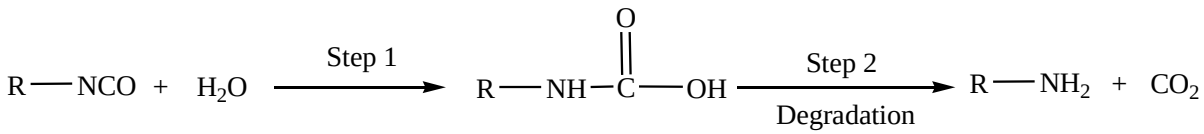


Figure 4. The reaction between NCO group and water producing carbon dioxide

Furthermore, the application of PEG can influence the conductivity of PU where Porcarelli et al. (2017) 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 molecular weight more that 1000 $g \cdot mol^{-1}$ tends to crystallize with deleterious effects on room temperature ionic conductivity (Porcarelli et al. 2017).

b. Morphological analysis

The Field Emission Scanning Electron Microscope (FESEM) micrograph in **Figure 5** shows the formation of a uniform polymer film contributed by the polymerization method applied. The magnification used for this surface analysis ranged from 200 to 5000 ×. 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 justified by the wavelengths obtained by the FTIR spectrums above.

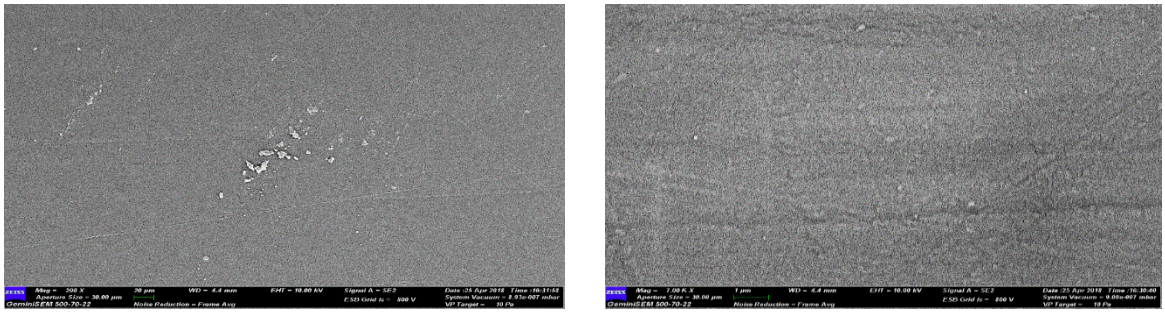


Figure 5. The micrograph of polyurethane films analysed by FESEM at (a) 200 × and (b) 5000× magnifications.

c. 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 (Cuve & Pascault 1991). Therefore, during the testing, it was very difficult to dissolve in toluene, as the testing reagent. The degree of the crosslinking is determined by the percentage of the gel content. The analysis result obtained from the Soxhlet testing indicating a 99.3 % gel content. This is significant in getting a stable polymer at higher working temperature (Rogulska et al. 2007).

$$\text{Gel content (\%)} = \frac{(0.6 - 0.301)\ \text{g}}{0.301\ \text{g}} \times 100\% = 99.33\%$$

d. The thermal analysis

Thermogravimetric analysis (TGA) can be used to observe the material mass based on temperature shift. It can also examine and estimate the thermal stability and materials properties such as the alteration weight owing to absorption or desorption, decomposition, reduction and oxidation. The material composition of polymer is specified by analysing the temperatures and the heights of the individual mass steps (Alamawi et al. 2019). **Figure 6** shows the TGA and 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 6** in the region of 45 – 180°C. This is due to the presence of condensation on moisture and solvent residues.

Table2 Weight loss percentage of (wt%) polyurethane film

Sample	% Weight loss (wt%)				Total of weight loss (%)	Residue after 550°C (%)
	$T_{max,}$ °C	T_{d1}, 200 – 290°C	T_{d2}, 350 – 500°C	T_{d3}, 500 – 550°C		
Polyurethane	240	8.04	39.29	34.37	81.7	18.3

The bio polyurethane is thermally stable up to 240 °C before it undergone thermal degradation (Agrawal et al. 2017). The first stage of thermal degradation (T_{d1}) on polyurethane films was shown in the region of 200 – 290 °C as shown in **Figure 6**. The T_{d1} is associated with degradation of the hard segments of the urethane bond, forming alcohol or degradation of the polyol chains and releasing of isocyanates (Berta et al. 2006), primary and secondary amines as well as carbon dioxide (Corcuera et al. 2011; Pan & Webster 2012). Meanwhile, the second thermal degradation stage (T_{d2}) of polyurethane films experienced a weight loss of 39.29 %. This endotherm of T_{d2} is related to dimmerization of isocyanates to form carbodiimides and release CO_2. The formed carbodiimide reacts with alcohol to form urea. For the third stage of thermal degradation (T_{d3}) is related to the degradation on urea (Berta et al. 2006) and the soft segment on polyurethane.

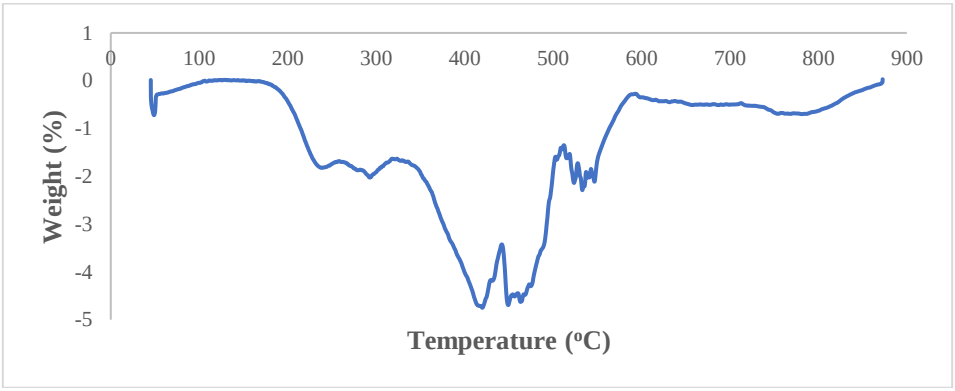


Figure 6. DTG thermogram of polyurethane film

Generally, DSC analysis exhibited thermal transitions as well as the initial crystallisation and melting temperatures of the polyurethane (Khairuddin et al. 2018). It serves to analyse changes in thermal behaviour due to changes occurring in the chemical chain structure based on the glass transition temperature (T_g) of the sample obtained from the DSC thermogram (**Figure 7**). DSC analysis on polyurethane films was performed in the temperature at range 100 ^oC to 200 ^oC using nitrogen gas as blanket as proposed by Furtwengler et al. (2017). The glass transition temperature (T_g) on polyurethane was above room temperature, at 78.1 ^oC indicated the state of glass on polyurethane. The presence of MDI contributes to the formation of hard segments in polyurethanes. Porcarelli et al. (2017) stated that possess a low glass transition (T_g) may contribute to PU conductivity.

During polymerization, this hard segment restricts the mobility of the polymer chain (Ren et al. 2013) owing to steric effect on benzene ring in hard segment. The endothermic peak of acetone used as the solvent in this study was supposedly be at 56^oC. However, it was detected in the DSC thermogram nor the TGA thermogram, which indicates that acetone was removed from the polyurethane during the synthesis process, owing to its volatility nature. The presence of acetone in the synthesis was to lower the reaction kinetics.

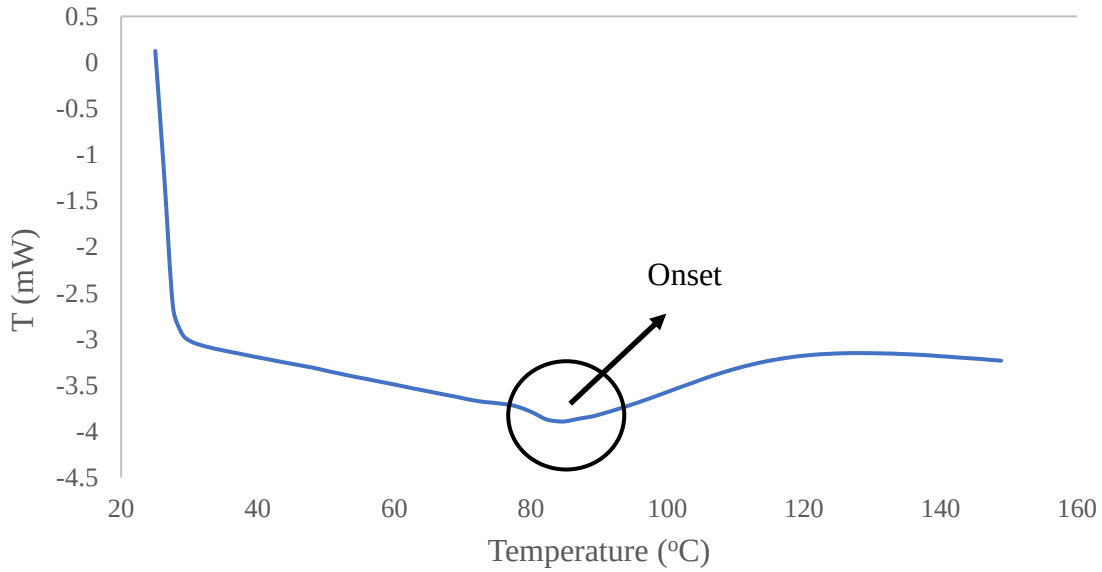


Figure 7. DSC thermogram of polyurethana film

e. The solubility and mechanical properties of the polyurethane film

The chemical resistivity of a polymer will be the determinant in performing as conductor. Thus, its solubility in various solvents was determined by dissolving the polymer in selected solvents such as hexane, benzene, acetone, tetrahydrofuran (THF), dimethylformamide (DMF) and dimethylformamide (DMSO). On the other hand, the mechanical properties of polyurethane were determined based on the standard testing following ASTM D 638 (Standard Test Method for Tensile Properties of Plastics). The results from the polyurethane film solubility and tensile test are shown in **Table 3**. Polyurethane films were insoluble with benzene, hexane and acetone and are only slightly soluble in tetrahydrofuran (THF), dimethylformamide (DMF) and dimethylformamide (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.

Table 3 The solubility and mechanical properties of the polyurethane film

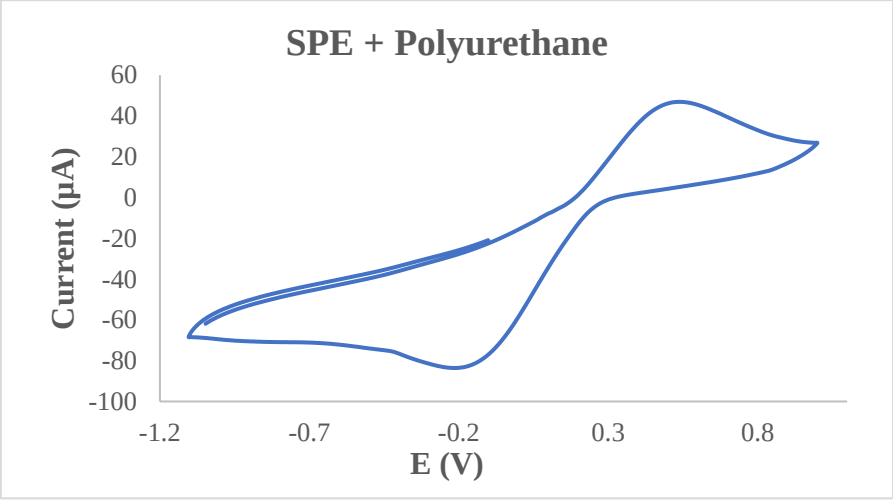
Parameters		Polyurethane film
Solubility	Benzene	Insoluble
	Hexane	Insoluble
	Acetone	Insoluble
	THF	Less soluble
	DMF	Less soluble
	DMSO	Less soluble
Stress (MPa)		8.53
Elongation percentage (%)		43.34
Strain modulus (100) (MPa)		222.10

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 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.

f. Conductivity of the polyurethane as polymeric film on SPE

Polyurethane film deposited onto the screen printed electrode by casting method as shown in **Figure 1**. After that, the modified electrode was analysed using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in order to study the behaviour of modified electrode. The modified electrode was tested in a 0.1 mmol/L KCl solution containing 5 mmol/L ($K_3Fe(CN)_6$). 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 voltametry method with a potential range of -1.00 to +1.00 with a scan rate of 0.05 V/s. The voltamogram at electrode have shown a specific redox reactions. Furthermore, the conductivity of the modified electrode is lower due to the use of polyurethane. This occurs due to PU is a natural polymer produced from the polyol of palm kernel oil. The electrochemical signal at the electrode is low if there is a decrease in electrochemical conductivity (El - Raheem et al. 2020). It can be conluded that polyurethane is a bio – polymer with a low conductivity value. The current of modified electrode was found at 5.3 x

382 10^{-5} A or 53 µA. Nevertheless, the electroconductivity of PU in this study shows better
383 conductivity several times compared to Bahrami et al. (2019) that reported the conductivity
384 of PU as 1.26 x 10^{-6} A, whereas Li et al. (2019) reported the PU conductivity in their study
385 was even very low, namely 10^{-14} A. The conductivity of PU owing to the benzene ring in
386 hard segment (MDI) could exhibit the conductivity by inducing electron delocalization along
387 the polyurethane chain (Wong et al. 2014). The conducivity of PU can also caused by PEG.
388 The application of PEG as polyol has been studied by Porcarelli et al. (2017), that reported
389 that conductivity of PU based on PEG – polyol was 9.2 x 10^{-8}.
390 Accoridng to **Figure 8**, it can be concluded that the anodic peak present in the modifed
391 electrode was at +0.5 V, it also represented the oxidation process of the modified electode.
392 The first oxidation scan on both electrodes ranged from -0.2 to +1.0 V, which showed a
393 significant anodic peak at a potential of +0.5 V.
394



395
396 **Figure 8**. The voltamogram of SPE – PU modified electrode after analysed using cyclic
397 voltammetry (CV) technique
398
399 **Figure 9** also presents the DPV voltammogram of modified electrode. DPV is a measurement
400 based on the difference in potential pulses that produce an electric current. Scanning the
401 capability pulses to the working electrode will produce different currents. Optimal peak

currents will be produced to the reduction capacity of the redox material. The peak current produced is proportional to the concentration of the redox substance and can be detected up to concentration below 10^{-8} M. DPV conducted to obtain the current value that more accurate than CV (Lee et al. 2018).

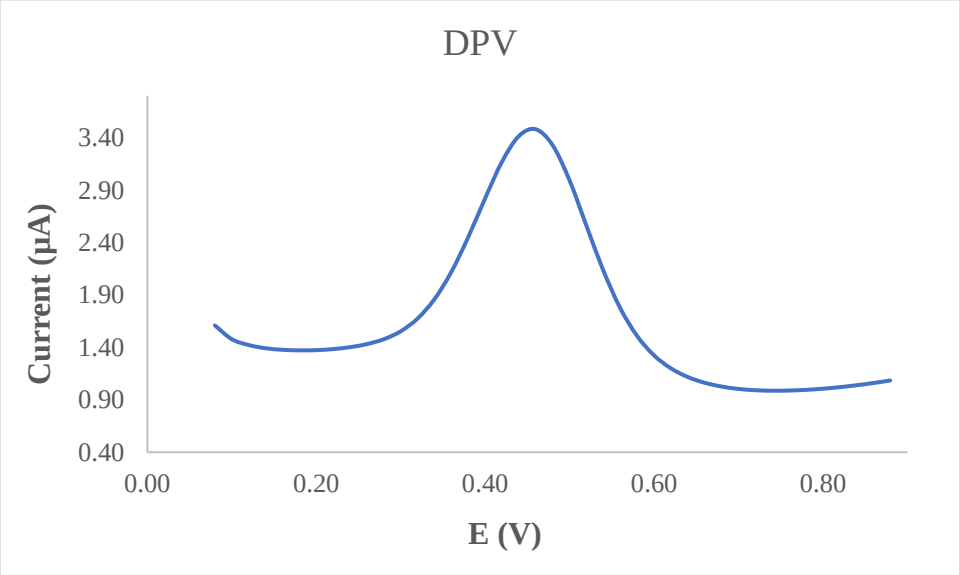


Figure 9. The voltammogram of SPE – PU modified electrode after analyzed using differential pulse voltammetry (DPV) technique

This study used a redox pair ($K_3Fe(CN)_6$) as a test device (probe). The currents generated by SPE-PU and proved by CV and DPV have shown conductivity on polyurethane films. This suggests that polyurethane films can conduct electron transfer. The electrochemical area on the modified electrode can be calculated using the formula from Randles-Sevcik (Butwong et al. 2019), where the electrochemical area for SPE-PU is considered to be A, using Equation 2:

$$\textbf{Current of SPE-PU , } I_p = 2.65 \times 10^5\, n^{3/2}\, A v^{1/2}\, C D^{1/2} \qquad (2)$$

Where, n – 1 is the amount of electron transfer involved, while C is the solvent concentration used (mmol/L) and the value of D is the diffusion constant of 5 mmol/L at ($K_3Fe(CN)_6$) dissolved using 0.1 mmol/L KCl. The estimated surface area of the electrode (**Figure 1**) was 0.2 cm^2 where the length and width of the electrode used during the study was 0.44 cm × 0.44

cm while the surface area of the modified electrode was 0.25 cm^2 with the length and width of the electrode estimated at 0.5 cm × 0.5 cm, and causing the modified electrode has a larger surface. The corresponding surface concentration (τ) (mol/cm^2) is calculated using Equation 3.

$$\mathbf{I_p = (n^2 F^2 / 4RT) A\tau v} \qquad (3)$$

I_p is the peak current (A), while A is the surface area 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 constant ideal gas (8.314 J/mol K) and T is the temperature used during the experiment being conducted (298 K) (Koita et al. 2014). The development of conducting polymer from palm oil – based biomaterials seems to be one of the potential future applications of palm oil products, as this novel material has the potential to contribute positively to the analytical industry. Likewise, other palm oil-based products, such as refined-bleached-deodorised (RBD) palm oil, palm oil, and palm stearin are abundantly available in Malaysia. They are known to be economical, sustainable, and environmentally biodegradable. These palm oil-based products are promising prospects for manufacturing biomaterials that become alternative products to other polymers from synthetic/chemical-based (Tajao et al. 2021). Several studies have been reported the application of PU to produce elastic conductive fibres and films owing to it is highly elastic, scratch resistant and adhesive (Tadese et al. 2019), thus it is easy for PU to adhere on the screen printed electrode in order to modify the electrode. PU is also being used as a composite material to make elastic conducting composite films (Khatoon & Ahmad 2017).

4. Conclusion

Polyurethane film was prepared by pre-polymerization between palm kernel oil-based polyol (PKO-p) with MDI. The presence of PEG 400 as the chain extender formed freestanding

flexible film. Acetone was used as the solvent to lower the reaction kinetics since the pre-polymerization was carried out at room temperature. The formation of urethane links (NHCO – backbone) after polymerization was confirmed by the absence of N=C=O peak at 2241 cm^{-1} 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 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 absence of phase separation and smooth surface. Meanwhile, the current of modified electrode was found at 5.2×10^{-5} A. This bio polyurethane film can be used as a conducting bio – polymer and it is very useful for other studies such as electrochemical sensor purpose. Furthermore, advanced technologies are promising and the future of bio – based polyols looks very bright.

5. Acknowledgement

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6. Conflict of Interest

The authors declare no conflict of interest.

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Design and Synthesis of Conducting Polymer Based on Polyurethane produced from Palm Kernel Oil

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— Editorial Comments

Peter Foot 15.11.2021

Decision

Major Revision Requested

Message for Author

* The synthetic chemistry and general polymer characterization are fine.
* I am satisfied with the revisions made by the authors, but I agree with the following comments of Reviewer #3:

1. The reported electrical properties are misleading and incorrect. A current of 53 microamps signifies nothing on its own, and it cannot be used as the basis of a comparison of the authors' polymer with other polymers. The mentions of "conductivity" in the following sentences should be corrected or preferably the sentences should be deleted completely:

Lines 432-435: "Nevertheless, the electroconductivity of PU in this study shows better conductivity several times compared to Bahrami et al. (2019) that reported the conductivity of PU as 1.26 x 10-6 A, whereas Li et al. (2019) reported the PU conductivity in their study was even very low, namely 10-14 A. "
and in lines 438-440: "The application of PEG as polyol has been studied by Porcarelli et al. (2017), that reported that the conductivity of PU based on PEG – polyol was 9.2 x 10-8." (This sentence doesn't even mention the units of the reported conductivity.)

2. The English is still poor and hard to follow in some places. This includes missing verbs, e.g. line 420 "Polyurethane film deposited" should be "Polyurethane film was deposited".; orthographic errors e.g. lines 123-125 "SPE becomes the best solution owing to its frugal manufacture, tiny size, able to produce on large-scale and can be applied for on-site detection".
Typographic errors should be corrected e.g. line 89: change Pus to PUs; and lines 138-139 "Polyurethane is possible to become an advanced frontier material is chemically modified electrodes.."
As noted by the reviewer, in line 299 "spectrums" is an incorrect word, which should change to "spectra".
Also repetitious or awkward sentences should be rewritten or deleted, e.g. line 53 "The application of petroleum as polyol in order to produce polyurethane has been applied." or lines 56-57 "These reasons have been considered and finding utilizing plants that can be used as alternative polyols should be done immediately."
The sentence in lines 37-38 must be deleted; readers of IJPS don't need to be told what a polymer is!
The authors are strongly advised to seek the help of a fluent English speaker when they revise their manuscript, or to use a professional scientific editing service.

− Response to Revision Request

Muhammad Abdurrahman Munir 01.10.2021

Your Reply

Greetings, Dear Editor, Hope you are doing well. I have attached several documents such as the manucript edited and the comments for reviewers. Best regards

File

Comments for Reviewers.docx **16 kB**

+ **Reviewer Reports**

Design and Synthesis of Conducting Polymer Based on Polyurethane produced from Palm Kernel Oil

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Abstract

Polyurethane (PU) is a unique polymer that has versatile processing methods and mechanical properties upon inclusion of selected additives. In this study, a freestanding bio-polyurethane film on 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 (PKOp) and 4,4-methylene diisocyanate. The PU has strong adhesion on SPE surface. The synthesized polyurethane was characterized using thermogravimetry analysis (TGA), differential scanning calorimetry (DSC), Fourier – transform infrared spectroscopy (FTIR), surface area analysis by field emission scanning electron microscope (FESEM) and

cyclic voltammetry (CV). Cyclic voltammetry was employed to study electro-catalytic 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 (DPV) method. Furthermore, the formation of urethane linkages (NHCO backbone) after polymerization was analysed using FTIR and confirmed by the absence of N=C=O peak at 2241 cm^{-1}. The glass transition temperature (T_g) of the polyurethane was detected at 78.1^oC.

Keywords: Polyurethane, polymerization, screen-printed electrode, voltammetry

1. Introduction

Polymers are molecules composed of many repeated sub-units referred to as monomers (Sengodu & Deshmukh 2015). Conducting polymers (CPs) are polymers that exhibit electrical behavior (Alqarni et al. 2020). The conductivity of CPs was first observed in polyacetylene, nevertheless owing to its instability led to the discovery of other forms of CPs such as polyaniline (PANI), poly (o-toluidine) (PoT), polythiophene (PTh), polyfluorene (PF) and polyurethane (PU). Furthermore, natural CPs have low conductivity and are often semi-conductive. Therefore, it is essential to increase their conductivity mainly for use in electrochemical sensor programs (Dzulkipli et al. 2021; Wang et al. 2018). Conducting polymers (CPs) represent a sizeable range of useful organic substances. Their unique electrical, chemical and physical properties; reasonable price; simple preparation; small dimensions and large surface area have enabled researchers to discover a wide variety of uses such as sensors, biochemical applications, solar cells and electrochromic devices (Alqarni et al. 2020; Ghosh et al. 2018). There are scientific documentation on the use of conductive polymers in various

studies such as polyaniline (Pan & Yu 2016), polypyrrole (Ladan et al. 2017) and polyurethane (Tran et al. 2020; Vieira et al. 2020; Guo et al. 2020; Fei et al. 2020).

The application of petroleum as polyol in order to produce polyurethane has been applied. Coal and crude oil were used as raw materials to produce it. 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. These reasons have been considered and finding utilizing plants that can be used as alternative polyols should be done immediately (Badri 2012). Furthermore, in order to avoid the application of petroleum as raw material for a polyol, vegetable oils become a better choice as polyol in order to obtain a biodegradable polyol. Vegetable oils that are generally used for synthesis polyurethane are soybean oil, corn oil, sunflower seed oil, coconut oil, nuts oil, rapeseed, olive oil and palm oil (Badri 2012; Borowicz et al. 2019).

It is very straightforward for vegetable oils to react with a specific group in order to form PU such as epoxy, hydroxyl, carboxyl and acrylate owing to the existence of (-C=C-) in vegetable oils. Thus, it has provided appealing profits to vegetable oils compared to petroleum considered the toxicity, price and harm to the environment (Mustapha et al. 2019; Mohd Noor et al. 2020). Palm oil becomes the chosen in this study to produce PU owing to it is largely cultivated in South Asia particularly in Malaysia and Indonesia. It has several profits 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 CO_2 from the atmosphere as net sequester (Tajau et al. 2021; Septevani et al. 2015). Biopolymer, a natural biodegradable polymer has attracted much attention in recent years. Global environmental awareness and fossil fuel depletion urged researchers to work in the

biopolymer field (Priya et al. 2018). Polyurethane is one of the most common, versatile and researched materials in the world. These materials combine the durability and toughness of metals with the elasticity of rubber, making them suitable to replace metals, plastics and rubber in several engineered products. They have been widely applied in biomedical applications, building and construction applications, automotive, textiles and in several other industries due to their superior properties in terms of hardness, elongation, strength and modulus (Zia et al. 2014; Romaskevic et al. 2006). Polyurethanes are also considered to be one of the most useful materials with many profits such as, possess low conductivity, low density, absorption capability and dimensional stability. They are clearly a great research subject owing to their mechanical, physical and chemical properties (Badan & Majka 2017).

The urethane group is the major repeating unit in PUs and is produced from the reaction between alcohol (-OH) and isocyanate (NCO); albeit polyurethanes also contain other groups such as ethers, esters, urea and some aromatic compounds. Due to the wide variety of sources from which Pus can be synthesized, thus a wide range of specific applications can be generated. They are grouped into several different classes based on the desired properties: rigid, flexible, thermoplastic, waterborne, binders, coating, adhesives, sealants and elastomers (Akindoyo et al. 2016).

Although, PU has low conductivity, it is lighter than other materials such as metals. The hardness of PU also relies on the number of the aromatic rings in the polymer structure (Janpoung et al, 2020; Su'ait et al. 2014), majorly contributed by the isocyanate derivatives. PU has also a conjugate structure where electrons can move in the main chain that causing electricity produced even the conductivity is low. The electrical conductivity of conjugated linear (π) can be explained by the distance between the highest energy level containing

electrons (HOMO) called valence band and the lowest energy level not containing electrons (LUMO) called the conduction band (Wang et al. 2017; Kotal et al. 2011).

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 users and environment (Kilele et al. 2020). Therefore, is is imperative to obtain and develop an alternative material that can be used to analyse 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, the 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 recorded (Chokkareddy et al. 2020). Few works have been reported on the electrochemical methods for the determination of analyte using electrode combined with several electrode modifiers such as carbon nanotube, gold and graphene (Chokkareddy et al. 2020; Kilele et al. 2021). Nevertheless, the materials are costly and the modification procedures are not straightforward. Thus, an electrochemical approach using inexpensive and easily available materials as electrode modifiers should be developed (Degefu et al. 2014).

Nowadays, screen-printed electrodes (SPEs) modified with conducting polymer have been developed for various electrochemical sensing. SPE becomes the best solution owing to its frugal manufacture, tiny size, able to produce on large-scale and can be applied for on-site

detection (Nakthong et al. 2020). Conducting polymers (CPs) become an alternative to modifying the screen-printed electrodes due to their electrical conductivity, able to capture analyte by chemical/physical adsorption, large surface area and making CPs are very appealing materials from electrochemical perspectives (Baig et al. 2019). 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 screen-printed electrode modified by 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 conductivity of polyurethane using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) attached to screen-printed electrode (SPE). To the best of our knowledge, this is the first attempt to use a modified polyurethane electrode. The electrochemistry of polyurethane mounted onto screen-printed electrode (SPE) is discussed in detail. Polyurethane is possible to become an advanced frontier material is chemically modified electrodes for bio/chemical sensing application.

2. Experimental

2.1 Chemicals

Synthesis of polyurethane film: Palm kernel oil (PKOp) supplied by UKM Technology Sdn Bhd through MPOB/UKM station plant, Pekan Bangi Lama, Selangor and prepared using Badri et al. (2000) method. 4, 4-diphenylmethane diisocyanate (MDI) was acquired from Cosmopolyurethane (M) Sdn. Bhd., Klang, Malaysia. Solvents and analytical reagents were benzene (≥ 99.8%), toluene (≥ 99.8%), hexane (≥ 99%), acetone (≥ 99%), tetrahydrofuran (THF), dimethylformamide (DMF) (≥ 99.8%), dimethylsulfoxide (DMSO) (≥ 99.9%) and

polyethylene glycol (PED) 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 638 (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 Perkin Elmer Pyris model with a heating rate of 10 °C/minute at a temperature range of 30 to 800 °C under a nitrogen gas atmosphere. The DSC analysis was performed using a thermal analyzer of Perkin Elmer Pyris model with a heating rate of 10 °C /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 -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 changes 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 film 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 film was coated with a thin layer of gold to increase the conductivity of the film. The coating method was carried out using a sputter-coater. The

observations were conducted at a magnification of 200× and 5000 × 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 hours. 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 hours in order to get a constant mass. The percentage of crosslinking content known as the gel content can be calculated using Equation (1).

$$\text{Gel content } (\%) = \frac{W_o - W}{W} \text{ x } 100\ \% \qquad (1)$$

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 (DATR) method to confirm the polyurethane, PKOp and MDI functional group. FTIR spectroscopic analysis was performed at a wave number 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) and carbamate group (-CN).

2.3 Synthesis of Polyurethane

Palm kernel oil (PKO)p and polyethylene glycol (PEG) 400 (100:40 g/g) were combined and dissolved by acetone 30% in order to form a polyol prepolymer solution. The mixture was mixed using centrifuge with 100 rpm for 5 min to acquire a homogenized solution. Whereas, diisocyanate prepolymer was obtained by mixing 4,4'-diphenyl-methane diisocyanate (MDI) (100 g) to acetone 30%, afterward the mixture was mixed using centrifuge for 1 min to obtain

a homogenized solution. Then, 10 g of diisocyanate solution was poured into a container that containing 10 g of a polyol prepolymer solution slowly in order to avoid an exothermic reaction occur. The mixture was mixed for 30 sec until a homogenized solution acquired. Lastly, the polyurethane solution was poured on the electrode surface by using casting method and dried at ambient temperature for 12 hours.

2.4 Modification of Electrode

Voltammetric tests were performed using Metrohm Autolab Software (**Figure 1**) analyzer using cyclic voltammetry (CV) method or known as amperometric mode and differential pulse voltammetry (DPV). All electrochemical experiments were carried out using screen-printed electrode (diameter 3 mm) modified using polyurethane film as working electrode, platinum wire as auxiliary electrode and Ag/AgCl electrode as a reference electrode. All experiments were conducted at a temperature of $20 \pm 2^{o}C$.

The PU was cast onto the screen – printed electrode (SPE + PU) 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 & 0.5) mg of palm-based prepolyurethane was dropped separately onto the surface of the SPE 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 screen-printed electrode that had been modified with polyurethane was applied as a working electrode.

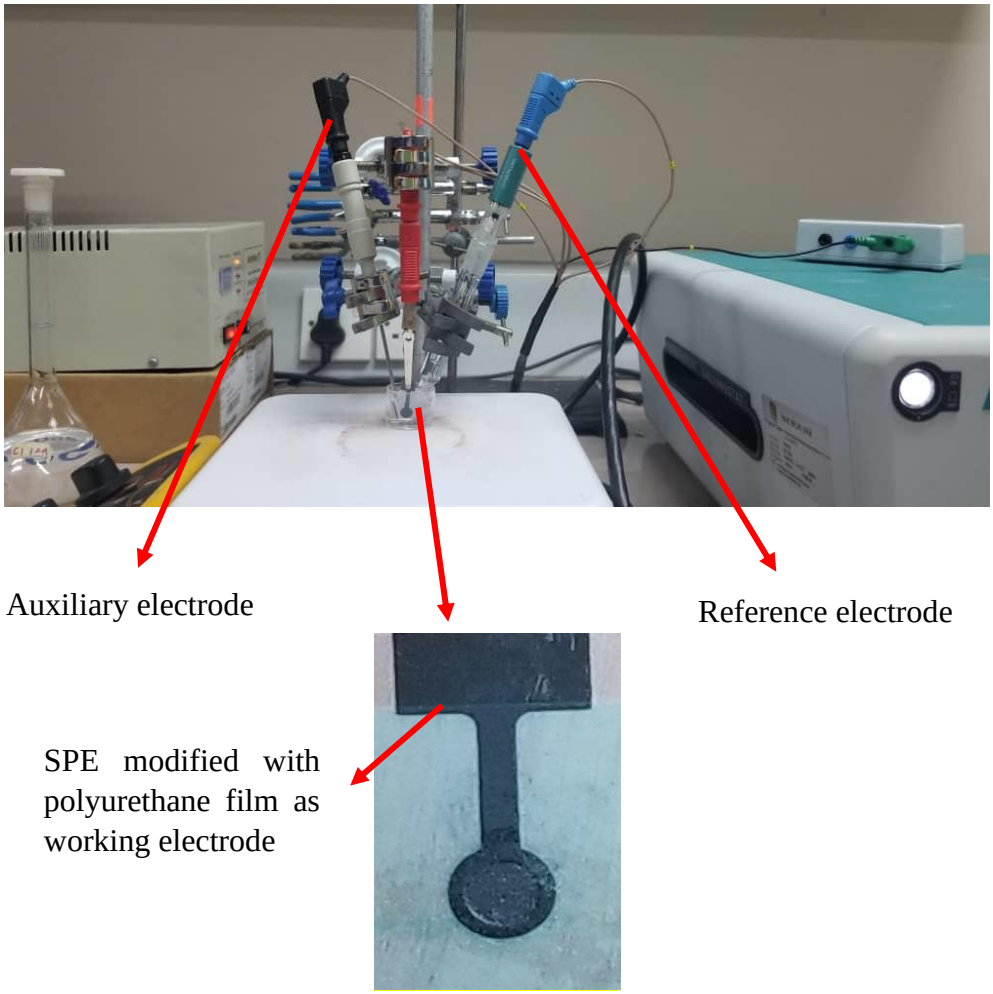


Figure 1. Potentiostat instrument to study the conductivity of SPE modified with polyurethane film using cyclic voltammetry (CV) and differential pulse voltammetry (DPV)

3. Results and Discussion

The synthesis of PU films was carried out using pre-polymerization method which involves the formation of urethane polymer at an early stage. The reaction took place between palm kernel oil-based polyol (PKOp) and diisocyanate (MDI). **Table 1** presents the PKO-p properties used in this study. The structural chain was extended with the aid of polyethylene glycol (PEG) to form flexible and elastic polyurethane film. In order to form the urethane prepolymer, one of the isocyanate groups (NCO) reacts with one hydroxyl group (OH) of polyol while the other isocyanate group attacks another hydroxyl group in the polyol (Wong & Badri 2012) as shown in **Figure 2**.

Table 1 The specification of PKO-p (Badri et al. (2000)).

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

a. FTIR analysis

Figure 3 shows the FTIR spectrum for polyurethane, exhibiting the important functional group peaks. According to a study researched by Wong & Badri 2012, PKO-p reacts with MDI to form urethane prepolymers. The NCO group on MDI reacts with the OH group on polyol whether PKOp or PEG. It can be seen there are no important peaks of MDI in the FTIR spectrums. This is further verified by the absence of peak at the 2400 cm^{-1} belongs 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 reacted with the carbonyl urethane group.

The reaction of polyurethane has been studied by Hamuzan & Badri (2016) 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 peaks at 2250 – 2270 cm^{-1} indicates the absence of NCO groups. It shows

257 that the polymerization reaction occurs entirely between NCO groups in MDI with hydroxyl
258 groups on polyols and PEG (Mishra et al. 2012). The absence of peaks at 1690 cm^{-1}
259 representing urea (C = O) in this study indicated, there is no urea formation as a byproduct
260 (Clemitson 2008) of the polymerization reaction that possibly occurs due to the excessive
261 water. For the amine (NH) group, hydrogen-bond to NH and oxygen to form ether and
262 hydrogen bond to NH and oxygen to form carbonyl on urethane can be detected at the peak of
263 3301 cm^{-1} and in the wavenumber at range 3326 – 3428 cm^{-1}. This has also been studied and
264 detected by Lampman et. al. (2010) and Mutsuhisa et al. (2007). In this study, the hydrogen
265 bond formed by C = O acts as a proton acceptor whereas NH acts as a proton donor. The
266 urethane group in the hard segment (MDI) has electrostatic forces on the oxygen, hydrogen
267 and nitrogen atoms and these charged atoms form dipoles that attract other opposite atoms.
268 These properties make isocyanates are highly reactive and having different properties (Leykin
269 et al. 2016).
270
271 MDI was one of the isocyanates used in this study, has an aromatic group and is more
272 reactive compared to aliphatic group isocyanates such as hexamethylene diisocyanate (HDI)
273 or isophorone diisocyanate (IPDI). Isocyanates have two groups of isocyanates on each
274 molecule. Diphenylmethane diisocyanate is an exception owing to its structure consists of two,
275 three, four or more isocyanate groups (Nohra et al. 2013). The use of PEG 400 in this study as
276 a chain extender for polyurethane increases the chain mobility of polyurethane at an optimal
277 amount. The properties of a polyurethane are contributed by hard and soft copolymer segments
278 of both polyol monomers and MDI. This makes the hard segment of urethane serves as a
279 crosslinking site between the soft segments of the polyol (Leykin et al. 2016).
280

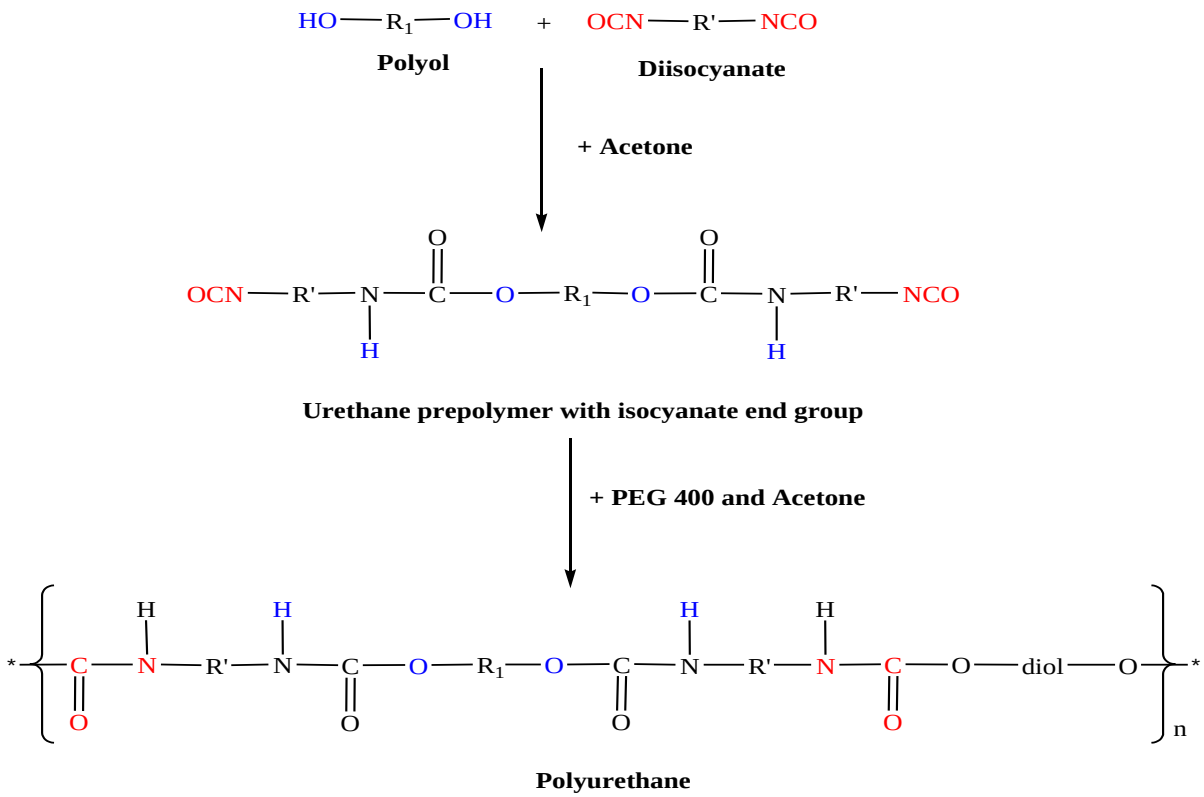
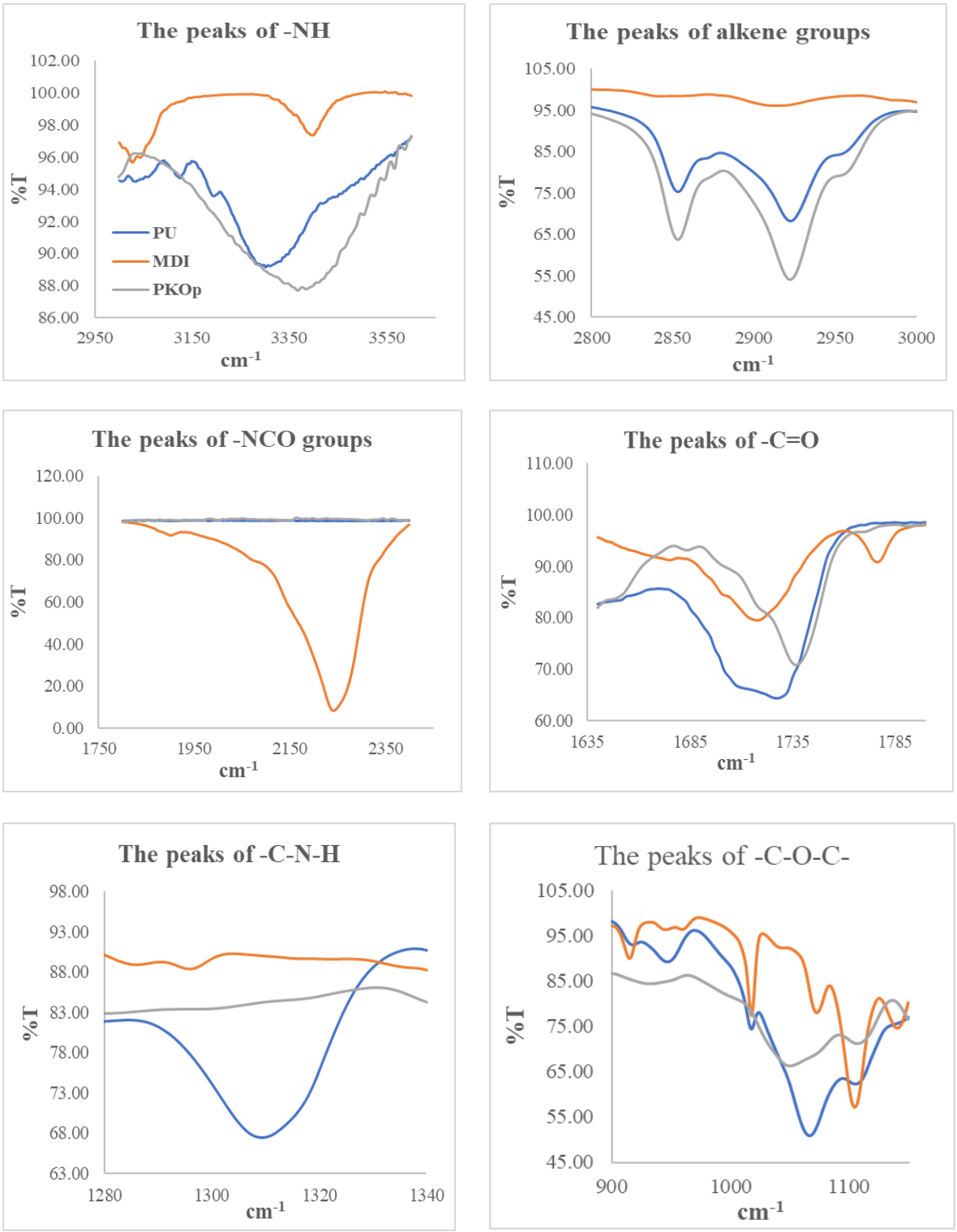


Figure 2. The chemical route of producing polyurethane via pre-polymerization method (Wong & Badri 2012).

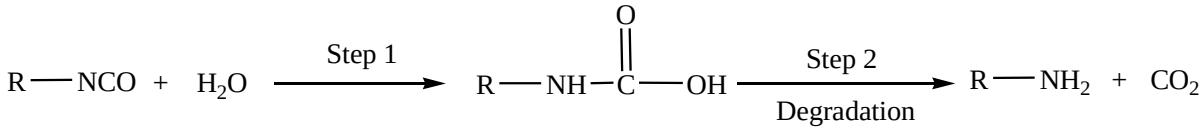
The mechanism of the pre-polymerization in urethane chains formation is a nucleophilic substitution reaction as studied by Yong et al. (2009). However, this study found amines as nucleophiles. Amine attacks carbonyl on isocyanate in MDI in order to form two resonance structures of intermediate complexes A and B. 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 who have conducted by Wong and Badri (2012). Moreover, nitrogen was more electropositive than oxygen, therefore, -CN bonds were more attracted to cations (H+) than -CO. The combination between long polymer chain and low cross-linking content gives the polymer elastic properties whereas short chain and high cross linking producing hard and rigid polymers. Cross-linking in polymers consists of three-

296 dimensional networks with high molecular weight. In some aspects, polyurethane can be a
297 macromolecule, a giant molecule (Petrovic 2008).
298



299 **Figure 3.** FTIR spectrums of several important peaks between polyurethane, PKO-p and MDI

300 However, the reaction between MDI and PEG as a chain extender where oxygen on the
301 nucleophile PEG attacks the NCO group in the MDI to form two intermediate complexes A
302 and B can occur. Nevertheless, nucleophilic substitution reactions have a greater tendency to
303 occur in PKOp compared to PEG because the presence of nitrogen atoms is more
304 electropositive than oxygen atoms in PEG. Amine has a higher probability of reacting
305 compared to hydroxyl (Herrington & Hock 1997). Amine with high alkalinity reacts with
306 carbon atoms on MDI as proposed by Wong and Badri (2012). PKOp contains long carbon
307 chains that can easily stabilize alkyl ions when intermediate complexes are formed. Therefore,
308 the polyol is more reactive than PEG to react with MDI. However, the addition of PEG will
309 increase the length of the polyurethane chain and prevent side effects such as the formation of
310 urea by-products of the NCO group reaction in urethane pre-polymer and water molecules from
311 the environment. If the NCO group reacts with the excess water in the environment, the
312 formation of urea and carbon dioxide gas will also occur excessively (**Figure 4**). This reaction
313 can cause a polyurethane foam, not polyurethane film as we studied the film.



314

315 **Figure 4**. The reaction between NCO group and water producing carbon dioxide

316

317 Furthermore, the application of PEG can influence the conductivity of PU where
318 Porcarelli et al. (2017) have reported the application of PEG using several molecular weights.
319 PEG 1500 decreased the conductivity of PU in consequence of the semicrystalline phase of
320 PEG 1500 that acted as a poor ion conducting phase for PU. It is also well known that PEG
321 with a molecular weight of more than 1000 $g \cdot mol^{-1}$ tends to crystallize with deleterious effects
322 on room temperature ionic conductivity (Porcarelli et al. 2017).

323

b. Morphological analysis

The Field Emission Scanning Electron Microscope (FESEM) micrograph in **Figure 5** shows the formation of a uniform polymer film contributed by the polymerization method applied. The magnification used for this surface analysis ranged from 200 to 5000 ×. 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 justified by the wavelengths obtained by the FTIR spectrums above.

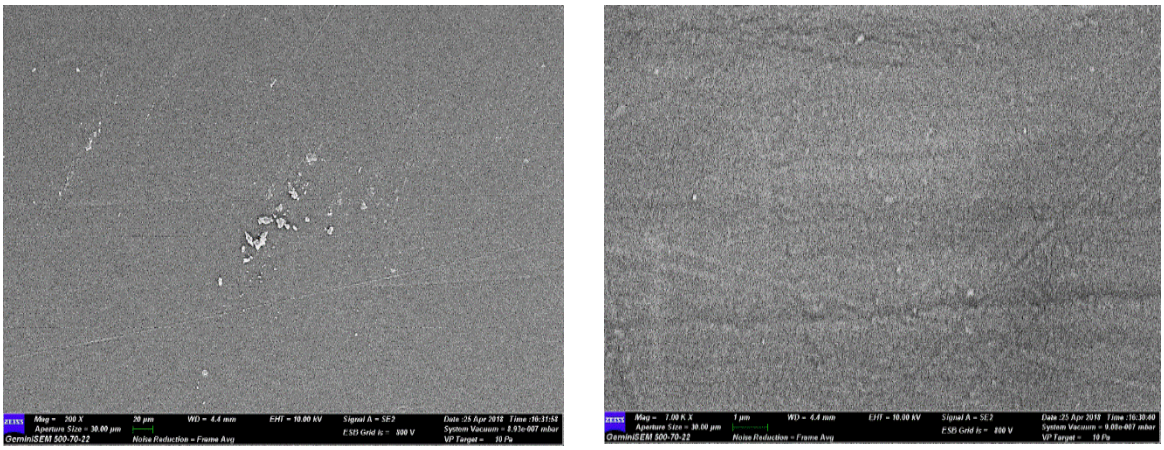


Figure 5. The micrograph of polyurethane films analysed by FESEM at (a) 200 × and (b) 5000× magnifications.

c. 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 (Cuve & Pascault 1991). 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 indicating a 99.3 % gel content. This is significant in getting a stable polymer at higher working temperature (Rogulska et al. 2007).

$$\text{Gel content (\%)} = \frac{(0.6 - 0.301)\ \text{g}}{0.301\ \text{g}} \times 100\% = 99.33\%$$

d. The thermal analysis

Thermogravimetric analysis (TGA) can be used to observe the material mass based on temperature shift. It can also examine and estimate the thermal stability and materials properties such as the alteration weight owing to absorption or desorption, decomposition, reduction and oxidation. The material composition of polymer is specified by analysing the temperatures and the heights of the individual mass steps (Alamawi et al. 2019). **Figure 6** shows the TGA and 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 6** in the region of 45 – 180ºC. This is due to the presence of condensation on moisture and solvent residues.

Table2 Weight loss percentage of (wt%) polyurethane film

Sample	% Weight loss (wt%)				Total of weight loss (%)	Residue after 550ºC (%)
	$T_{max,}$ ºC	T_{d1}, 200 – 290ºC	T_{d2}, 350 – 500ºC	T_{d3}, 500 – 550ºC		
Polyurethane	240	8.04	39.29	34.37	81.7	18.3

The bio polyurethane is thermally stable up to 240 °C before it has undergone thermal degradation (Agrawal et al. 2017). The first stage of thermal degradation (T_{d1}) on polyurethane films was shown in the region of 200 – 290 ºC as shown in **Figure 6**. The T_{d1} is associated with degradation of the hard segments of the urethane bond, forming alcohol or degradation of the polyol chains and releasing of isocyanates (Berta et al. 2006), primary and secondary amines as well as carbon dioxide (Corcuera et al. 2011; Pan & Webster 2012). Meanwhile, the 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 dimmerization of isocyanates to form carbodiimides and release CO_2. The formed carbodiimide reacts with alcohol to form urea. The third stage of thermal degradation (T_{d3}) is related to the degradation of urea (Berta et al. 2006) and the soft segment on polyurethane.

Generally, DSC analysis exhibited thermal transitions as well as the initial crystallisation and melting temperatures of the polyurethane (Khairuddin et al. 2018). It serves to analyse changes in thermal behavior due to changes occurring in the chemical chain structure based on the glass transition temperature (T_g) of the sample obtained from the DSC thermogram (**Figure 7**). DSC analysis on polyurethane film was performed in the temperature at the range 100 ^oC to 200 ^oC using nitrogen gas as a blanket as proposed by Furtwengler et al. (2017). The glass transition temperature (T_g) on polyurethane was above room temperature, at 78.1 ^oC indicated the state of glass on polyurethane. The presence of MDI contributes to the formation of hard segments in polyurethanes. Porcarelli et al. (2017) stated that possess a low glass transition (T_g) may contribute to PU conductivity.

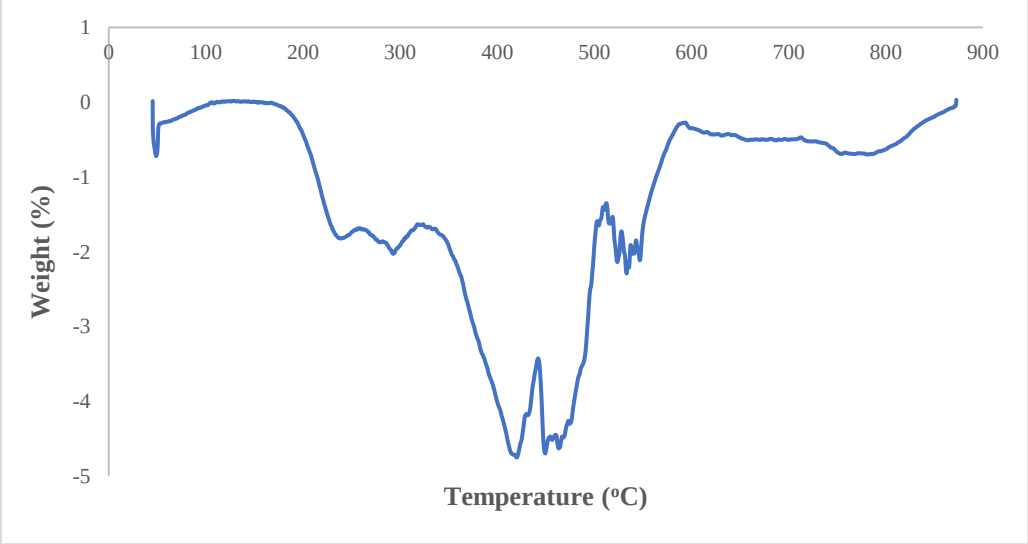


Figure 6. DTG thermogram of polyurethane film

During polymerization, this hard segment restricts the mobility of the polymer chain (Ren et al. 2013) 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 56ºC. However, it was detected in the DSC thermogram nor the TGA thermogram, which indicates that acetone was removed from the polyurethane during the synthesis process, owing to its volatility nature. The presence of acetone in the synthesis was to lower the reaction kinetics.

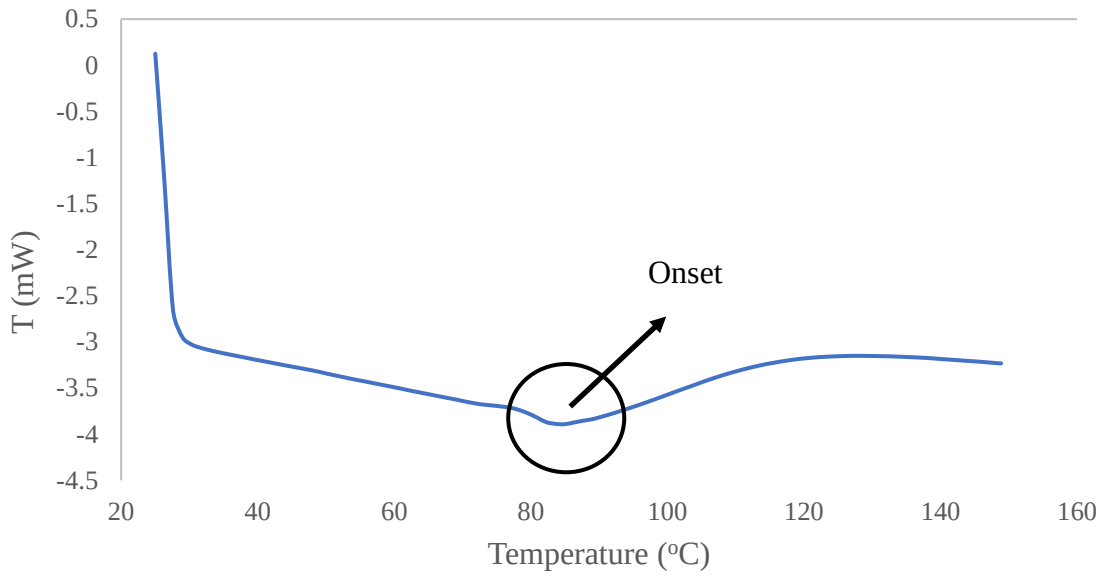


Figure 7. DSC thermogram of polyurethane film

e. 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, tetrahydrofuran (THF), dimethylformamide (DMF) and dimethylformamide (DMSO). On the other hand, the mechanical properties of polyurethane were determined based on the standard testing following ASTM D 638 (Standard Test Method for Tensile Properties of Plastics). The results from the polyurethane film solubility and tensile test are shown in **Table 3**. Polyurethane films were insoluble with

benzene, hexane and acetone and are only slightly soluble in tetrahydrofuran (THF), dimethylformamide (DMF) and dimethylformamide (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.

Table 3 The solubility and mechanical properties of the polyurethane film

Parameters		Polyurethane film
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

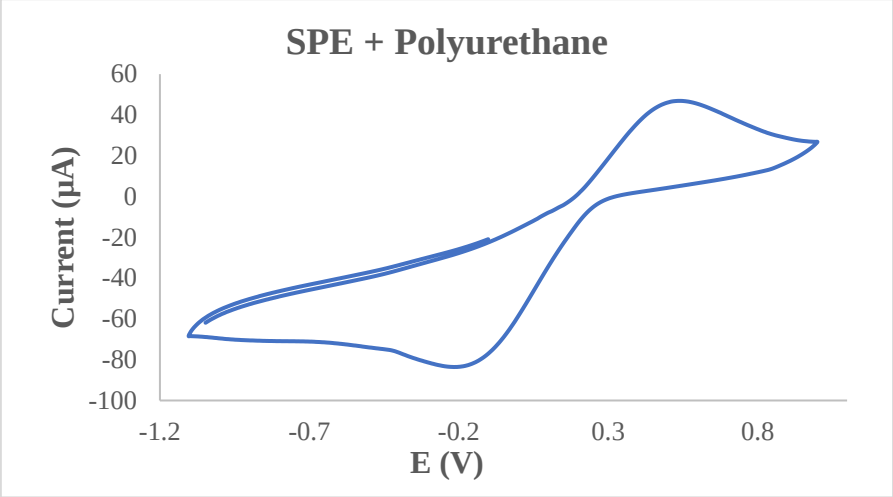
The tensile stress, strain and modulus of polyurethane film also indicated that polyurethane has good mechanical properties that are capable of being a supporting substrate for the next stage of study. In the production of polyurethane, the properties of a polyurethane are easily influenced by the content 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.

f. The conductivity of the polyurethane as a polymeric film on SPE

Polyurethane film deposited onto the screen-printed electrode by casting method as shown in **Figure 1**. After that, the modified electrode was analysed using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in order to study the behaviour of modified electrode. The modified electrode was tested in a 0.1 mmol/L KCl solution containing 5 mmol/L ($K_3Fe(CN)_6$). 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. The voltammograms at 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 is a natural polymer produced from the polyol of palm kernel oil. The electrochemical signal at the electrode is low if there is a decrease in electrochemical conductivity (El - Raheem et al. 2020). It can be concluded that polyurethane is a bio-polymer with a low conductivity value. The current of the modified electrode was found at 5.3×10^{-5} A or 53 µA. Nevertheless, the electroconductivity of PU in this study shows better conductivity several times compared to Bahrami et al. (2019) that reported the conductivity of PU as 1.26×10^{-6} A, whereas Li et al. (2019) reported the PU conductivity in their study was even very low, namely 10^{-14} A. The conductivity of PU owing to the benzene ring in the hard segment (MDI) could exhibit the conductivity by inducing electron delocalization along the polyurethane chain (Wong et al. 2014). The conductivity of PU can also be caused by PEG. The application of PEG as polyol has been studied by Porcarelli et al. (2017), that reported that the conductivity of PU based on PEG – polyol was 9.2×10^{-8}.

441 According to **Figure 8**, it can be concluded that the anodic peak present in the modifed
442 electrode was at +0.5 V, it also represented the oxidation process of the modified electrode.
443 The first oxidation scan on both electrodes ranged from -0.2 to +1.0 V, which showed a
444 significant anodic peak at a potential of +0.5 V.
445



446
447 **Figure 8**. The voltammogram of SPE – PU modified electrode after analysed using cyclic
448 voltammetry (CV) technique
449
450 **Figure 9** also presents the DPV voltammogram of modified electrode. DPV is a measurement
451 based on the difference in potential pulses that produce an electric current. Scanning the
452 capability pulses to the working electrode will produce different currents. Optimal peak
453 currents will be produced to the reduction capacity of the redox material. The peak current
454 produced is proportional to the concentration of the redox substance and can be detected up to
455 concentration below 10^{-8} M. DPV was conducted to obtain the current value that more accurate
456 than CV (Lee et al. 2018).
457
458 This study used a redox pair ($K_3Fe(CN)_6$) as a test device (probe). The currents generated by
459 SPE-PU and proved by CV and DPV have shown conductivity on polyurethane films. This
460 suggests that polyurethane films can conduct electron transfer. The electrochemical area on the

modified electrode can be calculated using the formula from Randles-Sevcik (Butwong et al. 2019), where the electrochemical area for SPE-PU is considered to be A, using Equation 2:

$$\textbf{Current of SPE-PU , } I_p = 2.65 \times 10^5\, n^{3/2}\, Av^{1/2}\, CD^{1/2} \qquad (2)$$

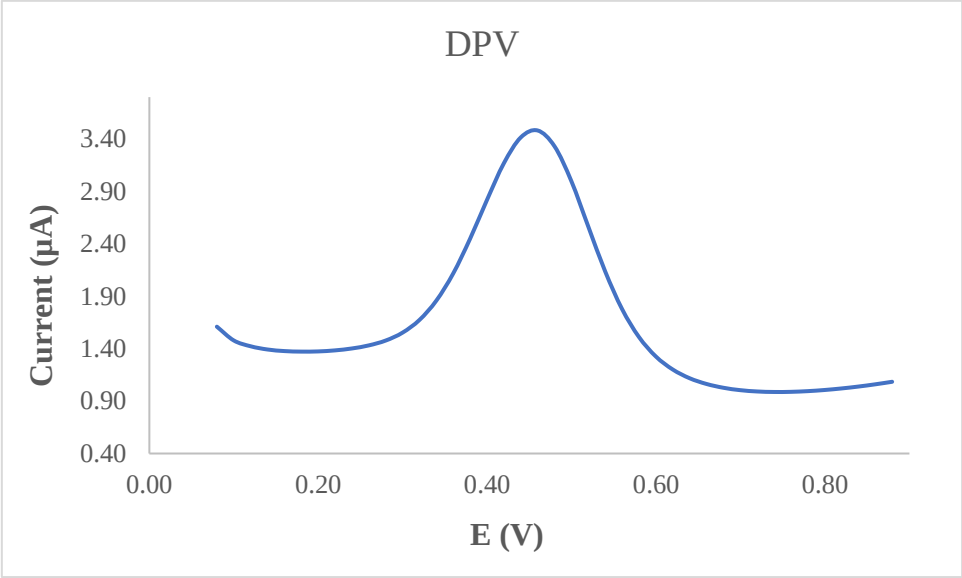


Figure 9. The voltammogram of SPE – PU modified electrode after analyzed using differential pulse voltammetry (DPV) technique

Where, n – 1 is the amount of electron transfer involved, while C is the solvent concentration used (mmol/L) and the value of D is the diffusion constant of 5 mmol/L at ($K_3Fe(CN)_6$) dissolved using 0.1 mmol/L KCl. The estimated surface area of the electrode (**Figure 1**) was 0.2 cm^2 where the length and width of the electrode used during the study was 0.44 cm × 0.44 cm while the surface area of the modified electrode was 0.25 cm^2 with the length and width of the electrode estimated at 0.5 cm × 0.5 cm, and causing the modified electrode has a larger surface. The corresponding surface concentration (τ) (mol/cm^2) is calculated using Equation 3.

$$\mathbf{I_p = (n^2\, F^2 / 4RT)\, A\tau v} \qquad (3)$$

I_p is the peak current (A), while A is the surface area 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 constant ideal gas (8.314 J/mol K) and T is the temperature used during the experiment being conducted

(298 K) (Koita et al. 2014). The development of conducting polymer from palm oil-based biomaterials seems to be one of the potential future applications of palm oil products, as this novel material has the potential to contribute positively to the analytical industry. Likewise, other palm oil-based products, such as refined-bleached-deodorised (RBD) palm oil, palm oil, and palm stearin are abundantly available in Malaysia. They are known to be economical, sustainable, and environmentally biodegradable. These palm oil-based products are promising prospects for manufacturing biomaterials that become alternative products to other polymers from synthetic/chemical-based (Tajao et al. 2021). Several studies have been reported the application of PU to produce elastic conductive fibres and films owing to it is highly elastic, scratch resistant and adhesive (Tadese et al. 2019), thus it is easy for PU to adhere on the screen-printed electrode in order to modify the electrode. PU is also being used as a composite material to make elastic conducting composite films (Khatoon & Ahmad 2017).

4. Conclusion

Polyurethane film was prepared by pre-polymerization between palm kernel oil-based polyol (PKO-p) with MDI. The presence of PEG 400 as the chain extender formed freestanding flexible film. Acetone was used as the solvent to lower the reaction kinetics since the pre-polymerization was carried out at room temperature. The formation of urethane links (NHCO – backbone) after polymerization was confirmed by the absence of N=C=O peak at 2241 cm^{-1} 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 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 modified electrode was found at 5.2×10^{-5} A. This bio polyurethane film can be used as a conducting bio-polymer 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.

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6. Conflict of Interest

The authors declare no conflict of interest.

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The reviewers have raised points that were not fully taken into consideration and revision of the manuscript before it is suitable for publication is still required.
The journal should follow certain standards, such as compliance with general recommendations (IUPAC, SI, manual for authors), so please review and correct manuscript again.
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Design and Synthesis of Conducting Polymer Based on Polyurethane produced from Palm Kernel Oil

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Abstract

Polyurethane (PU) is a unique polymer that has versatile processing methods and mechanical properties upon inclusion of selected additives. In this study, a freestanding bio-polyurethane film on 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 (PKOp) and 4,4-methylene diisocyanate. The PU has strong adhesion on SPE surface. The synthesized polyurethane was characterized using thermogravimetry analysis (TGA), differential scanning calorimetry (DSC), Fourier – transform infrared spectroscopy (FTIR), surface area analysis by field emission scanning electron microscope (FESEM) and

cyclic voltammetry (CV). Cyclic voltammetry was employed to study electro-catalytic 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 (DPV) method. Furthermore, the formation of urethane linkages (NHCO backbone) after polymerization was analysed using FTIR and confirmed by the absence of N=C=O peak at 2241 cm^{-1}. The glass transition temperature (T_g) of the polyurethane was detected at 78.1^oC.

Keywords: Polyurethane, polymerization, screen-printed electrode, voltammetry

1. Introduction

Polymers are molecules composed of many repeated sub-units referred to as monomers (Sengodu & Deshmukh 2015). Conducting polymers (CPs) are polymers that exhibit electrical behavior (Alqarni et al. 2020). The conductivity of CPs was first observed in polyacetylene, nevertheless owing to its instability led to the discovery of other forms of CPs such as polyaniline (PANI), poly (o-toluidine) (PoT), polythiophene (PTh), polyfluorene (PF) and polyurethane (PU). Furthermore, natural CPs have low conductivity and are often semi-conductive. Therefore, it is essential to increase their conductivity mainly for use in electrochemical sensor programs (Dzulkipli et al. 2021; Wang et al. 2018). Conducting polymers (CPs) represent a sizeable range of useful organic substances. Their unique electrical, chemical and physical properties; reasonable price; simple preparation; small dimensions and large surface area have enabled researchers to discover a wide variety of uses such as sensors, biochemical applications, solar cells and electrochromic devices (Alqarni et al. 2020; Ghosh et al. 2018). There are scientific documentation on the use of conductive polymers in various

studies such as polyaniline (Pan & Yu 2016), polypyrrole (Ladan et al. 2017) and polyurethane (Tran et al. 2020; Vieira et al. 2020; Guo et al. 2020; Fei et al. 2020).

The application of petroleum as polyol in order to produce polyurethane has been applied. Coal and crude oil were used as raw materials to produce it. 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. These reasons have been considered and finding utilizing plants that can be used as alternative polyols should be done immediately (Badri 2012). Furthermore, in order to avoid the application of petroleum as raw material for a polyol, vegetable oils become a better choice as polyol in order to obtain a biodegradable polyol. Vegetable oils that are generally used for synthesis polyurethane are soybean oil, corn oil, sunflower seed oil, coconut oil, nuts oil, rapeseed, olive oil and palm oil (Badri 2012; Borowicz et al. 2019).

It is very straightforward for vegetable oils to react with a specific group in order to form PU such as epoxy, hydroxyl, carboxyl and acrylate owing to the existence of (-C=C-) in vegetable oils. Thus, it has provided appealing profits to vegetable oils compared to petroleum considered the toxicity, price and harm to the environment (Mustapha et al. 2019; Mohd Noor et al. 2020). Palm oil becomes the chosen in this study to produce PU owing to it is largely cultivated in South Asia particularly in Malaysia and Indonesia. It has several profits 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 CO_2 from the atmosphere as net sequester (Tajau et al. 2021; Septevani et al. 2015). Biopolymer, a natural biodegradable polymer has attracted much attention in recent years. Global environmental awareness and fossil fuel depletion urged researchers to work in the

biopolymer field (Priya et al. 2018). Polyurethane is one of the most common, versatile and researched materials in the world. These materials combine the durability and toughness of metals with the elasticity of rubber, making them suitable to replace metals, plastics and rubber in several engineered products. They have been widely applied in biomedical applications, building and construction applications, automotive, textiles and in several other industries due to their superior properties in terms of hardness, elongation, strength and modulus (Zia et al. 2014; Romaskevic et al. 2006). Polyurethanes are also considered to be one of the most useful materials with many profits such as, possess low conductivity, low density, absorption capability and dimensional stability. They are clearly a great research subject owing to their mechanical, physical and chemical properties (Badan & Majka 2017).

The urethane group is the major repeating unit in PUs and is produced from the reaction between alcohol (-OH) and isocyanate (NCO); albeit polyurethanes also contain other groups such as ethers, esters, urea and some aromatic compounds. Due to the wide variety of sources from which Pus can be synthesized, thus a wide range of specific applications can be generated. They are grouped into several different classes based on the desired properties: rigid, flexible, thermoplastic, waterborne, binders, coating, adhesives, sealants and elastomers (Akindoyo et al. 2016).

Although, PU has low conductivity, it is lighter than other materials such as metals. The hardness of PU also relies on the number of the aromatic rings in the polymer structure (Janpoung et al, 2020; Su'ait et al. 2014), majorly contributed by the isocyanate derivatives. PU has also a conjugate structure where electrons can move in the main chain that causing electricity produced even the conductivity is low. The electrical conductivity of conjugated linear (π) can be explained by the distance between the highest energy level containing

electrons (HOMO) called valence band and the lowest energy level not containing electrons (LUMO) called the conduction band (Wang et al. 2017; Kotal et al. 2011).

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 users and environment (Kilele et al. 2020). Therefore, is is imperative to obtain and develop an alternative material that can be used to analyse 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, the 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 recorded (Chokkareddy et al. 2020). Few works have been reported on the electrochemical methods for the determination of analyte using electrode combined with several electrode modifiers such as carbon nanotube, gold and graphene (Chokkareddy et al. 2020; Kilele et al. 2021). Nevertheless, the materials are costly and the modification procedures are not straightforward. Thus, an electrochemical approach using inexpensive and easily available materials as electrode modifiers should be developed (Degefu et al. 2014).

Nowadays, screen-printed electrodes (SPEs) modified with conducting polymer have been developed for various electrochemical sensing. SPE becomes the best solution owing to its frugal manufacture, tiny size, able to produce on large-scale and can be applied for on-site

detection (Nakthong et al. 2020). Conducting polymers (CPs) become an alternative to modifying the screen-printed electrodes due to their electrical conductivity, able to capture analyte by chemical/physical adsorption, large surface area and making CPs are very appealing materials from electrochemical perspectives (Baig et al. 2019). 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 screen-printed electrode modified by 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 conductivity of polyurethane using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) attached to screen-printed electrode (SPE). To the best of our knowledge, this is the first attempt to use a modified polyurethane electrode. The electrochemistry of polyurethane mounted onto screen-printed electrode (SPE) is discussed in detail. Polyurethane is possible to become an advanced frontier material is chemically modified electrodes for bio/chemical sensing application.

2. Experimental

2.1 Chemicals

Synthesis of polyurethane film: Palm kernel oil (PKOp) supplied by UKM Technology Sdn Bhd through MPOB/UKM station plant, Pekan Bangi Lama, Selangor and prepared using Badri et al. (2000) method. 4, 4-diphenylmethane diisocyanate (MDI) was acquired from Cosmopolyurethane (M) Sdn. Bhd., Klang, Malaysia. Solvents and analytical reagents were benzene (≥ 99.8%), toluene (≥ 99.8%), hexane (≥ 99%), acetone (≥ 99%), tetrahydrofuran (THF), dimethylformamide (DMF) (≥ 99.8%), dimethylsulfoxide (DMSO) (≥ 99.9%) and

polyethylene glycol (PED) 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 638 (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 Perkin Elmer Pyris model with a heating rate of 10 °C/minute at a temperature range of 30 to 800 °C under a nitrogen gas atmosphere. The DSC analysis was performed using a thermal analyzer of Perkin Elmer Pyris model with a heating rate of 10 °C /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 -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 changes 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 film 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 film was coated with a thin layer of gold to increase the conductivity of the film. The coating method was carried out using a sputter-coater. The

observations were conducted at a magnification of 200× and 5000 × 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 hours. 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 hours in order to get a constant mass. The percentage of crosslinking content known as the gel content can be calculated using Equation (1).

$$\text{Gel content } (\%) = \frac{W_o - W}{W} \text{ x } 100\ \% \qquad (1)$$

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 (DATR) method to confirm the polyurethane, PKOp and MDI functional group. FTIR spectroscopic analysis was performed at a wave number 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) and carbamate group (-CN).

2.3 Synthesis of Polyurethane

Palm kernel oil (PKO)p and polyethylene glycol (PEG) 400 (100:40 g/g) were combined and dissolved by acetone 30% in order to form a polyol prepolymer solution. The mixture was mixed using centrifuge with 100 rpm for 5 min to acquire a homogenized solution. Whereas, diisocyanate prepolymer was obtained by mixing 4,4'-diphenyl-methane diisocyanate (MDI) (100 g) to acetone 30%, afterward the mixture was mixed using centrifuge for 1 min to obtain

a homogenized solution. Then, 10 g of diisocyanate solution was poured into a container that containing 10 g of a polyol prepolymer solution slowly in order to avoid an exothermic reaction occur. The mixture was mixed for 30 sec until a homogenized solution acquired. Lastly, the polyurethane solution was poured on the electrode surface by using casting method and dried at ambient temperature for 12 hours.

2.4 Modification of Electrode

Voltammetric tests were performed using Metrohm Autolab Software (**Figure 1**) analyzer using cyclic voltammetry (CV) method or known as amperometric mode and differential pulse voltammetry (DPV). All electrochemical experiments were carried out using screen-printed electrode (diameter 3 mm) modified using polyurethane film as working electrode, platinum wire as auxiliary electrode and Ag/AgCl electrode as a reference electrode. All experiments were conducted at a temperature of $20 \pm 2^{o}C$.

The PU was cast onto the screen – printed electrode (SPE + PU) 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 & 0.5) mg of palm-based prepolyurethane was dropped separately onto the surface of the SPE 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 screen-printed electrode that had been modified with polyurethane was applied as a working electrode.

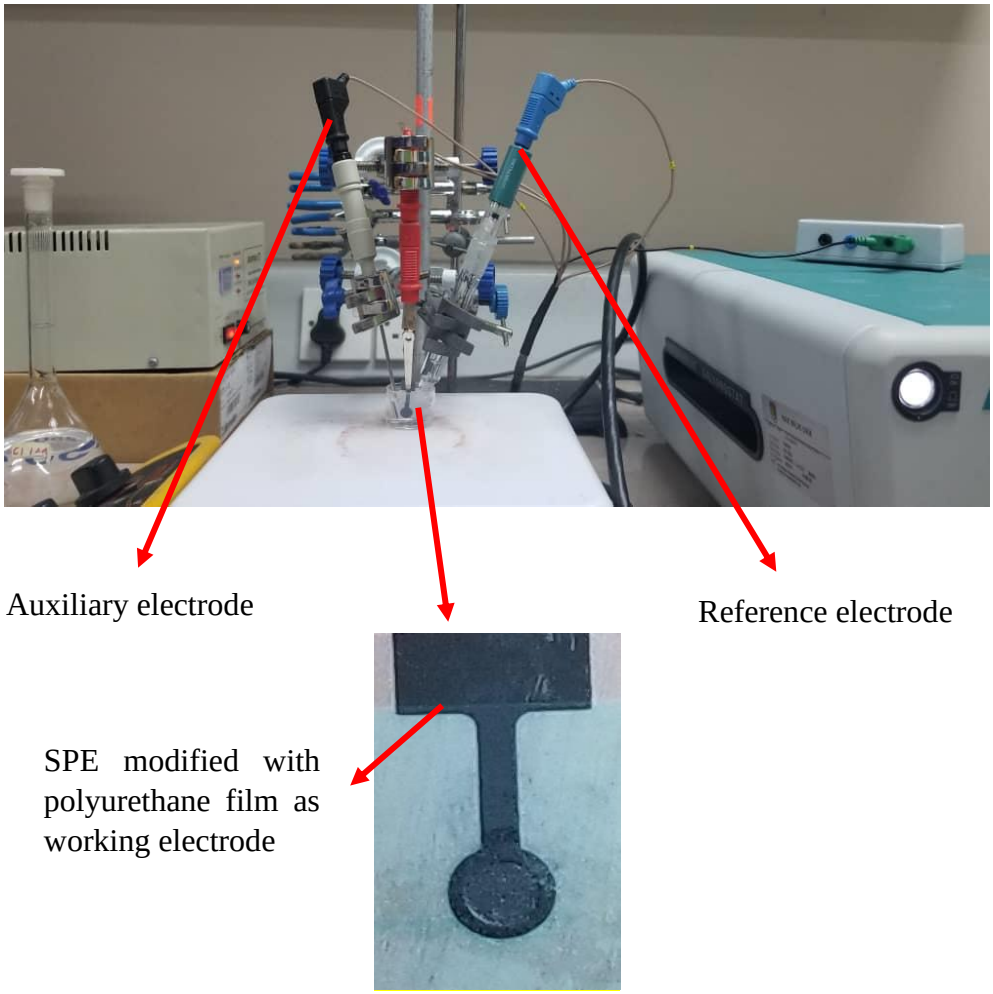


Figure 1. Potentiostat instrument to study the conductivity of SPE modified with polyurethane film using cyclic voltammetry (CV) and differential pulse voltammetry (DPV)

3. Results and Discussion

The synthesis of PU films was carried out using pre-polymerization method which involves the formation of urethane polymer at an early stage. The reaction took place between palm kernel oil-based polyol (PKOp) and diisocyanate (MDI). **Table 1** presents the PKO-p properties used in this study. The structural chain was extended with the aid of polyethylene glycol (PEG) to form flexible and elastic polyurethane film. In order to form the urethane prepolymer, one of the isocyanate groups (NCO) reacts with one hydroxyl group (OH) of polyol while the other isocyanate group attacks another hydroxyl group in the polyol (Wong & Badri 2012) as shown in **Figure 2**.

Table 1 The specification of PKO-p (Badri et al. (2000)).

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

a. FTIR analysis

Figure 3 shows the FTIR spectrum for polyurethane, exhibiting the important functional group peaks. According to a study researched by Wong & Badri 2012, PKO-p reacts with MDI to form urethane prepolymers. The NCO group on MDI reacts with the OH group on polyol whether PKOp or PEG. It can be seen there are no important peaks of MDI in the FTIR spectrums. This is further verified by the absence of peak at the 2400 cm^{-1} belongs 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 reacted with the carbonyl urethane group.

The reaction of polyurethane has been studied by Hamuzan & Badri (2016) 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 peaks at 2250 – 2270 cm^{-1} indicates the absence of NCO groups. It shows

257 that the polymerization reaction occurs entirely between NCO groups in MDI with hydroxyl
258 groups on polyols and PEG (Mishra et al. 2012). The absence of peaks at 1690 cm^{-1}
259 representing urea (C = O) in this study indicated, there is no urea formation as a byproduct
260 (Clemitson 2008) of the polymerization reaction that possibly occurs due to the excessive
261 water. For the amine (NH) group, hydrogen-bond to NH and oxygen to form ether and
262 hydrogen bond to NH and oxygen to form carbonyl on urethane can be detected at the peak of
263 3301 cm^{-1} and in the wavenumber at range 3326 – 3428 cm^{-1}. This has also been studied and
264 detected by Lampman et. al. (2010) and Mutsuhisa et al. (2007). In this study, the hydrogen
265 bond formed by C = O acts as a proton acceptor whereas NH acts as a proton donor. The
266 urethane group in the hard segment (MDI) has electrostatic forces on the oxygen, hydrogen
267 and nitrogen atoms and these charged atoms form dipoles that attract other opposite atoms.
268 These properties make isocyanates are highly reactive and having different properties (Leykin
269 et al. 2016).
270
271 MDI was one of the isocyanates used in this study, has an aromatic group and is more
272 reactive compared to aliphatic group isocyanates such as hexamethylene diisocyanate (HDI)
273 or isophorone diisocyanate (IPDI). Isocyanates have two groups of isocyanates on each
274 molecule. Diphenylmethane diisocyanate is an exception owing to its structure consists of two,
275 three, four or more isocyanate groups (Nohra et al. 2013). The use of PEG 400 in this study as
276 a chain extender for polyurethane increases the chain mobility of polyurethane at an optimal
277 amount. The properties of a polyurethane are contributed by hard and soft copolymer segments
278 of both polyol monomers and MDI. This makes the hard segment of urethane serves as a
279 crosslinking site between the soft segments of the polyol (Leykin et al. 2016).
280

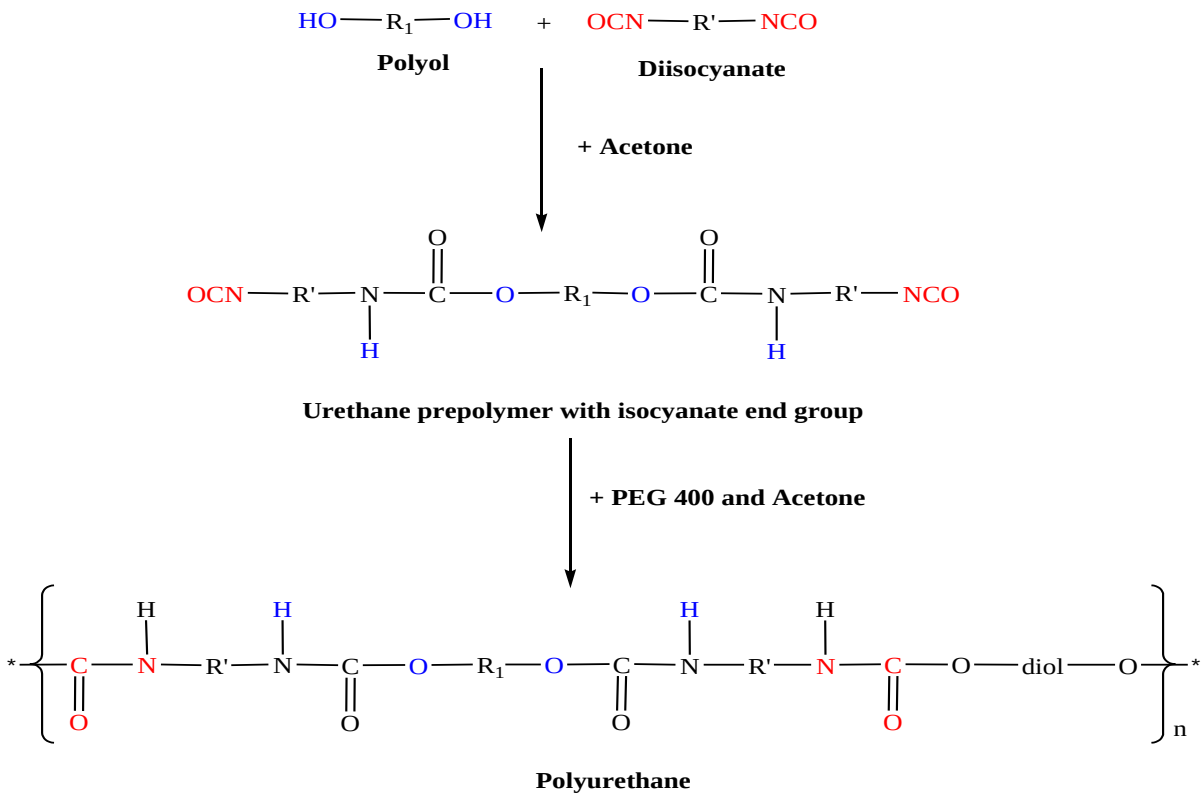
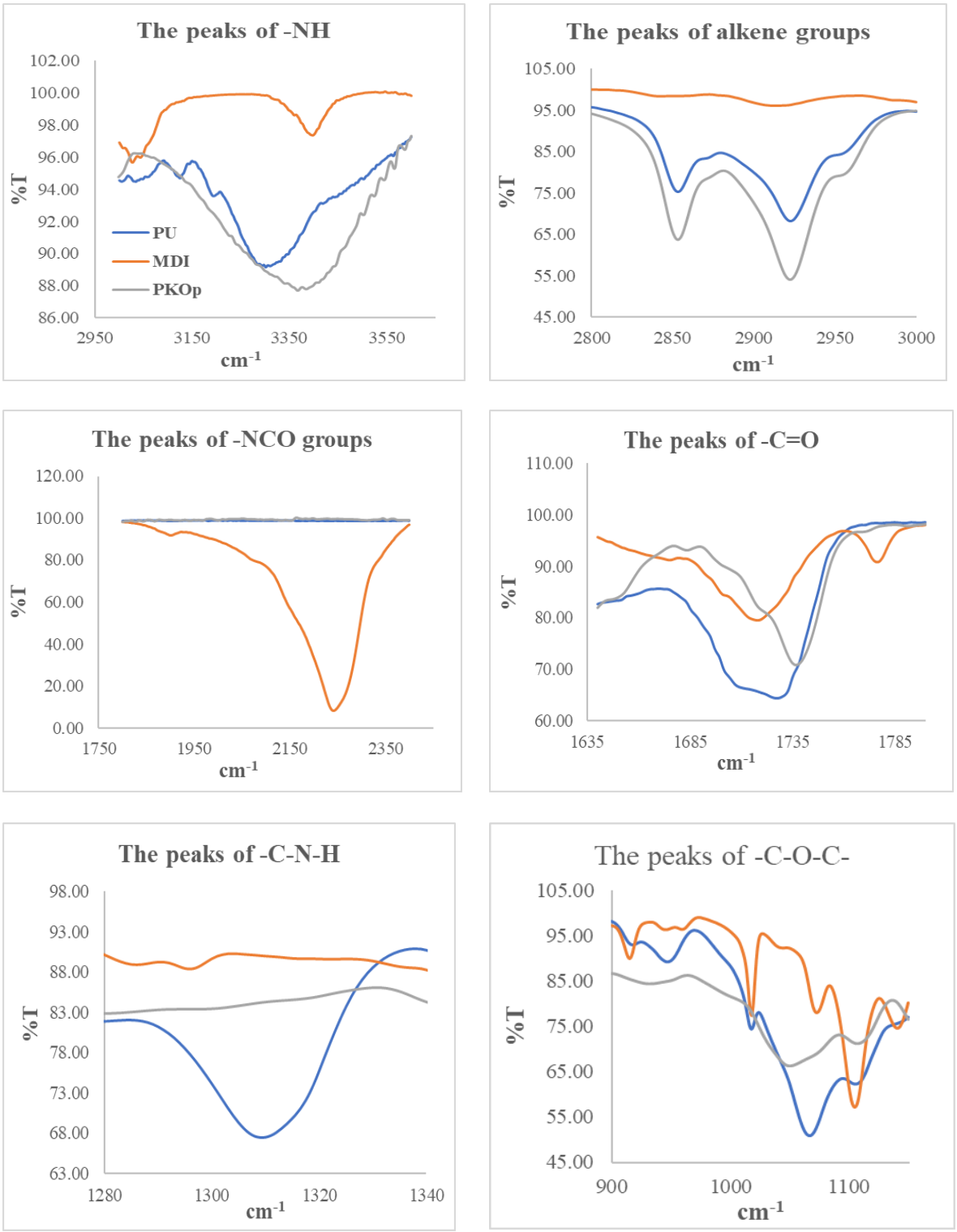


Figure 2. The chemical route of producing polyurethane via pre-polymerization method (Wong & Badri 2012).

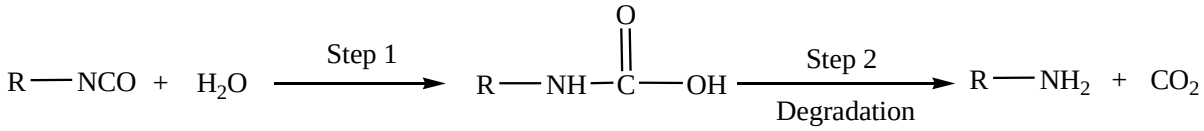
The mechanism of the pre-polymerization in urethane chains formation is a nucleophilic substitution reaction as studied by Yong et al. (2009). However, this study found amines as nucleophiles. Amine attacks carbonyl on isocyanate in MDI in order to form two resonance structures of intermediate complexes A and B. 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 who have conducted by Wong and Badri (2012). Moreover, nitrogen was more electropositive than oxygen, therefore, -CN bonds were more attracted to cations (H+) than -CO. The combination between long polymer chain and low cross-linking content gives the polymer elastic properties whereas short chain and high cross linking producing hard and rigid polymers. Cross-linking in polymers consists of three-

296 dimensional networks with high molecular weight. In some aspects, polyurethane can be a
297 macromolecule, a giant molecule (Petrovic 2008).
298



299 **Figure 3.** FTIR spectrums of several important peaks between polyurethane, PKO-p and MDI

300 However, the reaction between MDI and PEG as a chain extender where oxygen on the
301 nucleophile PEG attacks the NCO group in the MDI to form two intermediate complexes A
302 and B can occur. Nevertheless, nucleophilic substitution reactions have a greater tendency to
303 occur in PKOp compared to PEG because the presence of nitrogen atoms is more
304 electropositive than oxygen atoms in PEG. Amine has a higher probability of reacting
305 compared to hydroxyl (Herrington & Hock 1997). Amine with high alkalinity reacts with
306 carbon atoms on MDI as proposed by Wong and Badri (2012). PKOp contains long carbon
307 chains that can easily stabilize alkyl ions when intermediate complexes are formed. Therefore,
308 the polyol is more reactive than PEG to react with MDI. However, the addition of PEG will
309 increase the length of the polyurethane chain and prevent side effects such as the formation of
310 urea by-products of the NCO group reaction in urethane pre-polymer and water molecules from
311 the environment. If the NCO group reacts with the excess water in the environment, the
312 formation of urea and carbon dioxide gas will also occur excessively (**Figure 4**). This reaction
313 can cause a polyurethane foam, not polyurethane film as we studied the film.



314

315 **Figure 4**. The reaction between NCO group and water producing carbon dioxide

316

317 Furthermore, the application of PEG can influence the conductivity of PU where
318 Porcarelli et al. (2017) have reported the application of PEG using several molecular weights.
319 PEG 1500 decreased the conductivity of PU in consequence of the semicrystalline phase of
320 PEG 1500 that acted as a poor ion conducting phase for PU. It is also well known that PEG
321 with a molecular weight of more than 1000 $g \cdot mol^{-1}$ tends to crystallize with deleterious effects
322 on room temperature ionic conductivity (Porcarelli et al. 2017).

323

b. Morphological analysis

The Field Emission Scanning Electron Microscope (FESEM) micrograph in **Figure 5** shows the formation of a uniform polymer film contributed by the polymerization method applied. The magnification used for this surface analysis ranged from 200 to 5000 ×. 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 justified by the wavelengths obtained by the FTIR spectrums above.

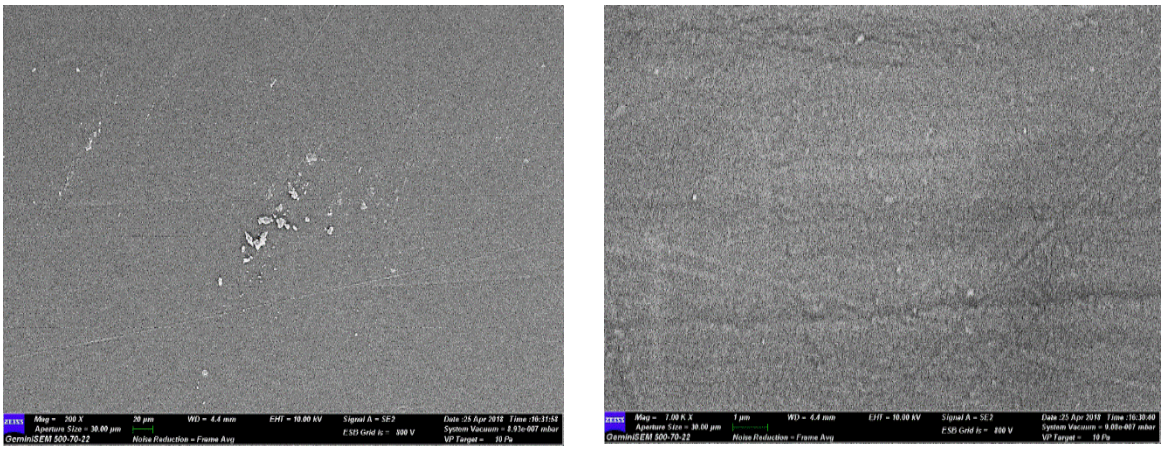


Figure 5. The micrograph of polyurethane films analysed by FESEM at (a) 200 × and (b) 5000× magnifications.

c. 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 (Cuve & Pascault 1991). 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 indicating a 99.3 % gel content. This is significant in getting a stable polymer at higher working temperature (Rogulska et al. 2007).

$$\text{Gel content (\%)} = \frac{(0.6 - 0.301)\ \text{g}}{0.301\ \text{g}} \times 100\% = 99.33\%$$

d. The thermal analysis

Thermogravimetric analysis (TGA) can be used to observe the material mass based on temperature shift. It can also examine and estimate the thermal stability and materials properties such as the alteration weight owing to absorption or desorption, decomposition, reduction and oxidation. The material composition of polymer is specified by analysing the temperatures and the heights of the individual mass steps (Alamawi et al. 2019). **Figure 6** shows the TGA and 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 6** in the region of 45 – 180ºC. This is due to the presence of condensation on moisture and solvent residues.

Table2 Weight loss percentage of (wt%) polyurethane film

Sample	% Weight loss (wt%)				Total of weight loss (%)	Residue after 550ºC (%)
	$T_{max,}$ ºC	T_{d1}, 200 – 290ºC	T_{d2}, 350 – 500ºC	T_{d3}, 500 – 550ºC		
Polyurethane	240	8.04	39.29	34.37	81.7	18.3

The bio polyurethane is thermally stable up to 240 °C before it has undergone thermal degradation (Agrawal et al. 2017). The first stage of thermal degradation (T_{d1}) on polyurethane films was shown in the region of 200 – 290 ºC as shown in **Figure 6**. The T_{d1} is associated with degradation of the hard segments of the urethane bond, forming alcohol or degradation of the polyol chains and releasing of isocyanates (Berta et al. 2006), primary and secondary amines as well as carbon dioxide (Corcuera et al. 2011; Pan & Webster 2012). Meanwhile, the 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 dimmerization of isocyanates to form carbodiimides and release CO_2. The formed carbodiimide reacts with alcohol to form urea. The third stage of thermal degradation (T_{d3}) is related to the degradation of urea (Berta et al. 2006) and the soft segment on polyurethane.

Generally, DSC analysis exhibited thermal transitions as well as the initial crystallisation and melting temperatures of the polyurethane (Khairuddin et al. 2018). It serves to analyse changes in thermal behavior due to changes occurring in the chemical chain structure based on the glass transition temperature (T_g) of the sample obtained from the DSC thermogram (**Figure 7**). DSC analysis on polyurethane film was performed in the temperature at the range 100 ^oC to 200 ^oC using nitrogen gas as a blanket as proposed by Furtwengler et al. (2017). The glass transition temperature (T_g) on polyurethane was above room temperature, at 78.1 ^oC indicated the state of glass on polyurethane. The presence of MDI contributes to the formation of hard segments in polyurethanes. Porcarelli et al. (2017) stated that possess a low glass transition (T_g) may contribute to PU conductivity.

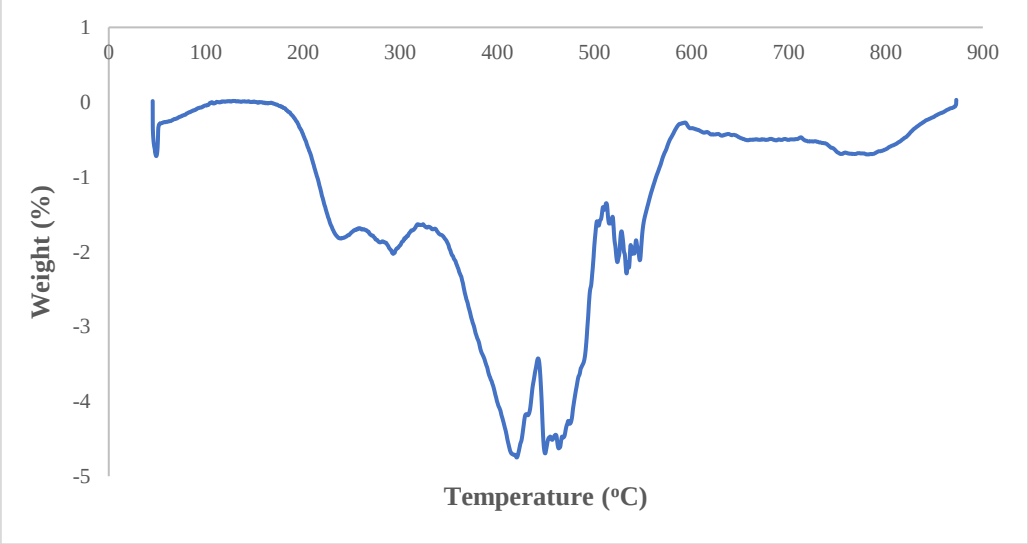


Figure 6. DTG thermogram of polyurethane film

During polymerization, this hard segment restricts the mobility of the polymer chain (Ren et al. 2013) 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 56ºC. However, it was detected in the DSC thermogram nor the TGA thermogram, which indicates that acetone was removed from the polyurethane during the synthesis process, owing to its volatility nature. The presence of acetone in the synthesis was to lower the reaction kinetics.

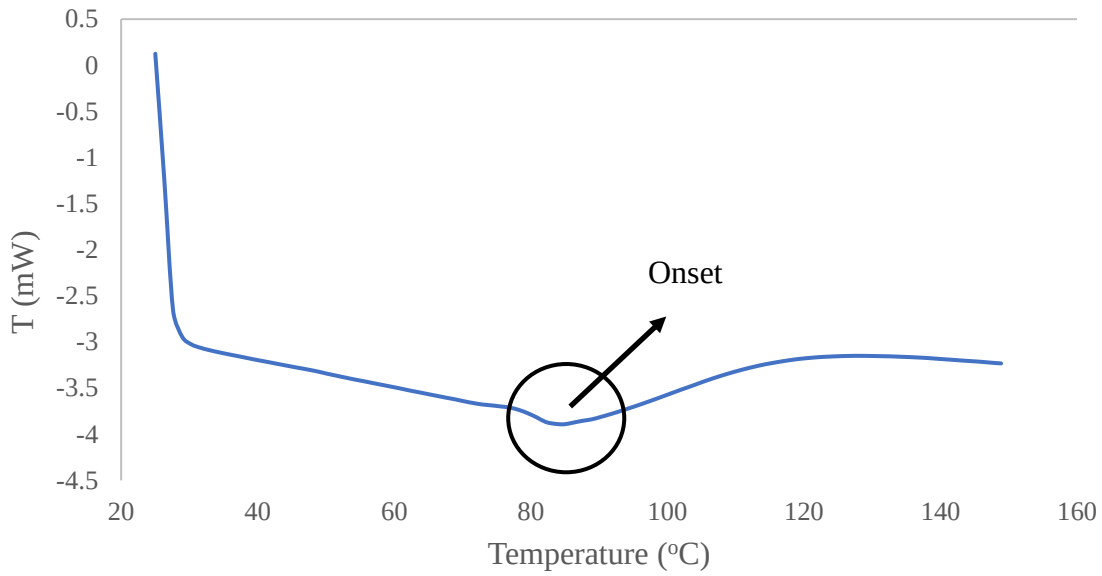


Figure 7. DSC thermogram of polyurethane film

e. 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, tetrahydrofuran (THF), dimethylformamide (DMF) and dimethylformamide (DMSO). On the other hand, the mechanical properties of polyurethane were determined based on the standard testing following ASTM D 638 (Standard Test Method for Tensile Properties of Plastics). The results from the polyurethane film solubility and tensile test are shown in **Table 3**. Polyurethane films were insoluble with

benzene, hexane and acetone and are only slightly soluble in tetrahydrofuran (THF), dimethylformamide (DMF) and dimethylformamide (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.

Table 3 The solubility and mechanical properties of the polyurethane film

Parameters		Polyurethane film
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

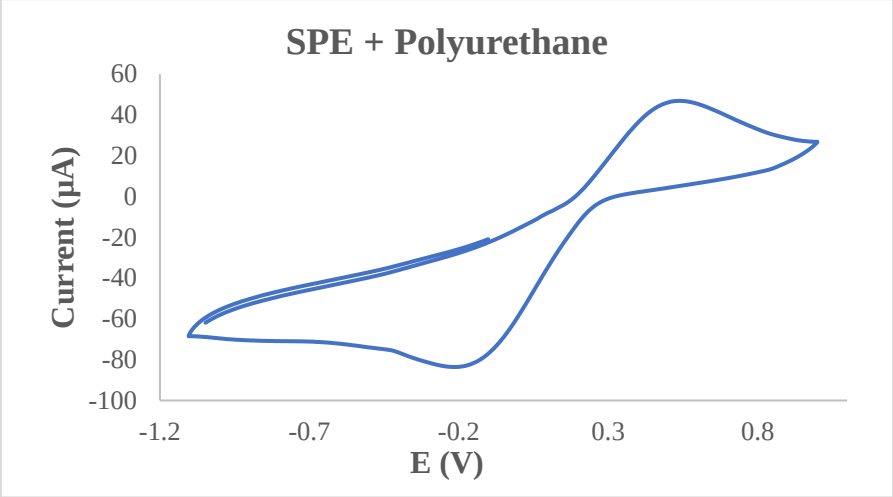
The tensile stress, strain and modulus of polyurethane film also indicated that polyurethane has good mechanical properties that are capable of being a supporting substrate for the next stage of study. In the production of polyurethane, the properties of a polyurethane are easily influenced by the content 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.

f. The conductivity of the polyurethane as a polymeric film on SPE

Polyurethane film deposited onto the screen-printed electrode by casting method as shown in **Figure 1**. After that, the modified electrode was analysed using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in order to study the behaviour of modified electrode. The modified electrode was tested in a 0.1 mmol/L KCl solution containing 5 mmol/L ($K_3Fe(CN)_6$). 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. The voltammograms at 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 is a natural polymer produced from the polyol of palm kernel oil. The electrochemical signal at the electrode is low if there is a decrease in electrochemical conductivity (El - Raheem et al. 2020). It can be concluded that polyurethane is a bio-polymer with a low conductivity value. The current of the modified electrode was found at 5.3×10^{-5} A or 53 µA. Nevertheless, the electroconductivity of PU in this study shows better conductivity several times compared to Bahrami et al. (2019) that reported the conductivity of PU as 1.26×10^{-6} A, whereas Li et al. (2019) reported the PU conductivity in their study was even very low, namely 10^{-14} A. The conductivity of PU owing to the benzene ring in the hard segment (MDI) could exhibit the conductivity by inducing electron delocalization along the polyurethane chain (Wong et al. 2014). The conductivity of PU can also be caused by PEG. The application of PEG as polyol has been studied by Porcarelli et al. (2017), that reported that the conductivity of PU based on PEG – polyol was 9.2×10^{-8}.

441 According to **Figure 8**, it can be concluded that the anodic peak present in the modifed
442 electrode was at +0.5 V, it also represented the oxidation process of the modified electrode.
443 The first oxidation scan on both electrodes ranged from -0.2 to +1.0 V, which showed a
444 significant anodic peak at a potential of +0.5 V.
445



446
447 **Figure 8**. The voltammogram of SPE – PU modified electrode after analysed using cyclic
448 voltammetry (CV) technique
449
450 **Figure 9** also presents the DPV voltammogram of modified electrode. DPV is a measurement
451 based on the difference in potential pulses that produce an electric current. Scanning the
452 capability pulses to the working electrode will produce different currents. Optimal peak
453 currents will be produced to the reduction capacity of the redox material. The peak current
454 produced is proportional to the concentration of the redox substance and can be detected up to
455 concentration below 10^{-8} M. DPV was conducted to obtain the current value that more accurate
456 than CV (Lee et al. 2018).
457
458 This study used a redox pair ($K_3Fe(CN)_6$) as a test device (probe). The currents generated by
459 SPE-PU and proved by CV and DPV have shown conductivity on polyurethane films. This
460 suggests that polyurethane films can conduct electron transfer. The electrochemical area on the

modified electrode can be calculated using the formula from Randles-Sevcik (Butwong et al. 2019), where the electrochemical area for SPE-PU is considered to be A, using Equation 2:

$$\textbf{Current of SPE-PU , } I_p = 2.65 \times 10^5\, n^{3/2}\, Av^{1/2}\, CD^{1/2} \qquad (2)$$

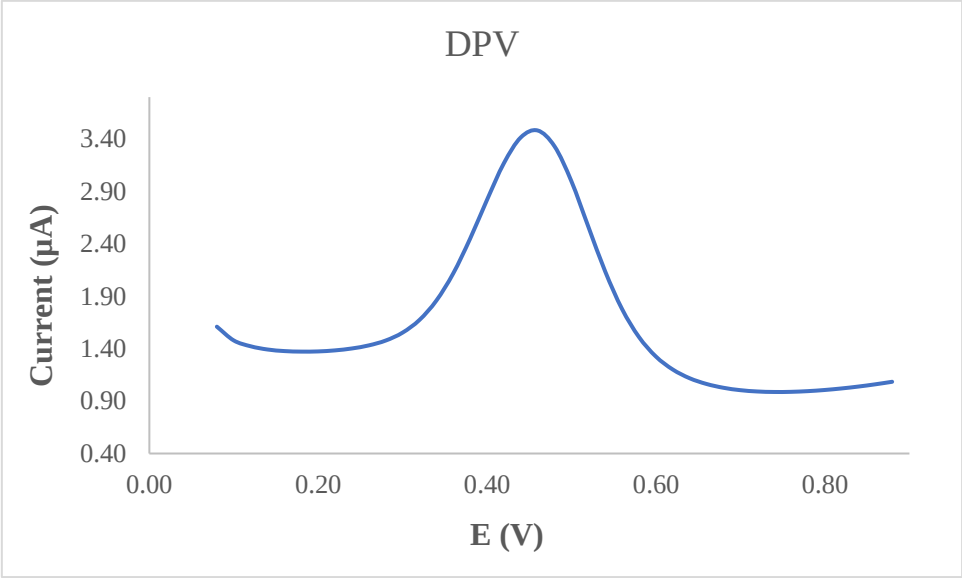


Figure 9. The voltammogram of SPE – PU modified electrode after analyzed using differential pulse voltammetry (DPV) technique

Where, n – 1 is the amount of electron transfer involved, while C is the solvent concentration used (mmol/L) and the value of D is the diffusion constant of 5 mmol/L at ($K_3Fe(CN)_6$) dissolved using 0.1 mmol/L KCl. The estimated surface area of the electrode (**Figure 1**) was 0.2 cm^2 where the length and width of the electrode used during the study was 0.44 cm × 0.44 cm while the surface area of the modified electrode was 0.25 cm^2 with the length and width of the electrode estimated at 0.5 cm × 0.5 cm, and causing the modified electrode has a larger surface. The corresponding surface concentration (τ) (mol/cm^2) is calculated using Equation 3.

$$\mathbf{I_p = (n^2\, F^2 / 4RT)\, A\tau v} \qquad (3)$$

I_p is the peak current (A), while A is the surface area 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 constant ideal gas (8.314 J/mol K) and T is the temperature used during the experiment being conducted

(298 K) (Koita et al. 2014). The development of conducting polymer from palm oil-based biomaterials seems to be one of the potential future applications of palm oil products, as this novel material has the potential to contribute positively to the analytical industry. Likewise, other palm oil-based products, such as refined-bleached-deodorised (RBD) palm oil, palm oil, and palm stearin are abundantly available in Malaysia. They are known to be economical, sustainable, and environmentally biodegradable. These palm oil-based products are promising prospects for manufacturing biomaterials that become alternative products to other polymers from synthetic/chemical-based (Tajao et al. 2021). Several studies have been reported the application of PU to produce elastic conductive fibres and films owing to it is highly elastic, scratch resistant and adhesive (Tadese et al. 2019), thus it is easy for PU to adhere on the screen-printed electrode in order to modify the electrode. PU is also being used as a composite material to make elastic conducting composite films (Khatoon & Ahmad 2017).

4. Conclusion

Polyurethane film was prepared by pre-polymerization between palm kernel oil-based polyol (PKO-p) with MDI. The presence of PEG 400 as the chain extender formed freestanding flexible film. Acetone was used as the solvent to lower the reaction kinetics since the pre-polymerization was carried out at room temperature. The formation of urethane links (NHCO – backbone) after polymerization was confirmed by the absence of N=C=O peak at 2241 cm^{-1} 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 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 modified electrode was found at 5.2×10^{-5} A. This bio polyurethane film can be used as a conducting bio-polymer 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.

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6. Conflict of Interest

The authors declare no conflict of interest.

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Design and Synthesis of Conducting Polymer Based on Polyurethane produced from Palm Kernel Oil

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> Abstract

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— Editorial Comments

Joanna Rydz 10.02.2022

Decision

Minor Revision Requested

Message for Author

Dear authors,
The text still needs to be improved.
1. Please properly describe the results from FTIR throughout the text also in Conclusion.
"N=C=O is not a peak. Functional groups give characteristic signals in a spectrum. Please use scientific language throughout your text and please describe the FTIR spectra properly"
"Thank you for your suggestion. Nevertheless, the reading of this spectrum based on Spectroscopy book 4th Edition by Lampman et al. It is written on Page 29, 77 and 78 (Figure 2.64) about the spectrum of N=C=O. According to their research, the isocyanates have sp-hydridized carbon atoms similar to the C≡C bond. The absorption occurs in 2100-2270 cm-1"
Exactly, then why do you write "N=C=O peak"? It is a scientific work and that is the language it should use.
"and confirmed by the absence of peak at 2241 cm-1 attributed to the sp-hydridized carbon atoms of ....."/or "absorption bands at 2241 cm-1 associated with N=C=O bond stretching...." Please correct.
2. "bio based" is one word and should be spelled the same way throughout the text, see lines 21 and 75 (correct). Please correct throughout the text (It is best to use the find options throughout the text).
3. Line 150-152: The reagent purity record was perfectly correct and please restore it. The note was about DMSO, which was 2 times.
4. Line 220: the parenthesis is missing.
5. Line 369, 507, 513: “bio polyurethane”. Should be bio-based polyurethane. A single comment applies to the entire text!
6. Table 2: Please explain variables such as Tmax, etc. under the table.
The table has not been corrected and is still incomprehensible. It not only shows the "weight loss percentage" as its caption suggests, but also other parameters. Please properly title it. Right now, the table shows that the weight loss percentage of sample Tmax has changed by 240!
The first row should be discarded. The table shows the TGA parameters of one sample, so there is no need to put it in the table. Please correct.

− Response to Revision Request

Muhammad Abdurrahman Munir 10.02.2022

Your Reply

Greetings, Dear Dr. Joanna Rydz We would like to inform you that the manuscript has been revised accroding to the reviewer's comments. Journal: International

Journal of Polymer Science Manuscript ID: 6815187 Title: "Design and Synthesis of Conducting Polymer Based on Polyurethane produced from Palm Kernel Oil" Comments and track changes are attached. We look forward to receiving your revision if any. Best Regards.

File

Manuscript - Munir.docx **916 kB**

Design and Synthesis of Conducting Polymer Based on Polyurethane produced from Palm Kernel Oil

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Abstract

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-polyurethane film 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 (PKOp) and 4,4-methylene diisocyanate. The PU has strong

adhesion on the SPE surface. The synthesized polyurethane was characterized using thermogravimetry analysis (TGA), differential scanning calorimetry (DSC), Fourier – transform infrared spectroscopy (FTIR), surface area analysis by field emission scanning electron microscope (FESEM), and cyclic voltammetry (CV). Cyclic voltammetry was employed to study electro-catalytic 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 (DPV) method. Furthermore, the formation of urethane linkages (NHCO backbone) after polymerization was analyzed using FTIR and confirmed by the absence of N=C=O peak at 2241 cm^{-1}. The glass transition temperature (T_g) of the polyurethane was detected at 78.1^oC.

Keywords: Polyurethane, polymerization, screen-printed electrode, voltammetry

1. Introduction

Conducting polymers (CPs) are polymers that can release a current (Alqarni et al. 2020). The conductivity of CPs was first observed in polyacetylene, nevertheless owing to its instability, the invention of various CPs have 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 semi-conductive. Therefore, it is imperative to improve their conductivity for electrochemical sensor purposes (Sengodu & Deshmukh 2015; Dzulkipli et al. 2021; Wang et al. 2018). 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, 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 (Alqarni et al. 2020; Ghosh et al. 2018). There is scientific documentation on the use of conductive polymers in various studies such as polyaniline (Pan & Yu 2016), polypyrrole (Ladan et al. 2017), and polyurethane (Tran et al. 2020; Vieira et al. 2020; Guo et al. 2020; Fei et al. 2020).

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 (Badri 2012). 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 (Badri 2012; Borowicz et al. 2019).

It is very straightforward for vegetable oils to react with a specific group to produce a PU such as epoxy, hydroxyl, carboxyl, and acrylate owing to the existence of (-C=C-) in vegetable oils. Thus, it provides appealing profits to vegetable oils compared to petroleum considering the toxicity, price, and harm to the environment (Mustapha et al. 2019; Mohd Noor et al. 2020). 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 profits 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 CO_2 from the atmosphere as a net sequester (Tajau et al. 2021; Septevani et al. 2015).

The application of biopolymer has appealed much attention until now. Global environmental activists have forced researchers to discover another material producing biopolymers (Priya et al. 2018). 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 (Zia et al. 2014; Romaskevic et al. 2006). Polyurethanes are also considered to be one of the most useful materials with many profits 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 (Badan & Majka 2017; Munir et al. 2021).

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 & MDI) and 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 (Akindoyo et al. 2016).

PUs have low conductivity and 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 (Janpoung et al, 2020; Su'ait et al. 2014), majorly 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 (π) 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 (Wang et al. 2017; Kotal et al. 2011).

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 users and environment (Kilele et al. 2020; Inayatullah et al. 2021; Munir et al. 2021; Harmayani et al. 2014; Nurwanti et al. 2018). 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 (Chokkareddy et al. 2020). 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 (Chokkareddy et al. 2020; Kilele et al. 2021). 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 (Degefu et al. 2014).

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 (Nakthong et al. 2020). Conducting polymers (CPs) become an alternative to modifying the screen-printed electrodes due to their electrical conductivity, able to capture analyte by chemical/physical adsorption, large surface area, and making CPs are very appealing materials from electrochemical perspectives (Baig et al. 2019). 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 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 electro behavior of polyurethane using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) attached to the screen-printed electrode (SPE). To the best of our knowledge, this is the first attempt to use a modified polyurethane electrode. The electrochemistry of polyurethane mounted onto screen-printed electrode (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

Synthesis of polyurethane film: Palm kernel oil (PKOp) supplied by UKM Technology Sdn Bhd through MPOB/UKM station plant, Pekan Bangi Lama, Selangor and prepared using Badri et al. (2000) method. 4, 4-diphenylmethane diisocyanate (MDI) was acquired from Cosmopolyurethane (M) Sdn. Bhd., Klang, Malaysia. Solvents and analytical reagents were benzene (≥ 99.8%), toluene (≥ 99.8%), hexane (≥ 99%), acetone (≥ 99%), dimethylsulfoxide (DMSO) (≥ 99.9%), dimethylformamide (DMF) (≥ 99.8%), tetrahydrofuran (THF) (≥ 99.8%), dimethylsulfoxide (DMSO) (≥ 99.9%), 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 638 (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 °C/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 °C /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 -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 changes 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 film 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 film was coated with a thin layer of gold to increase the conductivity of the film. The coating method was carried out using a sputter-coater. The observations were conducted at a magnification of 200× and 5000 × 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 hours. 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 hours in order to get a constant mass. The percentage of crosslinking content known as the gel content can be calculated using Equation (1).

$$\text{Gel content } (\%) = \frac{W_o - W}{W} \text{ x } 100\ \% \qquad (1)$$

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 (DATR) method to confirm the polyurethane, PKOp, 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

198 the formation of the polymer such as amide group (-NH), urethane carbonyl group (-C = O),
199 and carbamate group (-CN).
200
201 **2.3 Synthesis of Polyurethane**
202 Firstly, the polyol prepolymer solution was produced by combining palm kernel oil (PKO)p
203 and polyethylene glycol (PEG) 400 (100:40 g/g), acetone 30% was used as a solution. The
204 compound was homogenized using a centrifuge (100 rpm) for 5 min. Whereas diisocyanate
205 prepolymer was obtained by mixing 4,4'-diphenylmethane diisocyanate (MDI) (100 g) to
206 acetone 30%, afterward the mixture was mixed using a centrifuge for 1 min to obtain a
207 homogenized solution. Afterward, diisocyanate solution (10 g) was poured into a container that
208 contains polyol prepolymer solution (10 g) slowly to avoid an exothermic reaction occurring.
209 The mixture was mixed for 30 sec until a homogenized solution was acquired. Lastly, the
210 polyurethane solution was poured on the electrode surface by using the casting method and
211 dried at ambient temperature for 12 hours.
212
213 **2.4 Modification of Electrode**
214 Voltammetric tests were performed using Metrohm Autolab Software (**Figure 1**) analyzer
215 using cyclic voltammetry (CV) method or known as amperometric mode and differential pulse
216 voltammetry (DPV). All electrochemical experiments were carried out using screen-printed
217 electrode (diameter 3 mm) modified using polyurethane film as working electrode, platinum
218 wire as the auxiliary electrode, and Ag/AgCl electrode as a reference electrode. All experiments
219 were conducted at a temperature of 20 ± 2^{o}C.
220
221 The PU was cast onto the screen-printed electrode (SPE + PU) and analyzed using a single
222 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 & 0.5) mg of palm-based pre-polyurethane was dropped separately onto the surface of the SPE 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.

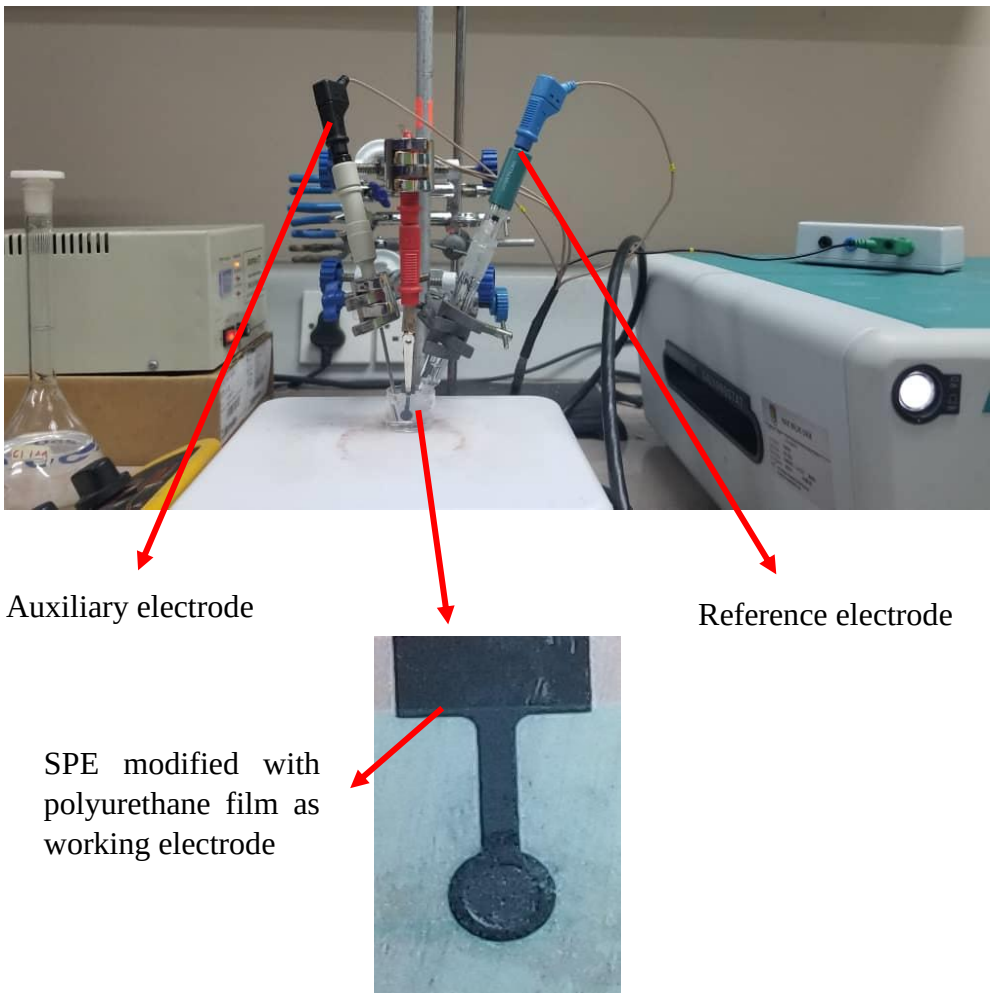


Figure 1. Potentiostat instrument to study the conductivity of SPE modified with polyurethane film using voltammetric approach: CV and DPV

3. Results and Discussion

The synthesis of PU films was carried out using a pre-polymerization 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 (PKOp). **Table 1** presents the PKO-p properties used in this study. The structural chain was extended with the aid of polyethylene glycol (PEG) 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 (PKOp) while the other hydroxyl group of the polyol is attacked by the other isocyanate group (Wong & Badri 2012) as shown in **Figure 2**.

Table 1 The specification of PKO-p (Badri et al. (2000)).

Property	**Values**
Viscosity at 25^{o}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

a. FTIR analysis

Figure 3 shows the FTIR spectra for polyurethane, exhibiting the important functional group peaks. According to a study researched by Wong & Badri 2012, PKO-p reacts with MDI to form urethane prepolymers. The NCO group on MDI reacts with the OH group on polyol whether PKOp 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 a peak 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 Hamuzan & Badri (2016) 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 peaks at 2250 – 2270 cm^{-1} indicates the absence of NCO groups. It shows that the polymerization reaction occurs entirely between NCO groups in MDI with hydroxyl groups on polyols and PEG (Mishra et al. 2012). The absence of peaks at 1690 cm^{-1} representing urea (C = O) in this study indicated, there is no urea formation as a byproduct (Clemitson 2008) 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 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. (2007) and Lampman et. al. (2010). 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. These properties make isocyanates are highly reactive, and have different properties (Leykin et al. 2016).

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 (Nohra et al. 2013). 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 (Leykin et al. 2016).

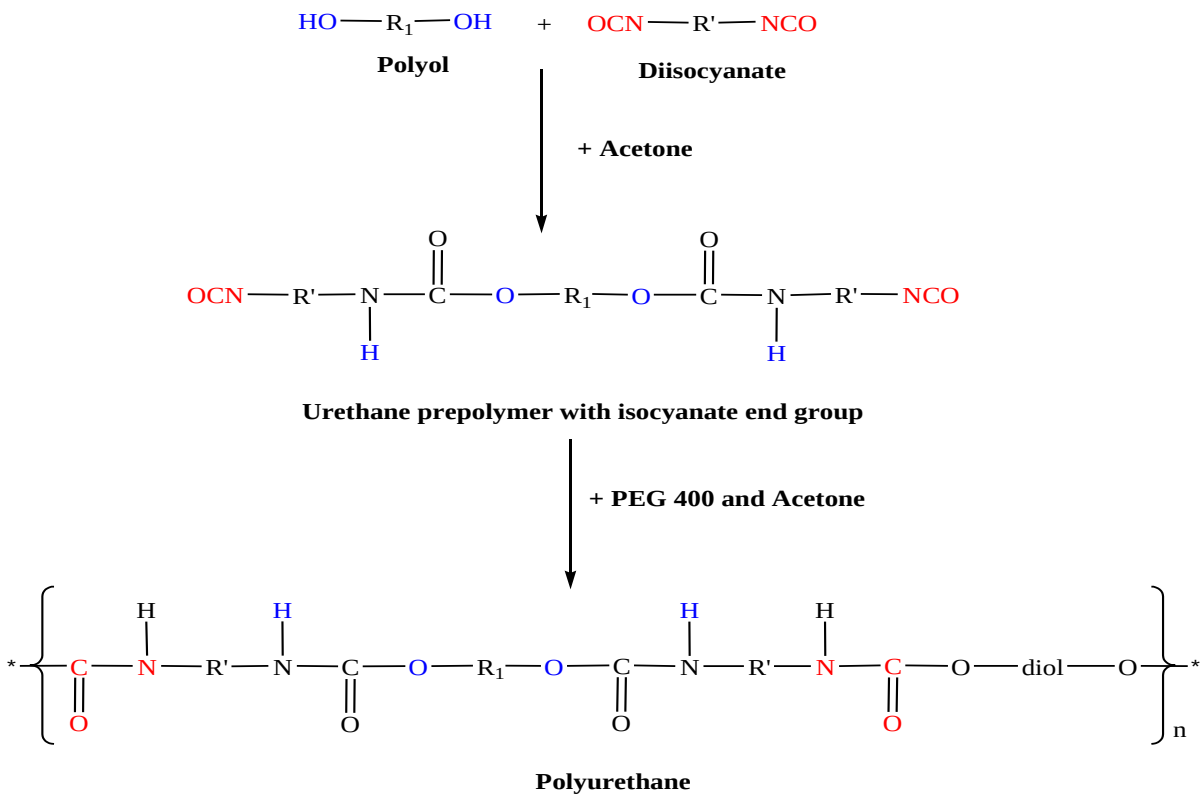
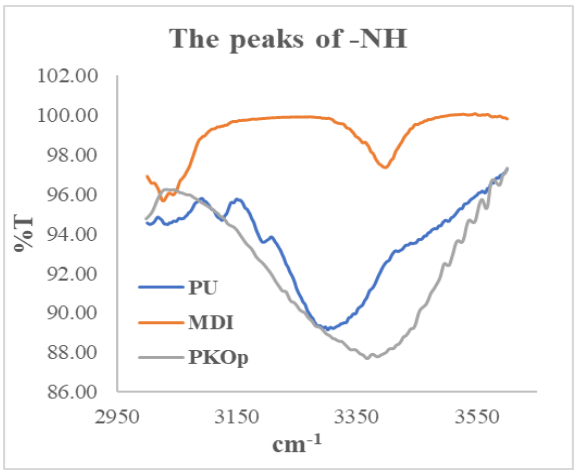


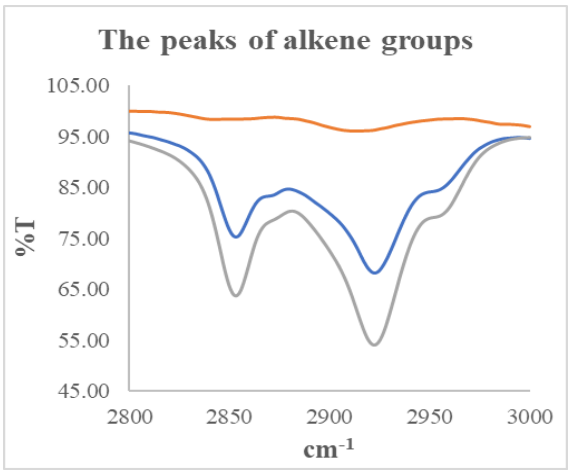
Figure 2. PU production via the pre-polymerization method (Wong & Badri 2012).

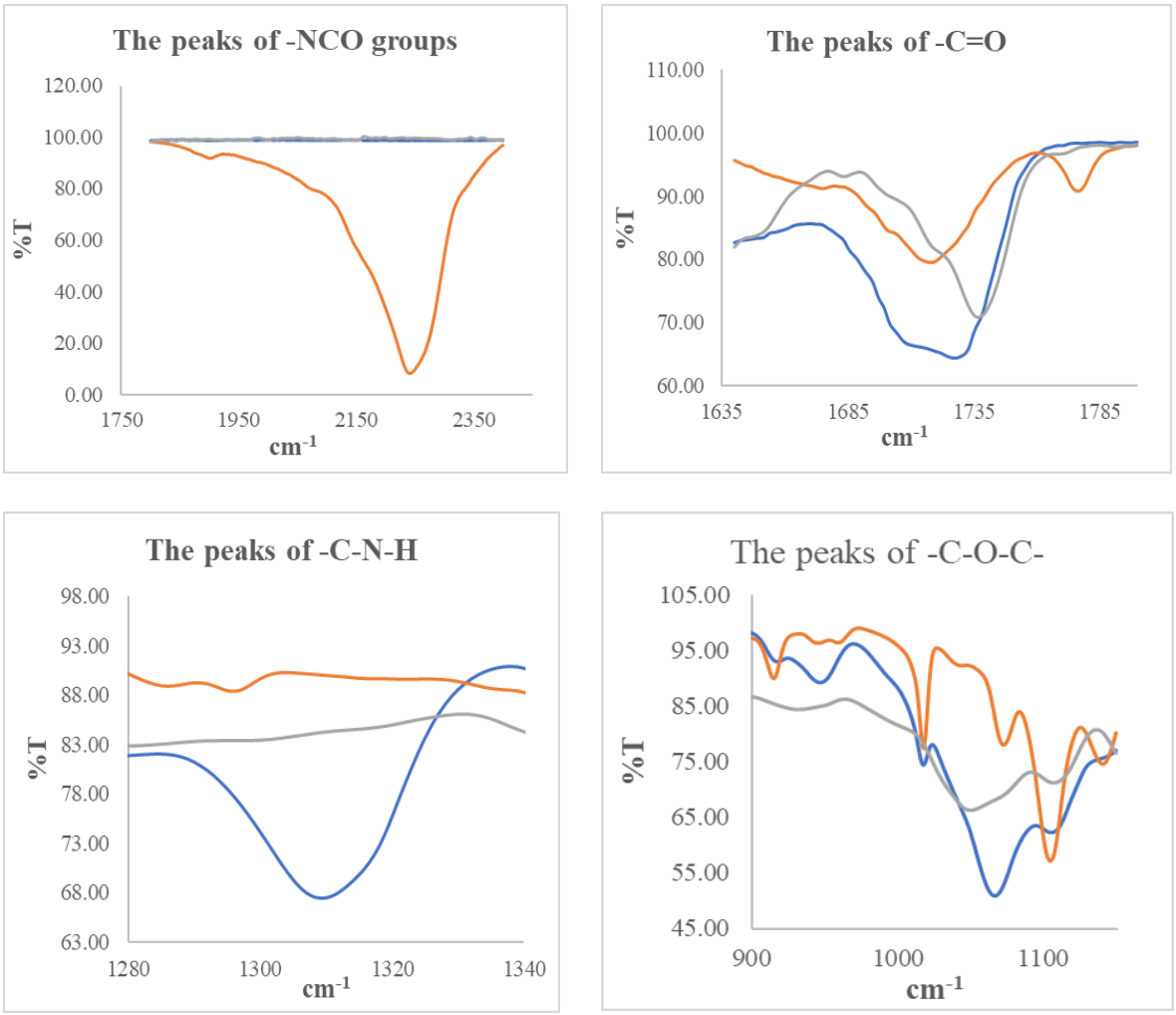
The mechanism of the pre-polymerization in urethane chains formation is a nucleophilic substitution reaction as studied by Yong et al. (2009). However, this study found amines as nucleophiles. Amine attacks carbonyl on isocyanate in MDI in order to form two resonance structures of intermediate complexes A and B. 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 who have conducted by Wong and Badri (2012). 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 cross-linking content gives the polymer elastic properties whereas short-chain and high cross-linking produce hard and rigid polymers. Cross-linking in polymers consists of three-dimensional networks with high molecular weight. In some aspects, polyurethane can be a macromolecule, a giant molecule (Petrovic 2008).

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 PKOp chemical structure causing the reaction of nucleophilic substitution that occurs in PKOp. Furthermore, amine has a higher probability of reacting compared to hydroxyl (Herrington & Hock 1997). Amine with high alkalinity reacts with carbon atoms on MDI as proposed by Wong and Badri (2012).







310 **Figure 3.** FTIR spectra of several important peaks between polyurethane, PKO-p, and MDI

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314 The production of intermediate complexes unstabilizes the alkyl ions, nevertheless, the
315 long carbon chains of PKOp ensure the stability of alkyl ions. The addition of PEG in this study
316 is imperative, not merely to increase the chain length of PU but also to avoid the production of
317 urea as a by-product after the NCO group reacts with H_2O from the environment. If the NCO
318 group reacts with the excess water in the environment, the formation of urea and carbon dioxide
319 gas will also occur excessively (**Figure 4**). This reaction can cause a polyurethane foam, not
320 polyurethane film as we studied the film.

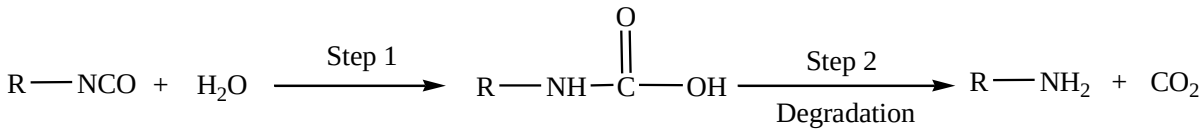

Figure 4. The reaction between the NCO group and water producing carbon dioxide

Furthermore, the application of PEG can influence the conductivity of PU whereby Porcarelli et al. (2017) 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 g·mol^{-1} tends to crystallize with deleterious effects on room temperature ionic conductivity (Porcarelli et al. 2017).

b. Morphological analysis

The Field Emission Scanning Electron Microscope (FESEM) micrograph in **Figure 5** shows the formation of a uniform polymer film contributed by the polymerization method applied. The magnification used for this surface analysis ranged from 200 to 5000 ×. 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 justified by the wavelengths obtained by the FTIR spectra above.

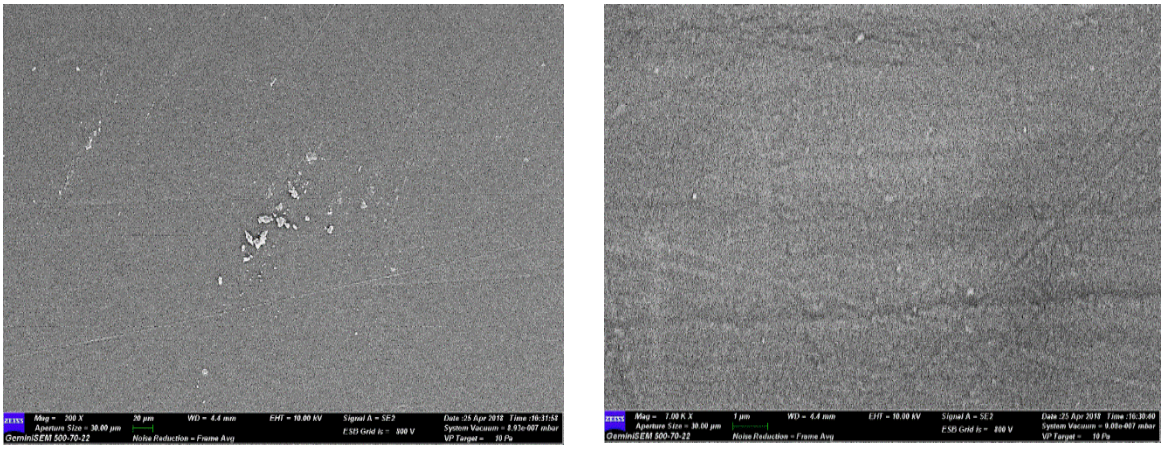

Figure 5. The micrograph of polyurethane films was analyzed by FESEM at (a) 200 × and (b) 5000× magnifications.

c. 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 (Cuve & Pascault 1991). 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 (Rogulska et al. 2007).

$$\text{Gel content (\%)} = \frac{(0.6 - 0.301)\ \text{g}}{0.301\ \text{g}} \times 100\% = 99.33\%$$

d. The thermal analysis

Thermogravimetric analysis (TGA) can be used to observe the material mass based on temperature shift. It can also examine and estimate the thermal stability and materials 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 heights of the individual mass steps (Alamawi et al. 2019). **Figure 6** shows the TGA and 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 6** in the region of 45 – 180°C. This is due to the presence of condensation on moisture and solvent residues.

Table2 Weight loss percentage of (wt%) polyurethane film

Sample	% Weight loss (wt%)				Total of weight loss (%)	Residue after 550°C (%)
	$T_{max,}$ °C	T_{d1}, 200 – 290°C	T_{d2}, 350 – 500°C	T_{d3}, 500 – 550°C		
Polyurethane	240	8.04	39.29	34.37	81.7	18.3

The bio polyurethane is thermally stable up to 240 °C before it has undergone thermal degradation (Agrawal et al. 2017). The first stage of thermal degradation (T_{d1}) on polyurethane films was shown in the region of 200 – 290 °C as shown in **Figure 6**. The T_{d1} is associated with degradation of the hard segments of the urethane bond, forming alcohol or degradation of the polyol chains and releasing of isocyanates (Berta et al. 2006), primary and secondary amines as well as carbon dioxide (Corcuera et al. 2011; Pan & Webster 2012). Meanwhile, the 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 CO_2. The formed carbodiimide reacts with alcohol to form urea. The third stage of thermal degradation (T_{d3}) is related to the degradation of urea (Berta et al. 2006) and the soft segment on polyurethane.

Generally, DSC analysis exhibited thermal transitions as well as the initial crystallization and melting temperatures of the polyurethane (Khairuddin et al. 2018). It serves to analyze changes in thermal behavior due to changes occurring in the chemical chain structure based on the glass transition temperature (T_g) of the sample obtained from the DSC thermogram

(**Figure 7**). DSC analysis on polyurethane film was performed in the temperature at the range 100 ^{o}C to 200 ^{o}C of using nitrogen gas as a blanket as proposed by Furtwengler et al. (2017). The glass transition temperature (T_g) on polyurethane was above room temperature, at 78.1 ^{o}C indicated the state of glass on polyurethane. The presence of MDI contributes to the formation of hard segments in polyurethanes. Porcarelli et al. (2017) stated that possessing a low glass transition (T_g) may contribute to PU conductivity.

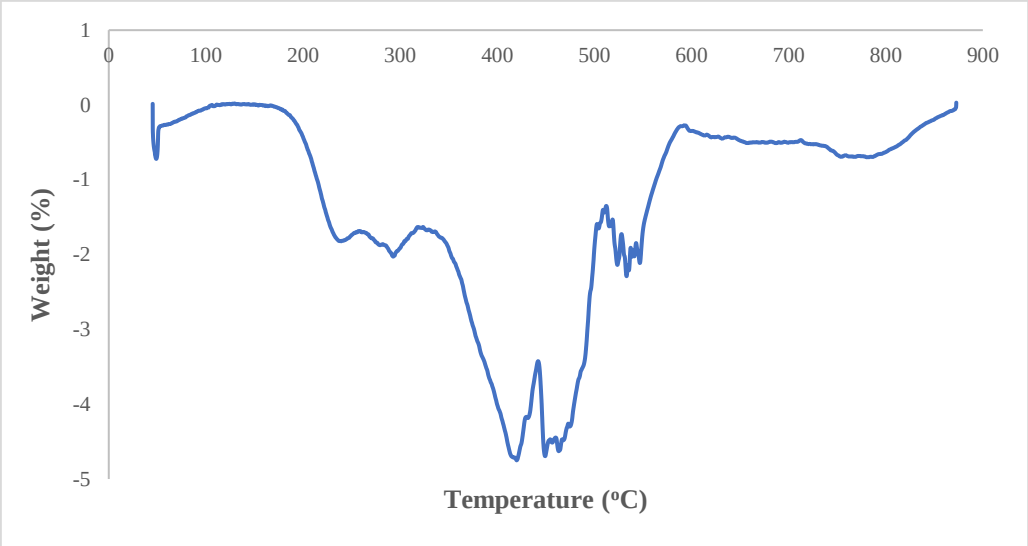

Figure 6. DTG thermogram of polyurethane film

During polymerization, this hard segment restricts the mobility of the polymer chain (Ren et al. 2013) 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^{o}C. However, it was detected in the DSC thermogram nor the TGA thermogram, which indicates that acetone was removed from the polyurethane during the synthesis process, owing to its volatile nature. The presence of acetone in the synthesis was to lower the reaction kinetics.

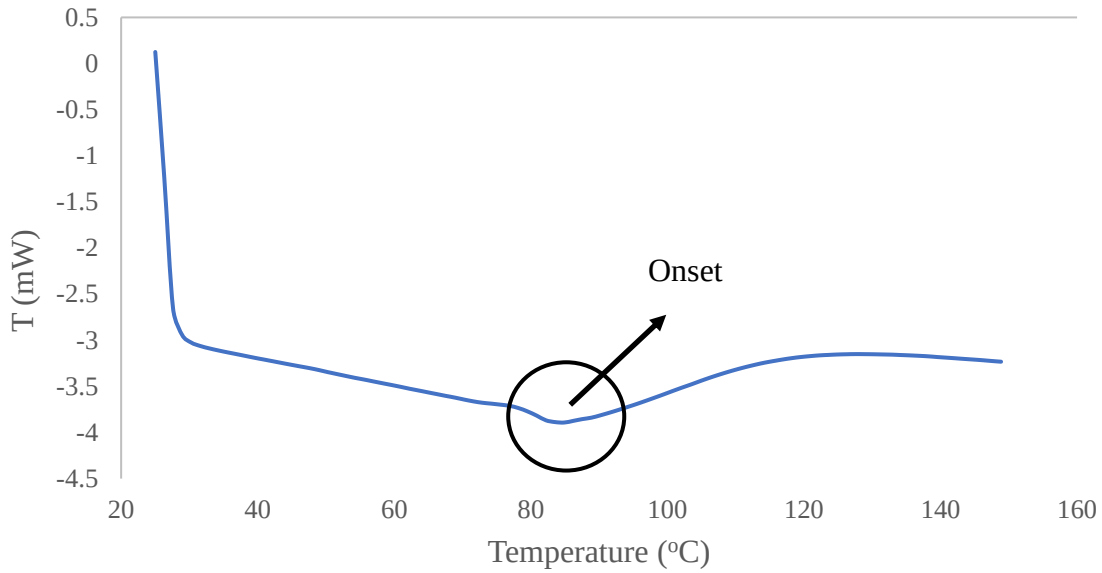

Figure 7. DSC thermogram of polyurethane film

e. 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, tetrahydrofuran (THF), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). On the other hand, the mechanical properties of polyurethane were determined based on the standard testing following ASTM D 638 (Standard Test Method for Tensile Properties of Plastics). The results from the polyurethane film solubility and tensile test are shown in **Table 3**. Polyurethane films were insoluble with acetone, hexane, and benzene and are only slightly soluble in tetrahydrofuran (THF), dimethylformamide (DMF), and dimethyl sulfoxide (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.

Table 3 The solubility and mechanical properties of the polyurethane film

Parameters	Polyurethane film

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

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.

f. 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 (CV) and differential pulse voltammetry (DPV) in order to study the behavior of the modified electrode. The modified electrode was tested in a 0.1 $mmol \cdot L^{-1}$ KCl solution containing 5 $mmol \cdot L^{-1}$ ($K_3Fe(CN)_6$). 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 $V \cdot s^{-1}$. 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. The electrochemical signal at the electrode is low if there is a decrease in electrochemical conductivity (El - Raheem et al. 2020). It can be concluded that polyurethane is a bio-polymer 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. (2019) 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 (Wong et al. 2014). The PU can also release a current caused by PEG. The application of PEG as polyol has been studied by Porcarelli et al. (2017), that reported that the current of PU based on PEG – polyol was 9.2×10^{-8} A.

According to **Figure 8**, it can be concluded that the anodic peak present in the modified electrode was at +0.5 V, 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.

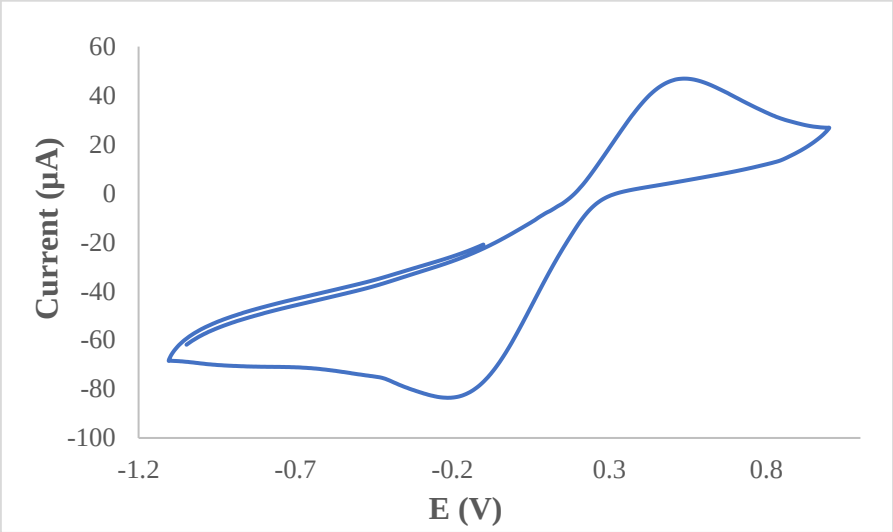

Figure 8. The voltammogram of SPE – PU modified electrode after analyzed using cyclic voltammetry (CV) technique

Figure 9 also presents the DPV voltammogram of the modified electrode. DPV is a measurement based on the difference in potential pulses that produce an electric current. Scanning the capability pulses to the working electrode will produce different currents. Optimal peak currents will be produced to the reduction capacity of the redox material. The peak current produced is proportional to the concentration of the redox substance and can be detected up to a concentration below 10^{-8} M. DPV was conducted to obtain the current value that is more accurate than CV (Lee et al. 2018).

This study used a redox pair ($K_3Fe(CN)_6$) as a test device (probe). The currents generated by SPE-PU and proved by CV and DPV have shown conductivity on polyurethane films. This suggests that polyurethane films can conduct electron transfer. The electrochemical area on the modified electrode can be calculated using the formula from Randles-Sevcik (Butwong et al. 2019), where the electrochemical area for SPE-PU is considered to be A, using Equation 2:

$$\textbf{Current of SPE-PU , } I_p = 2.65 \times 10^5 \, A C n^{3/2} \, v^{1/2} D^{1/2} \qquad (2)$$

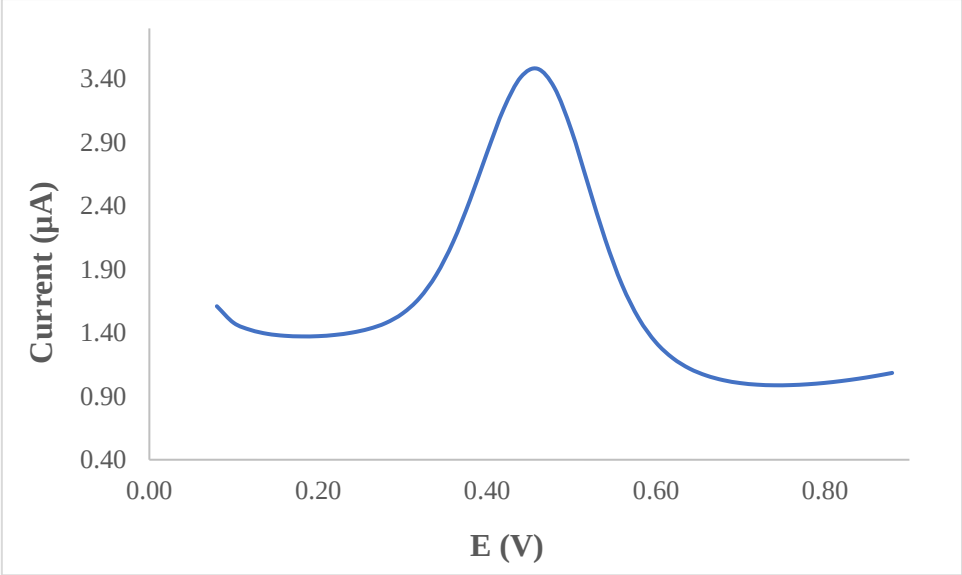

Figure 9. The voltammogram of SPE – PU modified electrode after analyzed using differential pulse voltammetry (DPV) technique

Where, n – 1 is the amount of electron transfer involved, while C is the solvent concentration used (mmol·L^{-1}) and the value of D is the diffusion constant of 5 mmol·L^{-1} at ($K_3Fe(CN)_6$) dissolved using 0.1 mmol·L^{-1} KCl. The estimated surface area of the electrode (**Figure 1**) was 0.2 cm^2 where the length and width of the electrode used during the study was 0.44 cm × 0.44 cm while the surface area of the SPE-PU was 0.25 cm^2 with the length and width of the electrode estimated at 0.5 cm × 0.5 cm, and causing the SPE-PU has a larger surface. The corresponding surface concentration (τ) (mol/cm^2) is measured using Equation 3.

$$\mathbf{I_p = (n^2 F^2 / 4RT) A\tau v} \qquad (3)$$

I_p is the peak current (A), while A is the surface area 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 constant ideal gas (8.314 J/mol K) and T is the temperature used during the experiment being conducted (298 K) (Koita et al. 2014). The application of PKOp to produce a conducting polymer will be a great prospect as this material can be employed in the analytical industry in order to modify electrodes for electrochemical purposes.

Furthermore, number of palm oils is 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 biomaterials that can be used to replace other polymers that are chemical-based (Tajao et al. 2021). 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 (Tadese et al. 2019), 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 (Khatoon & Ahmad 2017).

4. Conclusion

Polyurethane film was prepared by pre-polymerization between palm kernel oil-based polyol (PKO-p) with MDI. The presence of PEG 400 as the chain extender formed freestanding flexible film. Acetone was used as the solvent to lower the reaction kinetics since the pre-polymerization was carried out at room temperature. The formation of urethane links (NHCO – backbone) after polymerization was confirmed by the absence of N=C=O peak at 2241 cm^{-1} 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 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 polyurethane film can be used as a conducting bio-polymer 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.

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6. Conflict of Interest

The authors declare no conflict of interest.

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Comments for Reviewers

1. The reported electrical properties are misleading and incorrect. A current of 53 microamps signifies nothing on its own, and it cannot be used as the basis of a comparison of the authors' polymer with other polymers. The mentions of "conductivity" in the following sentences should be corrected or preferably the sentences should be deleted completely:

   Answer:

   The corrections have been made following the suggestion from reviewers.

2. Lines 432-435: "Nevertheless, the electroconductivity of PU in this study shows better conductivity several times compared to Bahrami et al. (2019) that reported the conductivity of PU as 1.26 x 10-6 A, whereas Li et al. (2019) reported the PU conductivity in their study was even very low, namely 10-14 A. "

   Answer:

   The corrections have been made following the suggestion from reviewers.
   So, these lines have been revised according to the reviewer's suggestions.

3. and in lines 438-440: "The application of PEG as polyol has been studied by Porcarelli et al. (2017), that reported that the conductivity of PU based on PEG – polyol was 9.2 x 10-8." (This sentence doesn't even mention the units of the reported conductivity.)

   Answer:

   The units of the reported conductivity have been added and revised based on the reviewer's suggestion.

4. The English is still poor and hard to follow in some places. This includes missing verbs, e.g. line 420 "Polyurethane film deposited" should be "Polyurethane film was deposited".; orthographic errors e.g. lines 123-125 "SPE becomes the best solution owing to its frugal manufacture, tiny size, able to produce on large-scale and can be applied for on-site detection".

   Answer:

   The grammars in this manuscript have been revised. The missing verb in Line 436 has been added.
   Lines 126-128 have been rephrased.

5. Typographic errors should be corrected e.g. line 89: change Pus to PUs; and lines 138-139 "Polyurethane is possible to become an advanced frontier material is chemically modified

electrodes." As noted by the reviewer, in line 299 "spectrums" is an incorrect word, which should change to "spectra".

Answer:

Lines 138-139 have been revised and they are shown in lines 141-143.

The spectrum words in this manuscript have been changed to spectra and the correction can be seen at lines: 250, 253, 315, and 342.

6. Also repetitious or awkward sentences should be rewritten or deleted, e.g. line 53 "The application of petroleum as a polyol in order to produce polyurethane has been applied." or lines 56-57 "These reasons have been considered and finding utilizing plants that can be used as alternative polyols should be done immediately."

Answer:

Lines 55-64 have been rephrased.

7. The sentence in lines 37-38 must be deleted; readers of IJPS don't need to be told what a polymer is! The authors are strongly advised to seek the help of a fluent English speaker when they revise their manuscript, or to use a professional scientific editing service.

Answer:

The suggestion of the reviewer has been followed.

Design and Synthesis of Conducting Polymer Bio-Based Polyurethane Produced from Palm Kernel Oil

VIEWING AN OLDER VERSION

ID 6815187

Muhammad Abdurrahman Munir SA CA [1], Khairiah Haji Badri[2], Lee Yook Heng[2]
+ Show Affiliations

Article Type

Research Article

Journal

International Journal of Polymer Science

Rydz Joanna
Submitted on 2021-06-14 (2 years ago)

> Abstract

> Author Declaration

> Files 2

— Editorial Comments

Joanna Rydz 13.02.2022

Decision

Minor Revision Requested

Message for Author

1. "bio based" is one word and should be spelled the same way throughout the text. Please correct throughout the text.
"Please correct throughout the text" means using the search option to find "bio based" throughout the text. The reviewer only has to point out what is wrong.
Please correct in lines 77 and 518.
2. Conclusion: “and the presence of N-H peak at 3300 cm-1”
N-H is also not a peak. Neither linkage is a peak.
Please correct on: “and the presence of absorption bands associated with N-H at 3300 cm-1”
Please also correct throughout the text!
3. Table 2.
The table shows the “Thermal degradation parameters determined by TGA”.
Please remove "% Weight loss (wt%) and thermal degradation (Td)" from the table and leave only two rows with variables (first) and data (second).
Thermogravimetric analysis is measurement of thermal stability of materials. In this method, changes in the weight of a specimen are measured while its temperature is increased. It does not need to be written in the row of table.
In this section (d. The thermal analysis), the authors write both mass and weight. Please change everything to mass.
Line 369 "Tmax: The temperature of polyurethane started to degrade"
Tmax represents the temperature at the maximum mass-loss rate. "The temperature of material started to degrade" is onset temperature usually given for 5% (T5%) because it is difficult to accurately determine the beginning (Tonset). What temperature did the authors mean?
The authors rightly speak of "individual mass steps"
Td1 is probably temperature at the first onset or at the first Tmax (at the first mas loss step).
Please use the IUPAC nomenclature and correctly present and describe the TGA variables (https://www.degruyter.com/database/iupac/html).

− Response to Revision Request

Muhammad Abdurrahman Munir 13.02.2022

Your Reply

Dear Dr. Joanna, Thank you for your comments and we have done revisions based on your comments above. Nevertheless, for the comment no. 6, we want to elaborate about the Tmax, where according to Figure 7. DTG thermogram of PU film, Page 19. The temperature was started to degrade at 240 C, that's why we called it as Tmax. So, the Td1, Td2 and Td3 in this manuscript are the thermal degradation

that we have plotted based on the specific region. However, if the revisions we have made are not sufficient, please guide us to improve this manuscript so it can be pubslished to this Journal. We are looking forward to hear from you. Best Regards.

File

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Design and Synthesis of Conducting Polymer Based on Polyurethane Produced from Palm Kernel Oil

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Abstract

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 film 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

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Bio-based or for medical purpose? The title given should be bio-based. Please correct.

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the SPE surface. The synthesized 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 electro-catalytic 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 N=C=O peak at 2241 cm^{-1}. The glass transition temperature of the polyurethane was detected at 78.1 °C.

Keywords: polyurethane, polymerization, screen-printed electrode, voltammetry

1. Introduction

Conducting polymers (CPs) are polymers that can release a current (Alqarni et al. 2020). The conductivity of CPs was first observed in polyacetylene, nevertheless owing to its instability, the invention of various CPs have 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 semi-conductive. Therefore, it is imperative to improve their conductivity for electrochemical sensor purposes (Sengodu & Deshmukh 2015; Dzulkipli et al. 2021; Wang et al. 2018). 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, 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

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Commented [j5]: N=C=O is not a peak. Functional groups give characteristic signals in a spectrum. Please use scientific language throughout your text and please describe the FTIR spectra properly.

Commented [MAM6R5]: Thank you for your suggestion. Nevertheless, the reading of this spectrum based on Spectroscopy book 4th Edition by Lampman et al. It is written on Page 29, 77 and 78 (Figure 2.64) about the spectrum of N=C=O.
According to their research, the isocyanates have *sp*-hydridized carbon atoms similar to the C≡C bond. The absorption occurs in 2100-2270 cm^{-1}.

Commented [j7]: What do "natural CPs" mean? Natural polymers occurring in nature?

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This paper has studied about the natural polymer and the synthetic polymer.

applications, electrochromic devices, and solar cells (Alqarni et al. 2020; Ghosh et al. 2018). There is scientific documentation on the use of conductive polymers in various studies such as polyaniline (Pan & Yu 2016), polypyrrole (Ladan et al. 2017), and polyurethane (Tran et al. 2020; Vieira et al. 2020; Guo et al. 2020; Fei et al. 2020).

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 (Badri 2012). 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 (Badri 2012; Borowicz et al. 2019).

It is very straightforward for vegetable oils to react with a specific group to produce a PU such as epoxy, hydroxyl, carboxyl, and acrylate owing to the existence of (-C=C-) in vegetable oils. Thus, it provides appealing profits to vegetable oils compared to petroleum considering the toxicity, price, and harm to the environment (Mustapha et al. 2019; Mohd Noor et al. 2020). 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 profits 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 CO_2 from the atmosphere as a net sequester (Tajau et al. 2021; Septevani et al. 2015).

The application of bio-based polymer has appealed much attention until now. Global environmental activists have forced researchers to discover another material producing polymers (Priya et al. 2018). 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 (Zia et al. 2014; Romaskevic et al. 2006). Polyurethanes are also considered to be one of the most useful materials with many profits 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 (Badan & Majka 2017; Munir et al. 2021).

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) and 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 (Akindoyo et al. 2016).

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 (Janpoung et al, 2020; Su'ait et al. 2014), majorly contributed by the isocyanate derivatives. PUs have also a conjugate

Commented [j9]: Authors should be careful when using the prefix "bio", as it gives words a strictly defined meaning (biopolymers, bioplastics, biomaterials). According IUPAC biopolymers are macromolecules formed by living organisms (including proteins, nucleic acids and polysaccharides). The authors, however, probably mean something else. Please correct.

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structure where electrons can move in the main chain that causes electricity produced even the current is low. The current of conjugated linear (π) 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 (Wang et al. 2017; Kotal et al. 2011).

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 users and environment (Kilele et al. 2020; Inayatullah et al. 2021; Munir et al. 2021; Harmayani et al. 2014; Nurwanti et al. 2018). 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 (Chokkareddy et al. 2020). 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 (Chokkareddy et al. 2020; Kilele et al. 2021). 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 (Degefu et al. 2014; Munir et al. 2022).

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 (Nakthong et al. 2020). Conducting polymers (CPs) become an alternative to modifying the screen-printed electrodes due to their electrical conductivity, able to capture analyte by chemical/physical adsorption, large surface area, and making CPs are very appealing materials from electrochemical perspectives (Baig et al. 2019). 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 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 electro behavior 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 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

Synthesis of polyurethane film: Palm kernel oil (PKOp) based polyol supplied by UKM Technology Sdn Bhd through MPOB/UKM station plant, Pekan Bangi Lama, Selangor and prepared using Badri et al. (2000) method. 4, 4-diphenylmethane diisocyanate (MDI) was

Commented [j15]: Is this palm kernel oil-based polyol? Please select one writing option also for the abbreviation. There are 3 types in the text. And please explain the abbreviation only once. This applies to all abbreviations. Please correct it throughout.

Commented [MAM16R15]: Yes, the Palm Kernel Oil acts as polyol for this study.
The revisions have been followed.

acquired from Cosmopolyurethane (M) Sdn. Bhd., Klang, Malaysia. Solvents and analytical reagents were benzene, toluene, hexane, acetone, dimethylsulfoxide (DMSO), dimethylformamide (DMF), tetrahydrofuran (THF), (the purity of solvents is ≥ 99.8%), and polyethylene glycol (PEG) with a molecular weight of 400 Da obtained from Sigma Aldrich Sdn Bhd, Shah Alam.

Commented [j17]: Different purity?

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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 °C/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 °C /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 film 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 film was coated with a thin layer of gold to increase the conductivity of the film. The coating method was carried out using a sputter-coater. The observations were conducted at a magnification of 200× and 5000× with 10.00 kV (Electron high tension – EHT).

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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 as the gel content can be calculated using Equation (1).

$$\text{Gel content (\%)} = \frac{W_o - W}{W} \text{ x } 100\ \% \qquad (1)$$

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 (DATR) method to confirm the polyurethane, PKOp, 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), 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.

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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 ± 2 °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 palm-based pre-polyurethane was dropped separately onto the surface of the SPE 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.

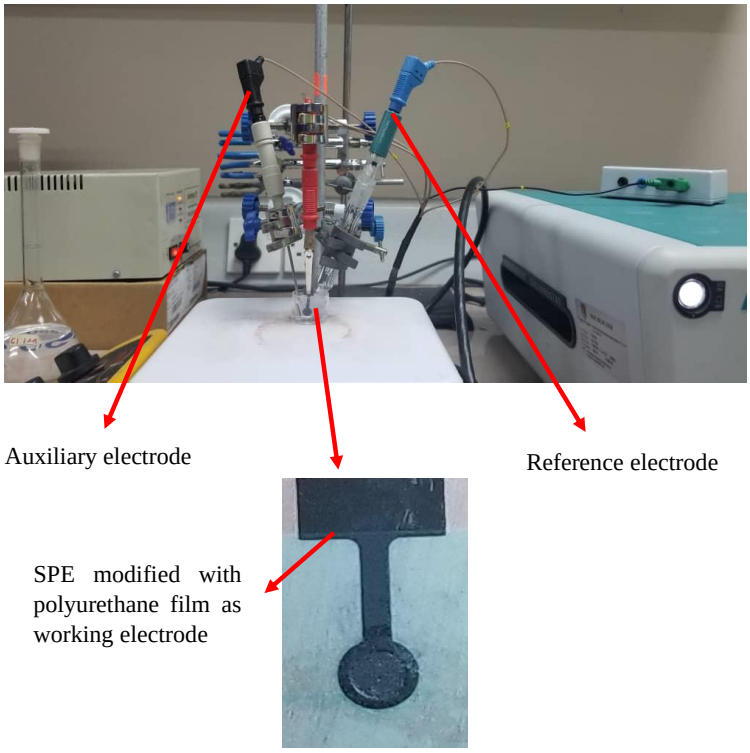


Figure 1. Potentiostat instrument to study the conductivity of SPE modified with polyurethane film using voltammetric approach: CV and DPV

3. Results and Discussion

The synthesis of PU films was carried out using a pre-polymerization method which involves the formation of urethane polymer at an early stage. The reaction took place between

237 diisocyanate (MDI) and palm kernel oil-based polyol. **Table 1** presents the PKO-p properties
238 used in this study.

239 **Table 1** The specification of PKO-p (Badri et al. (2000)).

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

240

241 The structural chain was extended with the aid of poly(ethylene glycol) to form flexible and
242 elastic polyurethane film. In order to produce the urethane prepolymer, the isocyanate group (-
243 NCO) attacks with the hydroxyl group (-OH) of polyol (PKOp) while the other hydroxyl group
244 of the polyol is attacked by the other isocyanate group (Wong & Badri 2012) as shown in
245 **Figure 2**.

246

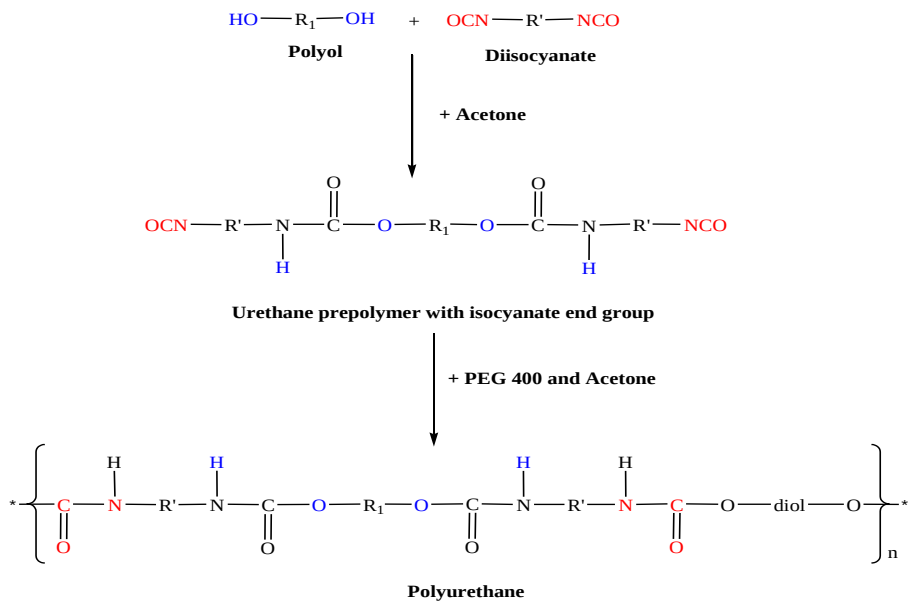
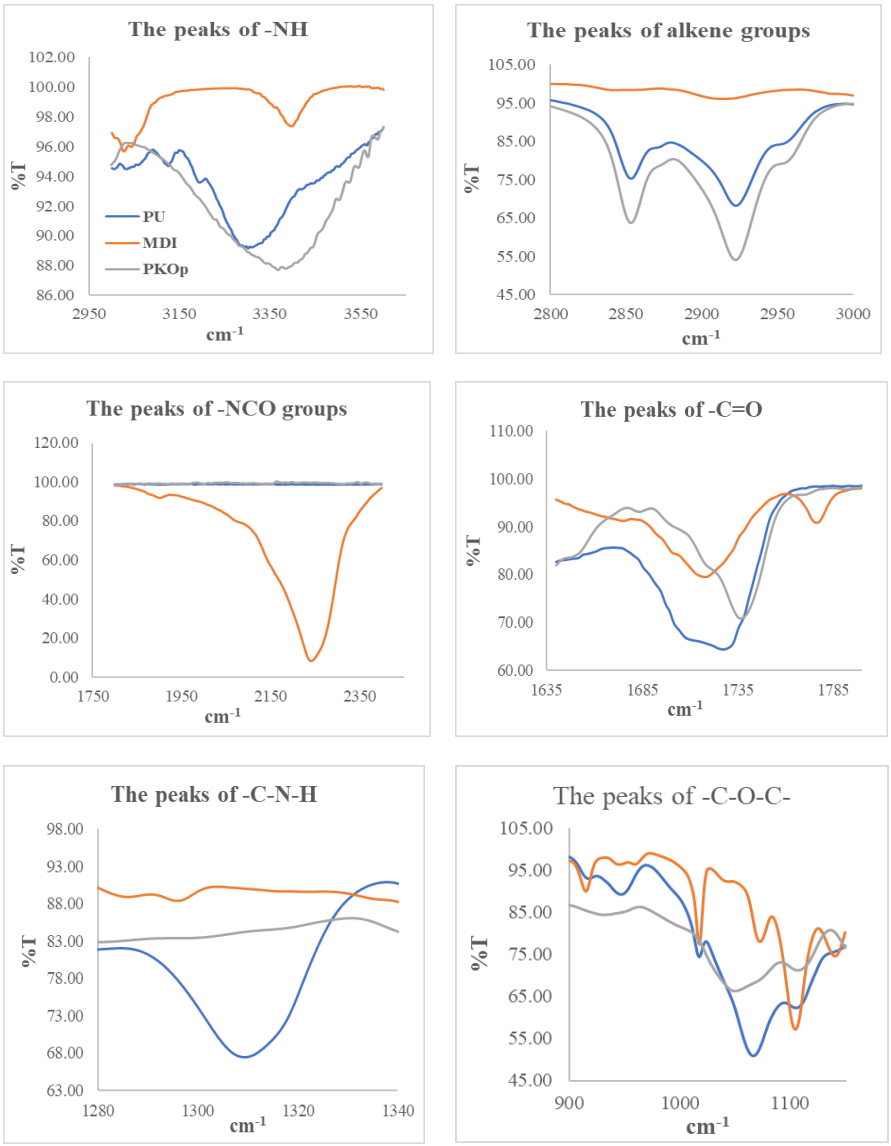


Figure 2. PU production via the pre-polymerization method (Wong & Badri 2012).

a. FTIR analysis

Figure 3 shows the FTIR spectra for polyurethane, exhibiting the important functional group peaks. According to a study researched by Wong & Badri 2012, PKO-p reacts with MDI to form urethane prepolymers. The NCO group on MDI reacts with the OH group on polyol whether PKOp 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 a peak 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.



262 **Figure 3.** FTIR spectra of several important peaks between polyurethane, PKO-p, and MDI

263

264 The reaction of polyurethane has been studied by Hamuzan & Badri (2016) where the urethane

265 carbonyl group was detected at 1730–1735 cm^{-1} while the MDI carbonyl was detected at 2400

266 cm^{-1}. The absence of peaks at 2250–2270 cm^{-1} indicates the absence of NCO groups. It shows
267 that the polymerization reaction occurs entirely between NCO groups in MDI with hydroxyl
268 groups on polyols and PEG (Mishra et al. 2012). The absence of peaks at 1690 cm^{-1}
269 representing urea (C=O) in this study indicated, there is no urea formation as a byproduct
270 (Clemitson 2008) of the polymerization reaction that possibly occurs due to the excessive
271 water. For the amine (-NH) group, hydrogen-bond to -NH and oxygen to form ether and
272 hydrogen bond to NH and oxygen to form carbonyl on urethane can be detected at the peak of
273 3301 cm^{-1} and in the wavenumber at range 3326–3428 cm^{-1}. This has also been studied and
274 detected by Mutsuhisa et al. (2007) and Lampman et. al. (2010). In this research, the proton
275 acceptor is carbonyl (-C=O) while the proton donor is an amine (-NH) to form a hydrogen
276 bond. The MDI chemical structure has the electrostatic capability that produces dipoles from
277 several atoms such as hydrogen, oxygen, and nitrogen atoms. These properties make
278 isocyanates are highly reactive, and have different properties (Leykin et al. 2016).
279
280 MDI was one of the isocyanates used in this study, has an aromatic group, and is more
281 reactive compared to aliphatic group isocyanates such as hexamethylene diisocyanate (HDI)
282 or isophorone diisocyanate (IPDI). Isocyanates have two groups of isocyanates on each
283 molecule. Diphenylmethane diisocyanate is an exception owing to its structure consisting of
284 two, three, four, or more isocyanate groups (Nohra et al. 2013). The use of PEG 400 in this
285 study as a chain extender for polyurethane increases the chain mobility of polyurethane at an
286 optimal amount. The properties of polyurethane are contributed by hard and soft copolymer
287 segments of both polyol monomers and MDI. This makes the hard segment of urethane serves
288 as a crosslinking site between the soft segments of the polyol (Leykin et al. 2016).
289
290

The mechanism of the pre-polymerization in urethane chains formation is a nucleophilic substitution reaction as studied by Yong et al. (2009). 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 who have conducted by Wong and Badri (2012).

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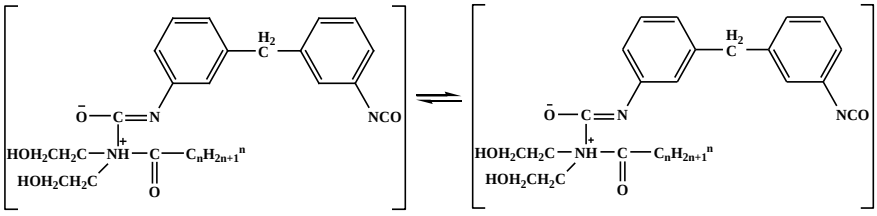

Intermediate complex A Intermediate complex B

Figure 4. The formation of intermediate complexes

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 cross-linking content gives the polymer elastic properties whereas short-chain and high cross-linking produce hard and rigid polymers. Cross-linking in polymers consists of three-dimensional networks with high molecular weight. In some aspects, polyurethane can be a macromolecule, a giant molecule (Petrovic 2008).

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 PKOp chemical structure causing the reaction of nucleophilic substitution that occurs in PKOp. Furthermore, amine has a higher probability

of reacting compared to hydroxyl (Herrington & Hock 1997). Amine with high alkalinity reacts with carbon atoms on MDI as proposed by Wong and Badri (2012).

The production of intermediate complexes unstabilizes the alkyl ions, nevertheless, the long carbon chains of PKOp 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 by-product after the NCO group reacts with H_2O 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 film as we studied the film.

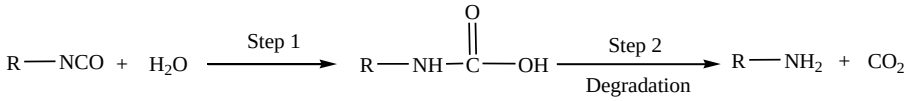

Figure 5. The reaction between the NCO group and water producing carbon dioxide

Furthermore, the application of PEG can influence the conductivity of PU whereby Porcarelli et al. (2017) 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 $g \cdot mol^{-1}$ tends to crystallize with deleterious effects on room temperature ionic conductivity (Porcarelli et al. 2017).

b. Morphological analysis

The field emission scanning electron microscope micrograph in **Figure 6** shows the formation of a uniform polymer film contributed by the polymerization method applied. The magnification used for this surface analysis ranged from 200 to 5000×. 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 justified by the wavelengths obtained by the FTIR spectra above.

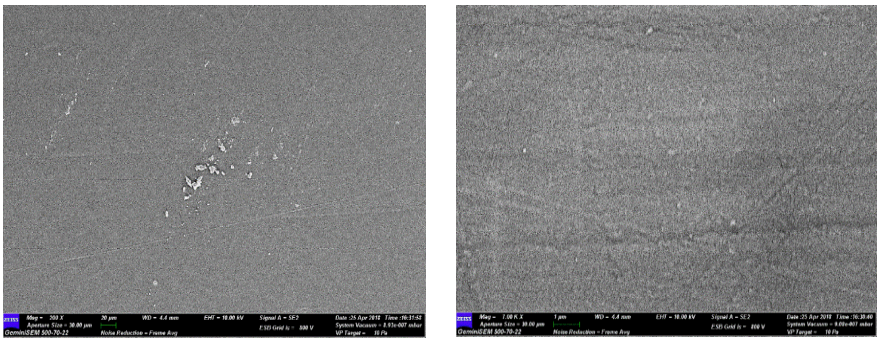

Figure 6. The micrograph of polyurethane films was analyzed by FESEM at (a) 200× and (b) 5000× magnifications.

c. 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 (Cuve & Pascault 1991). 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 (Rogulska et al. 2007).

$$\text{Gel content (\%)} = \frac{(0.6 - 0.301)\ \text{g}}{0.301\ \text{g}} \times 100\% = 99.33\%$$

d. 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 materials 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 heights of the individual mass steps (Alamawi et al. 2019). **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.

Table2 Weight loss percentage of (*wt%*) polyurethane film

Sample	% Weight loss (*wt%*)				Total of weight loss (%)	Residue after 550 ℃ (%)
	$T_{max.}$ (℃)	T_{d1}, 200– 90 ℃	T_{d2}, 350–500 ℃	T_{d3}, 500–550 ℃		
Polyurethane	240	8.04	39.29	34.37	81.7	18.3

The bio polyurethane is thermally stable up to 240 ℃ before it has undergone thermal degradation (Agrawal et al. 2017). 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 polyol chains and releasing of isocyanates (Berta et al. 2006), primary and secondary amines as well as carbon dioxide (Corcuera et al. 2011; Pan & Webster 2012). Meanwhile, the 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 CO_2. The formed carbodiimide reacts with alcohol to form urea. The third stage of

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thermal degradation (T_{d3}) is related to the degradation of urea (Berta et al. 2006) and the soft segment on polyurethane.

Generally, DSC analysis exhibited thermal transitions as well as the initial crystallization and melting temperatures of the polyurethane (Khairuddin et al. 2018). It serves 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 film 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. (2017). 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. (2017) stated that possessing a low T_g may contribute to PU conductivity.

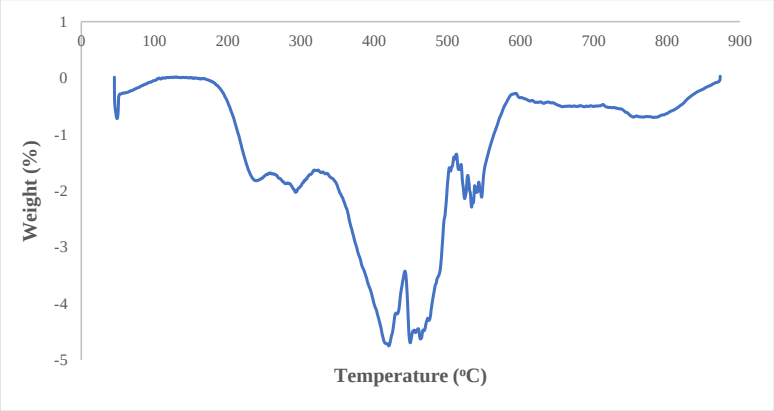

Figure 7. DTG thermogram of polyurethane film

During polymerization, this hard segment restricts the mobility of the polymer chain (Ren et al. 2013) 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, it was detected in the DSC thermogram nor the TGA thermogram, which indicates that acetone was removed from the polyurethane during the synthesis process, owing to its volatile nature. The presence of acetone in the synthesis was to lower the reaction kinetics.

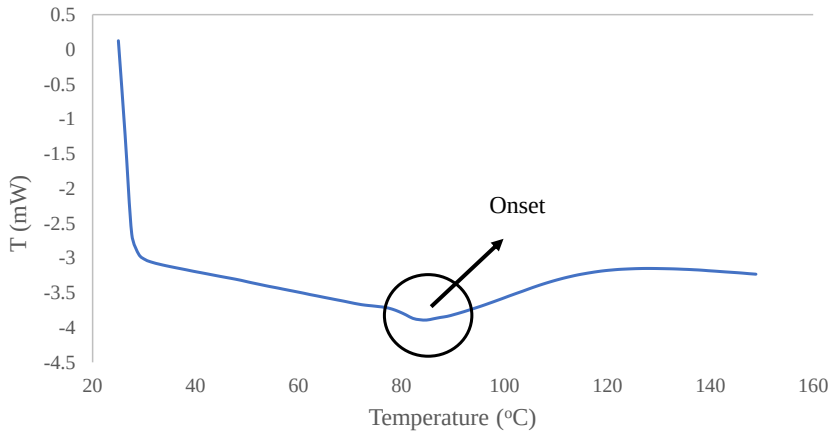

Figure 8. DSC thermogram of polyurethane film

e. 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 film solubility and tensile test are shown in **Table 3**. Polyurethane films 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.

Table 3 The solubility and mechanical properties of the polyurethane film

Parameters		Polyurethane film
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

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.

f. 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 $mmol \cdot L^{-1}$ KCl solution containing 5 $mmol \cdot L^{-1}$ ($K_3Fe(CN)_6$). 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 $V \cdot s^{-1}$. 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 polyol. The electrochemical signal at the electrode is low if there is a decrease in electrochemical conductivity (El - Raheem et al. 2020). It can be concluded that polyurethane is a bio-polymer with a low current value. The current of the modified electrode was found at 5.3 x 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 x 10^{-6} A, whereas Li et al. (2019) 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 (Wong et al. 2014). The PU can also release a current caused by PEG. The application of PEG as polyol has been studied by Porcarelli et al. (2017), that reported that the current of PU based on PEG – polyol was 9.2 x 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, 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.

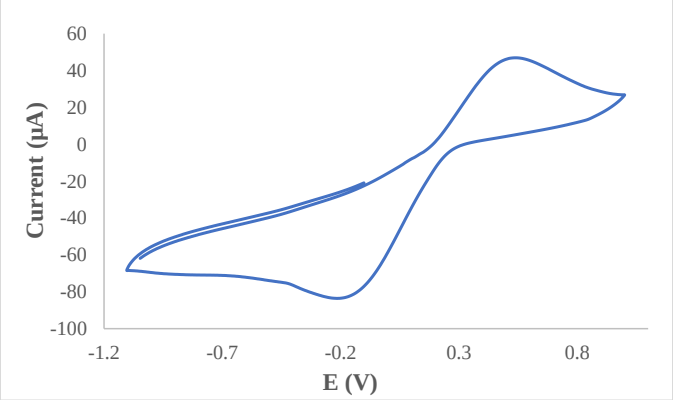

Figure 9. The voltammogram of SPE-PU modified electrode after analyzed using cyclic voltammetry technique

Figure 10 also presents the DPV voltammogram of the modified electrode. DPV is a measurement based on the difference in potential pulses that produce an electric current. Scanning the capability pulses to the working electrode will produce different currents. Optimal peak currents will be produced to the reduction capacity of the redox material. The peak current produced is proportional to the concentration of the redox substance and can be detected up to a concentration below 10^{-8} M. DPV was conducted to obtain the current value that is more accurate than CV (Lee et al. 2018).

This study used a redox pair ($K_3Fe(CN)_6$) as a test device (probe). The currents generated by SPE-PU and proved by CV and DPV have shown conductivity on polyurethane films. This suggests that polyurethane films can conduct electron transfer. The electrochemical area on the modified electrode can be calculated using the formula from Randles-Sevcik (Butwong et al. 2019), where the electrochemical area for SPE-PU is considered to be A, using Equation 2:

$$\textbf{Current of SPE-PU, } I_p = 2.65 \times 10^5 \, A C n^{3/2} \, v^{1/2} D^{1/2} \qquad (2)$$

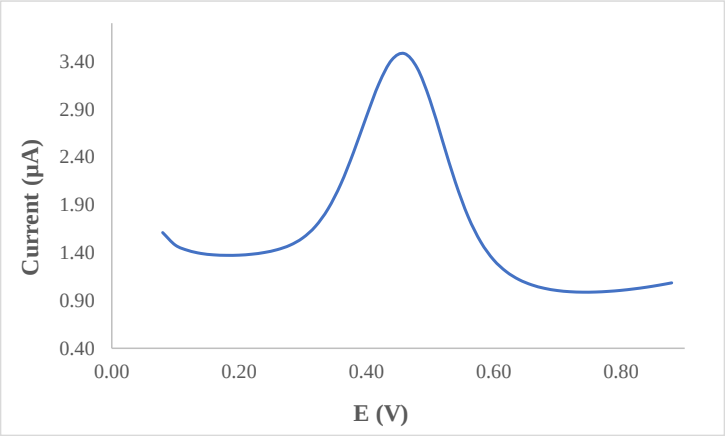

Figure 10. The voltammogram of SPE – PU modified electrode after analyzed using differential pulse voltammetry technique

Where, n – 1 is the amount of electron transfer involved, while C is the solvent concentration used (mmol·L^{-1}) and the value of D is the diffusion constant of 5 mmol·L^{-1} at ($K_3Fe(CN)_6$) dissolved using 0.1 mmol·L^{-1} KCl. The estimated surface area of the electrode (**Figure 1**) was 0.2 cm^2 where the length and width of the electrode used during the study was 0.44 cm × 0.44 cm while the surface area of the SPE-PU was 0.25 cm^2 with the length and width of the electrode estimated at 0.5 cm × 0.5 cm, and causing the SPE-PU has a larger surface. The corresponding surface concentration (τ) (mol/cm^2) is measured using Equation 3.

$$\mathbf{I_p = (n^2 F^2 / 4RT) A\tau v} \qquad (3)$$

I_p is the peak current (A), while A is the surface area 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 constant ideal gas (8.314 J/mol K) and T is the temperature used during the experiment being conducted (298 K) (Koita et al. 2014). The application of PKOp to produce a conducting polymer will be a great prospect as this material can be employed in the analytical industry in order to modify electrodes for electrochemical purposes.

Furthermore, number of palm oils is 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 biomaterials that can be used to replace other polymers that are chemical-based (Tajao et al. 2021). 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 (Tadese et al. 2019), 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 (Khatoon & Ahmad 2017).

4. Conclusion

Polyurethane film was prepared by pre-polymerization between palm kernel oil-based polyol (PKO-p) with MDI. The presence of PEG 400 as the chain extender formed freestanding flexible film. Acetone was used as the solvent to lower the reaction kinetics since the pre-polymerization was carried out at room temperature. The formation of urethane links (-NHC(O) backbone) after polymerization was confirmed by the absence of N=C=O peak at 2241 cm^{-1} 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 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 polyurethane film can be used as a conducting bio-polymer and it is very useful for

513 other studies such as electrochemical sensor purposes. Furthermore, advanced technologies are
514 promising and the future of bio-based polyol looks very bright.
515
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521
522 **6. Conflict of Interest**
523 The authors declare no conflict of interest.
524
525 **7. References**
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Design and Synthesis of Conducting Polymer Bio-Based Polyurethane Produced from Palm Kernel Oil

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Abstract

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 film 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 electro-catalytic 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-hydridized carbons atoms of C≡C bonds . The glass transition temperature of the polyurethane was detected at 78.1 °C.

Keywords: polyurethane, polymerization, screen-printed electrode, voltammetry

1. Introduction

Conducting polymers (CPs) are polymers that can release a current (Alqarni et al. 2020). The conductivity of CPs was first observed in polyacetylene, nevertheless owing to its instability, the invention of various CPs have 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 semi-conductive. Therefore, it is imperative to improve their conductivity for electrochemical sensor purposes (Sengodu & Deshmukh 2015; Dzulkipli et al. 2021; Wang et al. 2018). 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, 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 (Alqarni et al. 2020; Ghosh et al. 2018). There is scientific documentation on the use of conductive polymers in various studies such as polyaniline (Pan & Yu 2016), polypyrrole (Ladan et al. 2017), and polyurethane (Tran et al. 2020; Vieira et al. 2020; Guo et al. 2020; Fei et al. 2020).

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 (Badri 2012). 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 (Badri 2012; Borowicz et al. 2019).

It is very straightforward for vegetable oils to react with a specific group to produce a PU such as epoxy, hydroxyl, carboxyl, and acrylate owing to the existence of (-C=C-) in vegetable oils. Thus, it provides appealing profits to vegetable oils compared to petroleum considering the toxicity, price, and harm to the environment (Mustapha et al. 2019; Mohd Noor et al. 2020). 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 profits 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 CO_2 from the atmosphere as a net sequester (Tajau et al. 2021; Septevani et al. 2015).

The application of bio based polymer has appealed much attention until now. Global environmental activists have forced researchers to discover another material producing polymers (Priya et al. 2018). 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 (Zia et al. 2014; Romaskevic et al. 2006). Polyurethanes are also considered to be one of the most useful materials with many profits 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 (Badan & Majka 2017; Munir et al. 2021).

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) and 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 (Akindoyo et al. 2016).

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 (Janpoung et al, 2020; Su'ait et al. 2014), majorly 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 (π) 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 (Wang et al. 2017; Kotal et al. 2011).

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 users and environment (Kilele et al. 2020; Inayatullah et al. 2021; Munir et al. 2021; Harmayani et al. 2014; Nurwanti et al. 2018). 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 (Chokkareddy et al. 2020). 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 (Chokkareddy et al.

2020; Kilele et al. 2021). 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 (Degefu et al. 2014; Munir et al. 2022).

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 (Nakthong et al. 2020). Conducting polymers (CPs) become an alternative to modifying the screen-printed electrodes due to their electrical conductivity, able to capture analyte by chemical/physical adsorption, large surface area, and making CPs are very appealing materials from electrochemical perspectives (Baig et al. 2019). 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 electro behavior 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 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

Synthesis of bio-based polyurethane film: Palm kernel oil (PKOp) based polyol supplied by UKM Technology Sdn Bhd through MPOB/UKM station plant, Pekan Bangi Lama, Selangor and prepared using Badri et al. (2000) method. 4, 4-diphenylmethane diisocyanate (MDI) was acquired from Cosmopolyurethane (M) Sdn. Bhd., Klang, Malaysia. Solvents and analytical reagents were benzene (≥99.8%), toluene (≥99.8%), hexane (≥99%), acetone (≥99%), dimethylsulfoxide (DMSO) (≥99.9%), dimethylformamide (DMF) (≥99.8%), tetrahydrofuran (THF) (≥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 °C/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 °C /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 film 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 film was coated with a thin layer of gold to increase the conductivity of the film. The coating method was carried out using a sputter-coater. The observations were conducted at a magnification of 200× and 5000× 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 as the gel content can be calculated using Equation (1).

$$\text{Gel content } (\%) = \frac{W_o - W}{W} \text{ x } 100\ \% \qquad (1)$$

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 (DATR) method to confirm the polyurethane, PKOp, 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

198 formation of the polymer such as amide group (-NH), urethane carbonyl group (-C=O),
199 isocyanate group (-O=C=N-), and carbamate group (-CN).
200
201 **2.3 Synthesis of Polyurethane**
202 Firstly, the polyol prepolymer solution was produced by combining palm kernel oil-based
203 polyol and poly(ethylene glycol) (PEG) 400 (100:40 g/g), acetone 30% was used as a solution.
204 The compound was homogenized using a centrifuge (100 rpm) for 5 min. Whereas diisocyanate
205 prepolymer was obtained by mixing 4,4'-diphenylmethane diisocyanate (100 g) to acetone
206 30%, afterward the mixture was mixed using a centrifuge for 1 min to obtain a homogenized
207 solution. Afterward, diisocyanate solution (10 g) was poured into a container that contains
208 polyol prepolymer solution (10 g) slowly to avoid an exothermic reaction occurring. The
209 mixture was mixed for 30 sec until a homogenized solution was acquired. Lastly, the
210 polyurethane solution was poured on the electrode surface by using the casting method and
211 dried at ambient temperature for 12 h.
212
213 **2.4 Modification of Electrode**
214 Voltammetric tests were performed using Metrohm Autolab Software (**Figure 1**) analyzer
215 using cyclic voltammetry method or known as amperometric mode and differential pulse
216 voltammetry. All electrochemical experiments were carried out using screen-printed electrode
217 (diameter 3 mm) modified using polyurethane film as working electrode, platinum wire as the
218 auxiliary electrode, and Ag/AgCl electrode as a reference electrode. All experiments were
219 conducted at a temperature of 20 ± 2 °C.
220
221 The PU was cast onto the screen-printed electrode (SPE) and analyzed using a single
222 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 bio-based polyurethane was dropped separately onto the surface of the SPE 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.

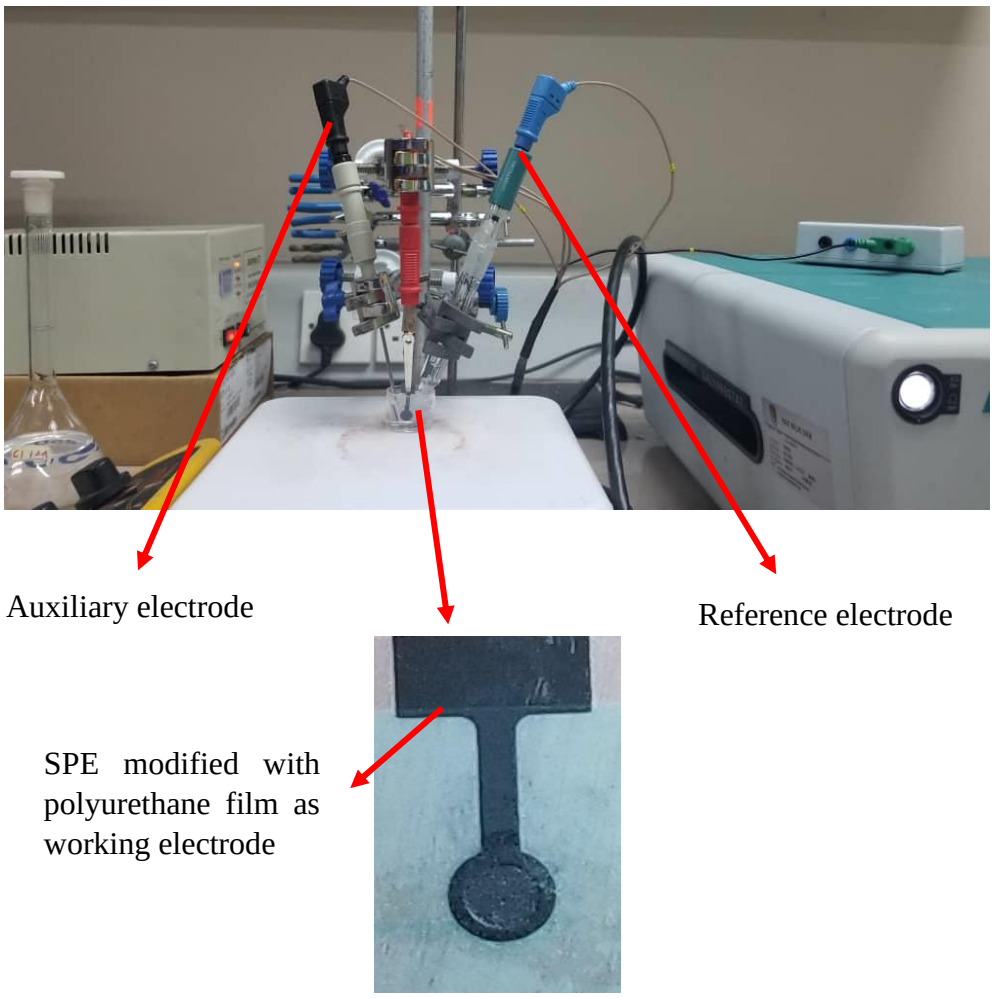


Figure 1. Potentiostat instrument to study the conductivity of SPE modified with polyurethane film using voltammetric approach: CV and DPV

3. Results and Discussion

The synthesis of PU films was carried out using a pre-polymerization 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.

Table 1 The specification of PKO-p (Badri et al. (2000)).

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

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 (PKOp) while the other hydroxyl group of the polyol is attacked by the other isocyanate group (Wong & Badri 2012) as shown in **Figure 2**.

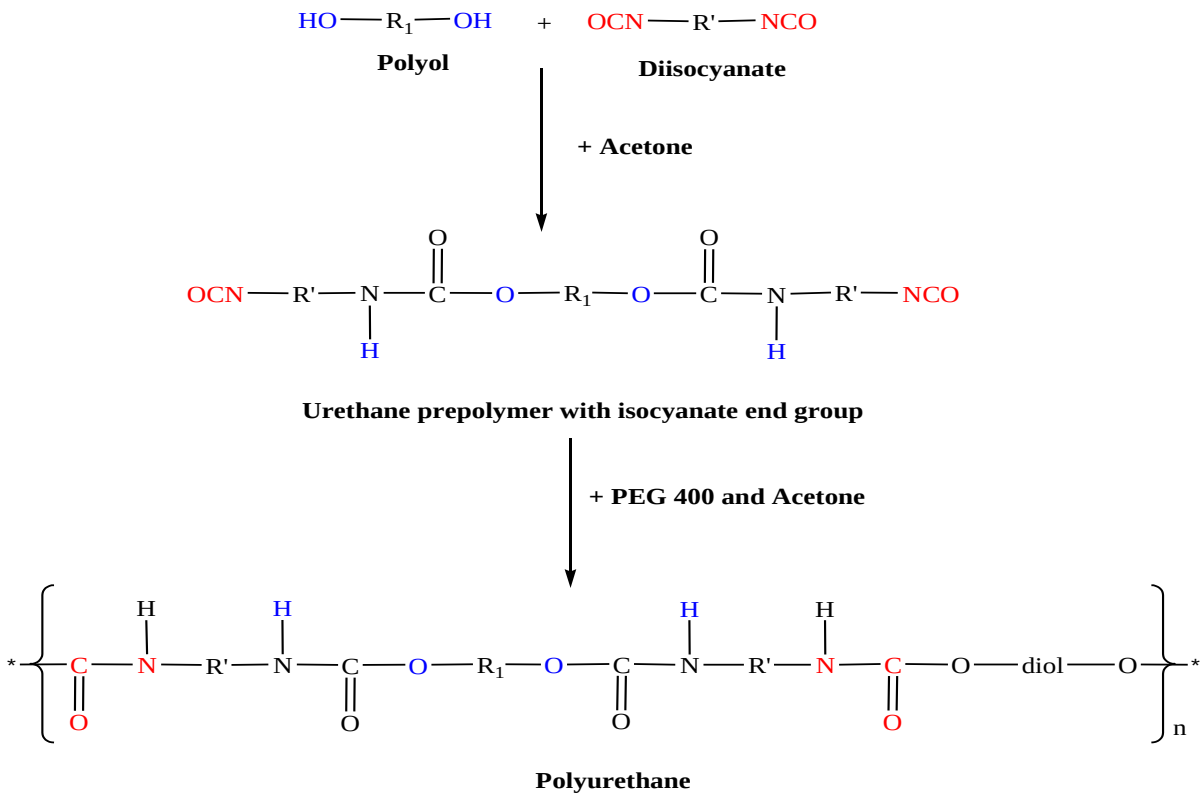
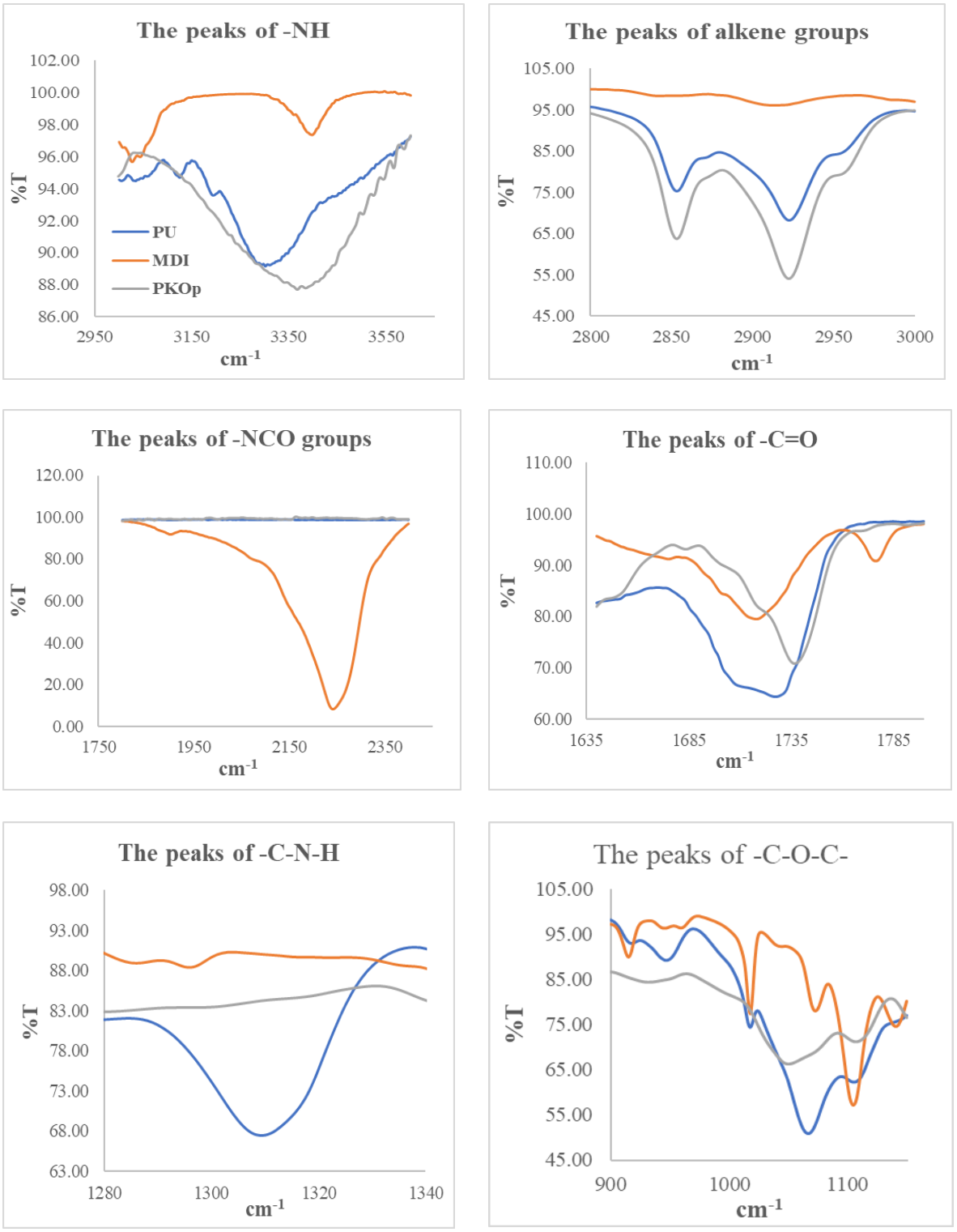


Figure 2. PU production via the pre-polymerization method (Wong & Badri 2012).

a. FTIR analysis

Figure 3 shows the FTIR spectra for polyurethane, exhibiting the important functional group peaks. According to a study researched by Wong & Badri 2012, PKO-p reacts with MDI to form urethane prepolymers. The NCO group on MDI reacts with the OH group on polyol whether PKOp 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.



263 **Figure 3.** FTIR spectra of several important peaks between polyurethane, PKO-p, and MDI

264

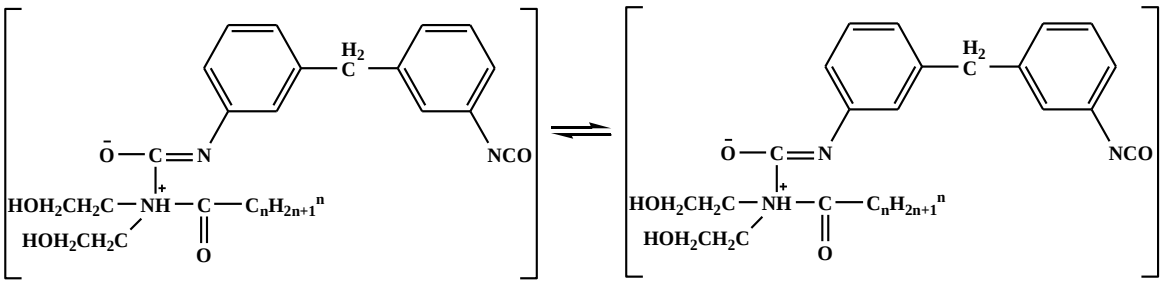
265 The reaction of polyurethane has been studied by Hamuzan & Badri (2016) where the urethane

266 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 polyols and PEG (Mishra et al. 2012). The absence of peaks at 1690 cm^{-1} representing urea (C=O) in this study indicated, there is no urea formation as a byproduct (Clemitson 2008) 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 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. (2007) and Lampman et. al. (2010). 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. These properties make isocyanates are highly reactive, and have different properties (Leykin et al. 2016).

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 (Nohra et al. 2013). 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 (Leykin et al. 2016).

The mechanism of the pre-polymerization in urethane chains formation is a nucleophilic substitution reaction as studied by Yong et al. (2009). 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 who have conducted by Wong and Badri (2012).



Intermediate complex A Intermediate complex B

Figure 4. The formation of intermediate complexes

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 cross-linking content gives the polymer elastic properties whereas short-chain and high cross-linking produce hard and rigid polymers. Cross-linking in polymers consists of three-dimensional networks with high molecular weight. In some aspects, polyurethane can be a macromolecule, a giant molecule (Petrovic 2008).

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 PKOp chemical structure causing the reaction

of nucleophilic substitution that occurs in PKOp. Furthermore, amine has a higher probability of reacting compared to hydroxyl (Herrington & Hock 1997). Amine with high alkalinity reacts with carbon atoms on MDI as proposed by Wong and Badri (2012).

The production of intermediate complexes unstabilizes the alkyl ions, nevertheless, the long carbon chains of PKOp 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 by-product after the NCO group reacts with H_2O 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 film as we studied the film.

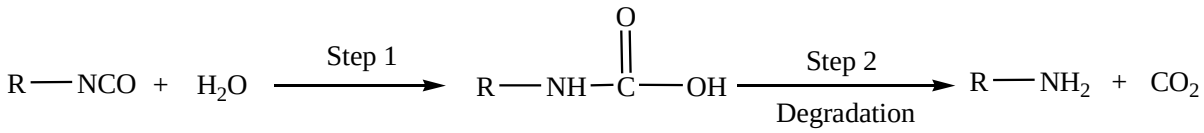


Figure 5. The reaction between the NCO group and water producing carbon dioxide

Furthermore, the application of PEG can influence the conductivity of PU whereby Porcarelli et al. (2017) 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 $g \cdot mol^{-1}$ tends to crystallize with deleterious effects on room temperature ionic conductivity (Porcarelli et al. 2017).

b. Morphological analysis

The field emission scanning electron microscope micrograph in **Figure 6** shows the formation of a uniform polymer film contributed by the polymerization method applied. The

magnification used for this surface analysis ranged from 200 to 5000×. 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 justified by the wavelengths obtained by the FTIR spectra above.

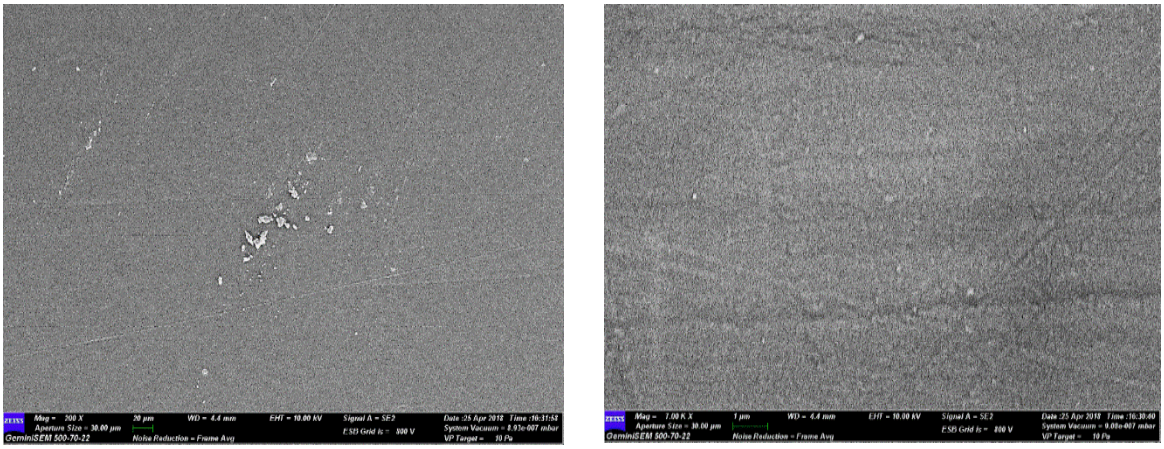


Figure 6. The micrograph of polyurethane films was analyzed by FESEM at (a) 200× and (b) 5000× magnifications.

c. 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 (Cuve & Pascault 1991). 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 (Rogulska et al. 2007).

$$\text{Gel content (\%)} = \frac{(0.6 - 0.301)\ \text{g}}{0.301\ \text{g}} \times 100\% = 99.33\%$$

d. 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 materials 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 heights of the individual mass steps (Alamawi et al. 2019). **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.

Table 2 Weight loss percentage (*wt%*) and thermal degradation (T_d) of polyurethane film

% Weight loss (*wt%*) and thermal degradation (T_d)				Total of weight loss (%)	Residue after 550 °C (%)
$T_{max,}$ (°C)	T_{d1}, 200–290 °C	T_{d2}, 350–500 °C	T_{d3}, 500–550 °C		
240	8.04	39.29	34.37	81.7	18.3

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 thermal degradation (Agrawal et al. 2017). 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 polyol chains and releasing of isocyanates (Berta et al. 2006), primary and secondary amines as well as carbon dioxide (Corcuera et al. 2011; Pan & Webster 2012). Meanwhile, the 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 CO_2. The formed carbodiimide reacts with alcohol to form urea. The third stage of

thermal degradation (T_{d3}) is related to the degradation of urea (Berta et al. 2006) and the soft segment on polyurethane.

Generally, DSC analysis exhibited thermal transitions as well as the initial crystallization and melting temperatures of the polyurethane (Khairuddin et al. 2018). It serves 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 film 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. (2017). 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. (2017) stated that possessing a low T_g may contribute to PU conductivity.

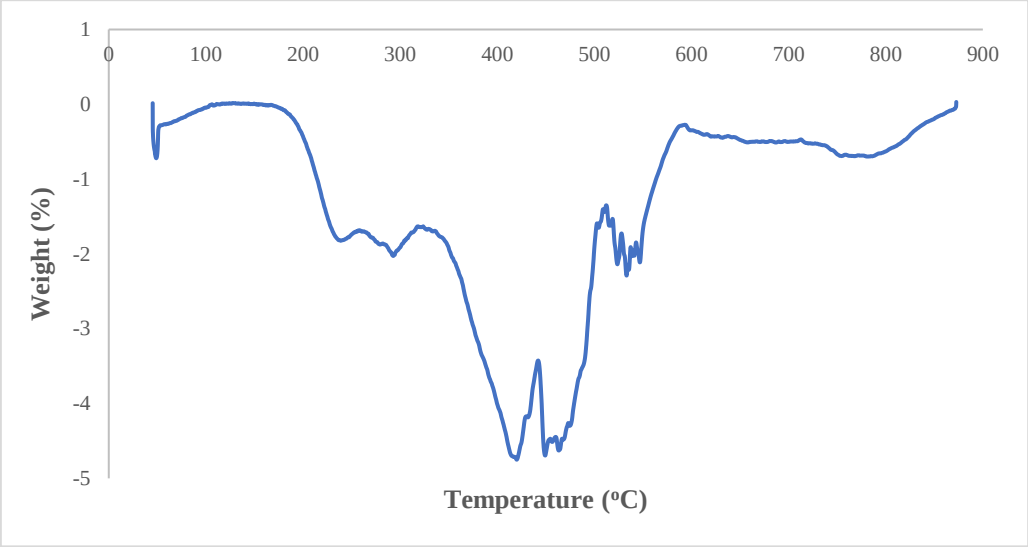


Figure 7. DTG thermogram of polyurethane film

During polymerization, this hard segment restricts the mobility of the polymer chain (Ren et al. 2013) 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, it was detected in the DSC thermogram nor the TGA thermogram, which indicates that acetone was removed from the polyurethane during the synthesis process, owing to its volatile nature. The presence of acetone in the synthesis was to lower the reaction kinetics.

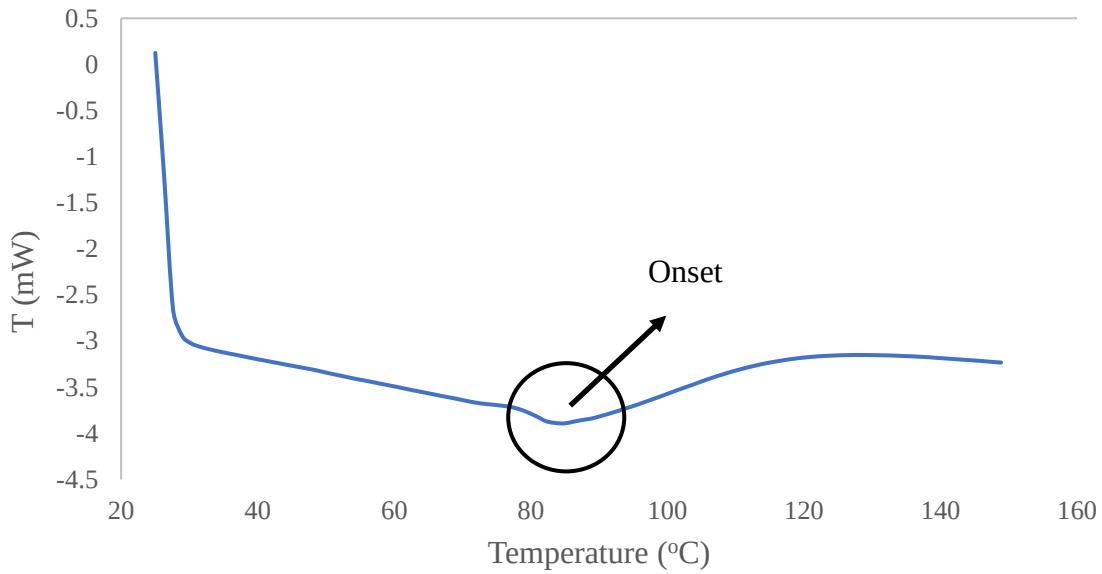


Figure 8. DSC thermogram of polyurethane film

e. 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 film solubility and tensile test are shown in **Table 3**. Polyurethane films 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.

Table 3 The solubility and mechanical properties of the polyurethane film

Parameters		Polyurethane film
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

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.

f. 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 $mmol \cdot L^{-1}$ KCl solution containing 5 $mmol \cdot L^{-1}$ ($K_3Fe(CN)_6$). 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 $V \cdot s^{-1}$. 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 polyol. The electrochemical signal at the electrode is low if there is a decrease in electrochemical conductivity (El - Raheem et al. 2020). It can be concluded that polyurethane is a bio-polymer with a low current value. The current of the modified electrode was found at 5.3 x 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 x 10^{-6} A, whereas Li et al. (2019) 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 (Wong et al. 2014). The PU can also release a current caused by PEG. The application of PEG as polyol has been studied by Porcarelli et al. (2017), that reported that the current of PU based on PEG – polyol was 9.2 x 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, 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.

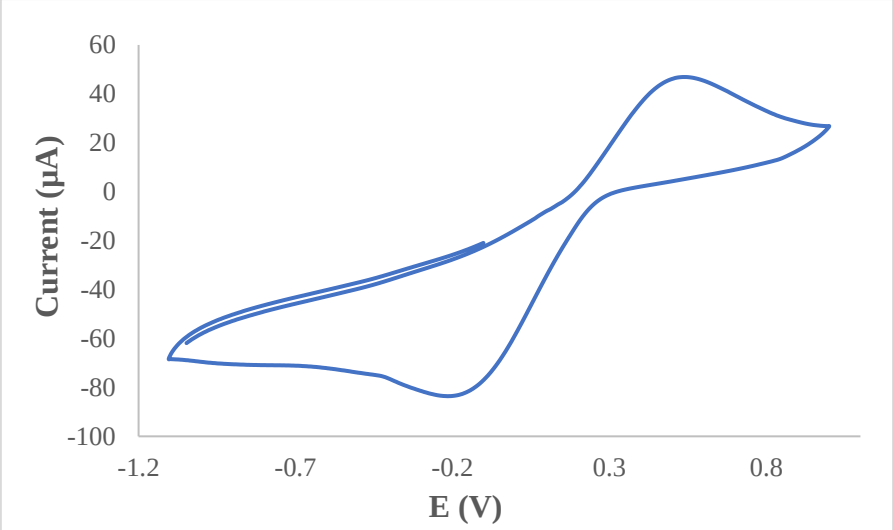


Figure 9. The voltammogram of SPE-PU modified electrode after analyzed using cyclic voltammetry technique

Figure 10 also presents the DPV voltammogram of the modified electrode. DPV is a measurement based on the difference in potential pulses that produce an electric current. Scanning the capability pulses to the working electrode will produce different currents. Optimal peak currents will be produced to the reduction capacity of the redox material. The peak current produced is proportional to the concentration of the redox substance and can be detected up to a concentration below 10^{-8} M. DPV was conducted to obtain the current value that is more accurate than CV (Lee et al. 2018).

This study used a redox pair ($K_3Fe(CN)_6$) as a test device (probe). The currents generated by SPE-PU and proved by CV and DPV have shown conductivity on polyurethane films. This suggests that polyurethane films can conduct electron transfer. The electrochemical area on the modified electrode can be calculated using the formula from Randles-Sevcik (Butwong et al. 2019), where the electrochemical area for SPE-PU is considered to be A, using Equation 2:

$$\textbf{Current of SPE-PU, } I_p = 2.65 \times 10^5 \, A C n^{3/2} \, v^{1/2} D^{1/2} \qquad (2)$$

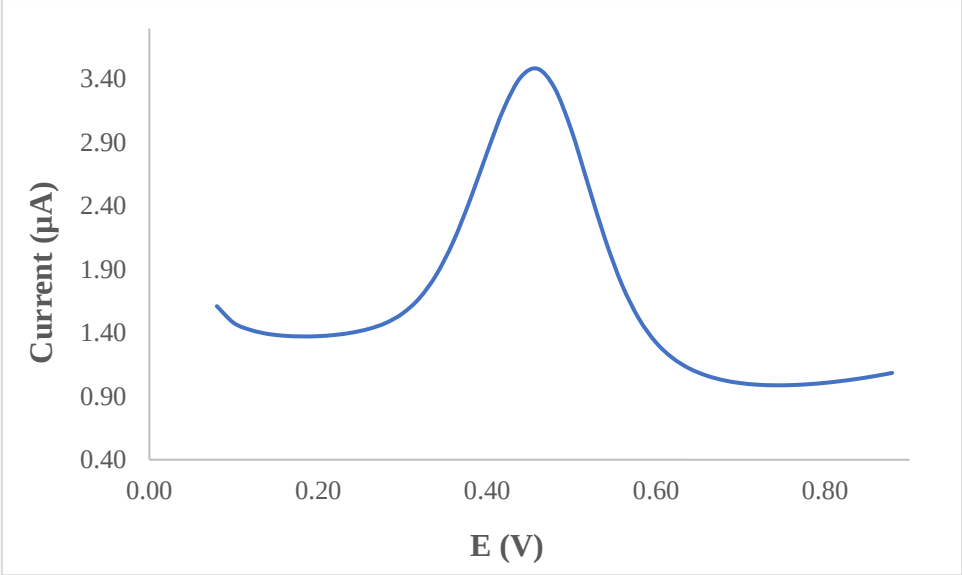


Figure 10. The voltammogram of SPE – PU modified electrode after analyzed using differential pulse voltammetry technique

Where, n – 1 is the amount of electron transfer involved, while C is the solvent concentration used (mmol·L^{-1}) and the value of D is the diffusion constant of 5 mmol·L^{-1} at ($K_3Fe(CN)_6$) dissolved using 0.1 mmol·L^{-1} KCl. The estimated surface area of the electrode (**Figure 1**) was 0.2 cm^2 where the length and width of the electrode used during the study was 0.44 cm × 0.44 cm while the surface area of the SPE-PU was 0.25 cm^2 with the length and width of the electrode estimated at 0.5 cm × 0.5 cm, and causing the SPE-PU has a larger surface. The corresponding surface concentration (τ) (mol/cm^2) is measured using Equation 3.

$$\mathbf{I_p = (n^2 F^2 / 4RT) A\tau v} \qquad (3)$$

I_p is the peak current (A), while A is the surface area 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 constant ideal gas (8.314 J/mol K) and T is the temperature used during the experiment being conducted (298 K) (Koita et al. 2014). The application of PKOp to produce a conducting polymer will be a great prospect as this material can be employed in the analytical industry in order to modify electrodes for electrochemical purposes.

Furthermore, number of palm oils is 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 biomaterials that can be used to replace other polymers that are chemical-based (Tajao et al. 2021). 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 (Tadese et al. 2019), 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 (Khatoon & Ahmad 2017).

4. Conclusion

Polyurethane film was prepared by pre-polymerization between palm kernel oil-based polyol (PKO-p) with MDI. The presence of PEG 400 as the chain extender formed freestanding flexible film. Acetone was used as the solvent to lower the reaction kinetics since the pre-polymerization 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 bio-polymer 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.

5. Acknowledgment

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6. Conflict of Interest

The authors declare no conflict of interest.

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Design and Synthesis of Conducting Polymer Bio-Based Polyurethane Produced from Palm Kernel Oil

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