Synthesis of Bio – Polyurethane from Palm Kernel Oil and Characterization Using FTIR and NMR

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Abstract- Polyurethane (PU) becomes one of the bio-based polymers and produced by pre-polymerization method. In this study, polyurethane (PU) was synthesised using aromatic isocyanate (4,4'-diphenylmethane disocyanate) as a hard segment and palm kernel-based monoester polyol (PKO-p) as a soft segment by using prepolymerization method with polyethylene glycol (PEG) 400 as a chain extender. Urea added into polyurethane in order to show the characteristic of polyurethane urea. Polyurethane – urea films with various concentration were studied and showing different tensile properties with polyurethane film. The tensile strains of PU – Urea films decreased owing to the addition of urea. The carbonyl peak (C=O) were detected using FTIR in polyurethane and polyurethane – urea around 1727 cm\(^{-1}\) and 1725 cm\(^{-1}\), respectively. Meanwhile, thermal properties of the PU – urea films were determined using thermogravimetry (TGA) method and indicated satisfactory result.

Index Terms- Polyurethane, pre-polymerization, urea, FTIR, TGA

I. INTRODUCTION

Varioius organic polymer materials nowadays are very popular among industry polymer. Polyurethane is one of the polymer materials considered to substitute materials originated from petroleum and can be applied as bio-based materials (Kizuka & Inoue 2015). Polyurethane (PU) is the largest volume commodity polymer that cannot be characterized by a simple structure. Instead, PU represents a class of polymers and any polymer with a urethane repeat unit is classified as a PU regardless of the other functional or polymer structures incorporated. As commodity products, PU have obtain acknowledgement by academic sciences and showed significant activity in PU science owing to its high potential for design and innovation (Sonnenschein & Koonce 2012; Szycher 2013; Prisacariu 2011).

Polyurethane (PU) can be produced by various techniques such as quasipolymer, single-step polymerization and prepolymerization. Quasipolymer technique is a reaction between diisocyanate reacted with polyol. Furthermore, the higher content of free isocyanate at 15 – 30% in urethane prepolymer and called semiprepolymer or isocyanate quasiprepolymers owing to half of diisocyanate molecules are reacted with polyol (Wong & Badri 2012), whereas for single-step polymerization takes place when polyol, diisocyanate and catalyst are mixed simultaneously with the extend of chain takes place simultaneously (Clemiston 2008).

On the other hand, prepolymerization technique divided into several steps, the initial step is a formation of urethane polymer where the reaction between polyol and disocyanate occurred. The final step is the chain of urethane prepolymer extended using water or diol to produce PU.

This study used palm kernel oil (PKO) as a monooester polyol. Production of PU in this study went prepolymerization technique which specifically designed by structoset prepolymer. Structoset prepolymer is polymerized in the final step by catalyst addition as shown in Figure 1. Here, this study report a synthesis of polyurethane using the aromatic isocyanate (4,4’-diphenyl-methane disocyanate (MDI)) as a hard segment, whereas for soft segment is polyol based on palm kernel oil (PKO) used and PEG 400 as a chain-extender.

II. EXPERIMENTAL PROCEDURE

2.1 Materials
The palm kernel oil – based monoester polyol (PKO-p) was prepared as described by Badri et al. (2000). 2,4-diphenylmethane disocyanate (MDI) was acquired from Cosmopolyurethane (M) Sdn. Bhd., Klang, Malaysia. Benzene, hexane, acetone, tetrahydrofuran (THF), dimethylformamide (DMF), dimethylsulfoxide (DMSO) and polyethylene glycol (PEG) 400 were purchased from UKM laboratory.

2.2 Synthesis of Polyurethane film
The PKO-p and PEG 400 were put into the vessel A and dissolved with acetone in order to form a polyol prepolymer solution. Afterward, the solution mixed using centrifuge in 100 rpm for 5 min to obtain homogenized solution. Disocyanate prepolymer produced with 4,4-diphenyl-methane diisocyanate (MDI) dissolved with acetone in vessel B, mixed for 20 sec in order to acquire a homogenized solution. Then, 10 g of disocyanate prepolymer solution poured slowly into vessel B that containing 10 g of polyol prepolymer solution, mixed using stirrer for 10 sec to obtain a homogenized prepolyurethane solution. Afterward, the solution poured into mold and dried at room temperature. The recipe and urea content for each polyurethane are listed in Table 1.

2.3 Characterization
In this research, characterizations applied were tensile test, surface analysis using FESEM, thermal properties using TGA and DSC, NMR and FTIR spectroscopy applied to identify the
chemical structures. All analyses and tests were performed at room temperature (23°C ± 2°C) unless otherwise indicated.

2.3.1 Chemical Properties

Solubility tests were performed using 10 x 10 mm test pieces. Each test piece was soaked in a solvent (benzene, hexane, acetone, tetrahydrofuran (THF), dimethylformamide (DMF), dimethylsulfoxide (DMSO); 10 mL) at room temperature (23°C ± 2°C) for 24 h.

2.3.2 Cross-Section Determination

Soxhlet extraction method used in order to determine the percent of cross-section. 1 cm x 1 cm of PU film weighed and put into the soxhlet and used toluene and poured into flask. This method was carried out for 24 hours. Mass of PU film weighed before and after reflux done.

2.3.3 Mechanical Properties

Tensile tests were performed on an Instron 5566 model. The value of tensile stress, strain and modulus recorded.

2.3.4 Thermal Properties

Thermogravimetric analyses (TGA) were performed on a Perkin Elmer Pyris 1 thermal at a heating rate of 10°C/min from 30°C to 600°C under an N2 atmosphere.

Different scanning calorimetry (DSC) measurements were performed on a Perkin Elmer Pyris 1 thermal at a heating rate of 10°C/min from 30°C to 250°C and at 20 Hz under a N2 atmosphere. Approximately 5 - 10 mg of PU was weighed and sealed in an aluminium pan. The samples were heated from 30°C to 150°C for 1 min then rapidly cooled from 150°C to -100°C for 1 min and then heated to 250°C at a rate of 10°C/min.

2.3.5 Surface Analysis

The field emission scanning electron microscope (FESEM) uses a focused beam of high-energy electrons to generate a variety of signals at the samples surface. The electron/sample interactions release signals that unveil information about the sample such as external morphology (texture) which forms the image observed. FESEM analyses were performed on dried sheets at room temperature in air using a Zeiss Gemini SEM 500-70-22. All the images presented here were reproduced from images acquired from at least three points on each sample surface.

2.3.6 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectroscopy was performed on a Perkin-Elmer Spectrum BX using the Diamond Attenuation Total Reflectance (DART) in order to identify several important functional groups in PU such as urethane carbonyl (C=O) group, carbamate (-CN), hydroxyl (-OH) and amide (-NH).

2.3.7 Nuclear Magnetic Resonance (NMR) Spectroscopy

The NMR spectroscopy ¹H NMR and ¹³C NMR 600 MHz spectra of PU were performed on an ECP spectrometer in dimethyl sulfoxide-d₆ (DMSO-d₆) with tetramethylsilane (Me₄Si, TMS) as an internal standard at room temperature.

III. RESULTS AND DISCUSSION

3.3.1 Chemical Properties

The solvent resistances of polyurethane films containing urea were tested by immersing polyurethane film sheet in various solvents such as hexane, benzene, acetone, THF, DMF and DMSO. The results are presented in Table 2.

All the PU films containing urea were resistant to benzene, hexane and acetone and slightly dissolved in THF, DMF and DMSO at room temperature (23°C ± 2°C) for 24 h. It shows the chemical bonds of PU are very strong and are not easy to be separated.

3.3.2 Crosslinking determination, Tensile and Thermal Properties

All results are reported in Table 3. Soxhlet extraction method was applied in order to determine the percentage of crosslinking part in polyurethane. Percentage different of PU mass before and after reflux process acquire the percentage of the sample crosslink. The content of crosslinked portion determined by the percentage of gel content (Rogul ska et al. 2007). Gel content of each sample was calculated using the following equation below:

\[
\text{Gel content (\%)} = \frac{(W_i - W_f)}{W_i} \times 100\%
\]

Where

\( W_i \) = initial mass of the sample before reflux (g)

\( W_f \) = final mass of the sample after reflux (g)

The tensile strength of PU, PU1, PU2 and PU3 films show how much elongating stress the film will endure before failure. The tensile properties of the PU films containing urea are reported below. The tensile stress, strain and modulus for polyurethane showed satisfactory result compared to polyurethane that containing urea. It can be concluded that urea has capacity to reduce the tensile properties of polyurethane film. Furthermore, the results of DSC and TGA are presented in Table 3.

Apart from different IR absorption, polymers also having variety in their thermal stability. TGA and DSC have been used in order to verify the purity of the synthetic materials, detect thermal degradation or phase transitions (Majewsky et al. 2016). During DSC analysis, a sample heats using a controlled temperature gradient with a defined heating rate, e.g. 10°C/min. The heat flow is interpreted by comparing the sample with a reference (Menczel & Prime 2008).

TGA analysis was applied to analyse the material degradation behaviour through the change in mass of the sample function of temperature and time in a controlled environment. This measurement was applied to determine the thermal stability and disintegrate the material composition. The thermal stabilities of the polyurethane films containing urea were analysed using TGA under a N₂ atmosphere. Table 3 presents four types of polyurethane films with and without urea with different urea concentration. Polyurethane films with and without urea were began degrading at above 170°C. Martel – Estrada et al. (2010) stated that polymer can be justified as a good polymer and mixed well when only one peak resulting in DTG thermogram. Nevertheless, this study showed the appearance more than one peak in DTG thermogram indicated that the PU prepolymer was likely to have residues.

DSC is a method with objective to analyse the changes of physical properties of the sample based on the glass transition temperature \( T_g \) from the thermogram. DSC and TGA curves were measured for all polyurethane with and without urea to analyse characteristic endothermic reactions. DSC analyses of the polyurethane film containing urea were performed over 30°C to 250°C under a N₂ atmosphere. From the data in Table 3, one main transition appeared in polyurethane films containing urea. The values for the glass transition temperatures \( T_g \), detected as the
peak temperature in the E’ curves of the corresponding polyurethane with and without urea content were 78.1°C, 117.6°C, 130.2°C and 132.2°C for PU, PU1, PU2 and PU3, respectively. $T_g$ values of polyurethane films containing urea increased. It is because the composition of urea inside the polyurethane have influenced the $T_g$ value of each sample.

### 3.3.4 Surface Analysis

FESEM images of the polyurethane films are presented in Figure 3. The surfaces of the polyurethane film were compared to polyurethane film that containing urea with various concentrations. The concentration, viscosity and conductivity of the solutions as well as the applied voltage and distance between the charged electrode and the grounded target (Kaur et al. 2016). FESEM images of polyurethane films containing urea revealed that all investigated samples were organic layer with a roughness less than the sheet thickness. The urea incorporation into the polyurethane film surface was visible. Furthermore, the surface of polyurethane films containing urea were not satisfactory uniform owing to the presence of urea.

### 3.3.5 Fourier Transform Infrared (FTIR) Spectroscopy

Figure 4 showed the FTIR spectra of polyurethane, polyurethane containing urea and urea. The PKO-p reacted with disocyanate to form urethane polymer in order to remove the free disiocyanate of MDI. Furthermore, there are no traces of NCO namely C-N (ester amide) at 1611 cm$^{-1}$ detected in the FTIR spectrum of the PU formed via addition polymerization. This indicates the disiocyanate group has completely reacted with PKO-p to from polyurethane.

The presence of the amide (-NH), carbonyl urethane group (C=O), carbamate group (CNH) and -C-O-C indicated the urethane linkages in the PU. The carbonyl peak (C=O) were detected in polyurethane and polyurethane – urea around 1727 cm$^{-1}$ and 1725 cm$^{-1}$, respectively which means a hydrogen bonded carbonyl urethane group. The identification peak around 1730 cm$^{-1}$ known as a non-hydrogen bonded carbonyl urethane group according to Clemiston (2008). Furthermore, there is no possibility of forming urea as the by product since the peak of C=O urea is no exist in polyurethane at 1690 cm$^{-1}$ (Clemiston 2008). Nevertheless, FTIR spectrum of polyurethane-urea and urea having the peak of C=O at 1660 cm$^{-1}$ and 1674 cm$^{-1}$, respectively. It indicates there are no reaction between polyurethane and urea owing to the peak of C=O presence in FTIR spectrum of polyurethane-urea. The free NH band, hydrogen – bonded NH with oxygen (ether) and hydrogen – bonded NH with oxygen (carbonyl) in the urethane are observed at 3301 cm$^{-1}$ and 3326 cm$^{-1}$ – 3428 cm$^{-1}$ (Lampman et al. 2010; Mutsuhisa et al. 2007). The urethane groups in the hard segment (MDI) have electrostatic charges at oxygen, hydrogen and nitrogen atoms and these charged atoms form dipoles which attract another atom of opposite charge (Boyd 1983). In this study, the hydrogen bond formed by C=O acts as proton acceptor whereas NH acts as proton donor.

The reaction mechanism in the formation of the urethane linkage via prepolymerization method is by nucleophilic substitution reactions (Yong et al. 2009) where in this research amine as the nucleophile. Amine attacks the carbonyl of the isocyanate (MDI) to form two resonance structures of the intermediate complexes A and B. The intermediate complex B has a greater tendency to react with polyl owing to the carbonyl bond (C=O) is stronger than the C=N bond the intermediate complex A. Thus, intermediate complex B is more stable than intermediate complex A (Wong & Badri 2012). Furthermore, nitrogen is more electropositive than oxygen, which -CN bond is more attracted to the cation (H$^+$) compared to -CO (Lampman et al. 2010).

The other reaction appeared in this study with PEG where the oxygen of PEG nucleophile attacks disiocyanate of MDI to form two intermediate complexes A and B. Nevertheless, nucleophilic substitution reaction has greater tendency to polyl compared to PEG owing to the nitrogen atom presence in polyl which is more electropositive than oxygen atom in PEG. Amine has higher possibility to react with isocyanate compared to hydroxyl (Herrington & Hock 1997). The other study stated that amine with a stronger alkalinity has more ability to react with carbon atom of the isocyanate (Wong & Badri 2012). Polyl contains a very long carbon chain that it can easily stabilize the alkyl ion when an intermediate complex is formed. Thus, the polyl is more reactive than PEG to react with MDI. Nevertheless, the use of PEG will increase the chain length of PU and prevent side reaction to occur such as the formation of urea between the reaction of NCO group in urethane prepolymer and water molecules from surrounding.

### 3.3.6 Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR spectra are applied to analysed the structure of the polymeric chains. The $^{13}$C NMR spectrum of the polyurethane and polyurethane containing urea are shown in Figure 5 and depicted as follows:

$^{13}$C NMR for polyurethane: $\delta$ (ppm) = 153.9 (C=OONH), 129.3 – 130.1 (C = C), 118.8 (C=CN(H)), 72.8 (CH$_2$O), 69.2 – 69.8 (CH$_2$(C=OC)), 60.7 – 63.9 (C=OCN), 59.3 – 59.6 (C = OH), 22.5 – 33.9 (CH$_3$), 14.4 (CH$_3$).

$^{13}$C NMR for polyurethane – urea: $\delta$ (ppm) = 129.3 (C = C), 118.9 (C=CN(H)), 72.8 (CH$_2$O), 69.2 – 70.2 (CH$_2$(C=OC)), 60.7 – 63.6 (C=OCN), 39.6 – 40.6 (C – N), 22.5 – 33.9 (CH$_3$), 14.4 (CH$_3$).

The presence of peak at 153.9 ppm and the disappearance of NCO peak of MDI at 125.7 ppm concluded that the disiocyanate of MDI reacted to -OH of polyl completely to form urethane polymeric chains (Wong & Badri 2012). Furthermore, the C-OH peak in polyurethane was detected around 59.3 – 59.4 ppm indicating an excess of polyl and PEG. Whereas, the C-N peak in polyurethane – urea was detected owing to the presence of urea. The CH$_2$ peaks in both spectrums also showing varieties around 22.5 – 33.9 ppm owing to numerous fatty acid contents in PKO such as linoleic acid, linolenic acid, palmitic acid, lauric acid and so on.

### IV. Conclusions

In summary, this study achieved the synthesis of polyurethane containing urea using the prepolymerization method. The use of urea showing that urea was entrapped inside the polyurethane films owing to the properties of polyurethane film has pores on the surface. The film of polyurethane is transparent and has pores on the surface. The film of polyurethane is transparent and has pores on the surface.

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polyurethane and urea. The experiment results showed that the tensile properties of polyurethane containing higher concentration of urea decrease and their flexibility are also unsatisfactory and the films containing urea are brittle.

Regarding its applications, the polyurethane – urea film is expected for use in chemical sensors. This study needs to be further extended by studying the capability of polyurethane – urea as a chemical sensor.

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REFERENCES


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Figure 1. The chemical route of producing polyurethane via prepolymerization method (Wong & Badri 2012).

Table 1. Synthesis of polyurethane films containing urea.

<table>
<thead>
<tr>
<th>Sample</th>
<th>MDI (g)</th>
<th>Polyol (g)</th>
<th>Urea (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyurethane</td>
<td>1.5</td>
<td>2.1</td>
<td>0</td>
</tr>
<tr>
<td>Polyurethane – 1</td>
<td>1.5</td>
<td>2.1</td>
<td>1</td>
</tr>
<tr>
<td>Polyurethane – 2</td>
<td>1.5</td>
<td>2.1</td>
<td>3</td>
</tr>
<tr>
<td>Polyurethane – 3</td>
<td>1.5</td>
<td>2.1</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 2. Solubilities of polyurethane films containing urea.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Benzene</th>
<th>Hexane</th>
<th>Acetone</th>
<th>THF</th>
<th>DMF</th>
<th>DMSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>PU1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>PU2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>PU3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

-: undissolved, x: slightly dissolved.
Table 3. Physical properties of polyurethane films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stress(^a) (Mpa)</th>
<th>Strain(^a) (%)</th>
<th>Modulus(^a) (Mpa)</th>
<th>(100)</th>
<th>Tg(^b) (°C)</th>
<th>Tc(^c) (°C)</th>
<th>Cross-section (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyurethane</td>
<td>8.53</td>
<td>43.34</td>
<td>222.10</td>
<td></td>
<td>78.1</td>
<td>171.8</td>
<td>99.36</td>
</tr>
<tr>
<td>Polyurethane – urea 1%</td>
<td>6.73</td>
<td>26.27</td>
<td>163.67</td>
<td></td>
<td>117.6</td>
<td>(\geq190)</td>
<td>90.12</td>
</tr>
<tr>
<td>Polyurethane – urea 3%</td>
<td>4.93</td>
<td>16.79</td>
<td>117.79</td>
<td></td>
<td>130.2</td>
<td>(\geq190)</td>
<td>88.27</td>
</tr>
<tr>
<td>Polyurethane – urea 5%</td>
<td>2.95</td>
<td>10.47</td>
<td>87.11</td>
<td></td>
<td>132.2</td>
<td>(\geq190)</td>
<td>85.31</td>
</tr>
</tbody>
</table>

\(^a\)Measurement conditions: using tensile instruments, total thickness = 1 mm, room temperature (23°C ± 2°C). \(^b\)Differential scanning calorimetry was performed at a heating rate of 10°C/min from -100°C to 200°C under a N\(_2\) atmosphere. \(^c\)Thermogravimetric analysis was performed at a heating rate of 10°C/min from 30°C to 300°C under an N\(_2\) atmosphere.
Figure 3. FESEM images of polyurethane with and without urea. (a) polyurethane, (b) polyurethane – urea 1%, (c) polyurethane – urea 3%, (d) polyurethane – urea 5%.
Figure 4. FTIR spectrum of polyurethane, polyurethane-urea and urea.
Figure 5. $^{13}$C NMR spectrum: (a) the polyurethane and (b) the polyurethane – urea.