Green waste cooking oil-based rigid polyurethane foam

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Abstract. Polyurethane is a versatile polymer traditionally prepared using petroleum-based raw material. Petroleum, however, is a non-renewable material and polyurethane produced was found to be non-biodegradable. In quest for a more environmentally friendly alternative, waste cooking oil, a highly abundant domestic waste with easily derivatized structure, is a viable candidate to replace petroleum. In this study, an investigation to determine physical and chemical properties of rigid polyurethane (PU) foam from waste cooking oil (WCO) was carried out. WCO was first adsorbed by using coconut husk activated carbon adsorbent prior to be used for polyol synthesis. The purified WCO was then used to synthesize polyol via transesterification reaction to yield alcohol groups in the WCO chains structure. Finally, the WCO-based polyol was used to prepare rigid PU foam. The optimum formulation for PU formation was found to be 90 polyol: 60 glycerol: 54 water: 40 diethanolamine: 23 diisocyanate. The rigid PU foam has density of 208.4 kg/m$^3$ with maximum compressive strength and capability to receive load at 0.03 MPa and 0.09 kN, respectively. WCO-based PU can potentially be used to replace petroleum-based PU as house construction materials such as insulation panels.

1. Introduction
Polyurethane (PU) is known as linear block copolymers prepared by reacting polyol and diisocyanate in the presence of surfactant, catalyst, blowing agent and other additives like fire retardants and smoke suppressants. Since variety of diisocyanates and polyols available to produce polyurethane, a broad spectrum of PU properties can be produced to meet the needs of specific applications. PU can be found in four main forms; 1) rigid, 2) flexible, 3) coatings, adhesives, sealants and elastomers, and 4) thermoplastic. Each type of PU has its own applications. For example, flexible PU are used as cushioning in bedding, furniture and in automotive industry, while rigid PU are used as insulation materials in house construction [1].

Currently, most PU products used petroleum as raw materials for polyol. Petroleum are non-renewable, not environmentally friendly and require high production costs with high technology processing system. PU made from vegetable oil based polyol such as rapeseed oil, palmieri oil, vernonia oil, castor oil and cardanol oil, are renewable and has been found to be more biodegradable than petroleum-based [2-3]. However, virgin vegetable oil is also expensive. Recently, lots of effort has been devoted to synthesize polyol for rigid PU foam from waste cooking oil (WCO).

WCO is waste materials from food industry. During frying, oil will be degraded due to presence of air, heat and water via oxidation, polymerization and hydrolysis processes. Degradation reaction will reduce the quality of oil and will give adverse effect to human if consumed. Uncontrolled dumping of WCO to the drainage system without proper treatment can lead to severe environmental problems. WCO has potential as raw material for PU production due to its physical and chemical
properties. However, an adsorbent is needed to remove the dissolved materials presence in WCO resulted from the degradation reaction[4-7].

Coconut husk, an agricultural waste material has been used as a low-cost adsorbent to adsorb dissolved materials in WCO. The bulk of coconut husk is composed of cellulose and lignin. The presence of hydroxyl groups in both polymeric substances provide sites for adsorption of dissolved materials in WCO [8].

In this study, WCO will be pretreated using coconut husk activated carbon, followed by transesterification reaction to synthesize polyol. The polyol was then used to prepare WCO-based PU rigid foam and the chemical and physical properties were studied.

2. Experimental

2.1. Materials
The raw materials used for this study are WCO and coconut husk. For preparation of adsorbent, 1M potassium hydroxide solution (KOH) and 0.1M hydrochloric acid (HCl) were purchased from R&M Chemicals. For preparation of polyol, diethanolamine (DEA) and monoethyleneglycol (MEG) were purchased from R&M Chemicals while potassium acetate (PA) was purchased from HmbG Chemical. For synthesis of rigid PU foam, 2,4-diphenylmethane diisocyanate (MDI) was purchased from Merck, diethanolamine (DEA) from R&M Chemicals and glycerol from HmbG Chemicals.

2.2. Methodology
Coconut husk used for preparation of activated carbon was obtained locally from coconut milk producer located in Kuala Terengganu. Coconut husk was first cut, washed with distilled water, oven dried for 12 hours at 85°C and grinded to 0.1 mm mesh size using Grinder Machine EFL2000. The powder was then sieved into 150 microns. 10 g of coconut husk powder mixed with 500 mL of 1 M KOH solution and placed into oven for 6 hours at 150 °C. The solution was filtered using filter paper. Next, the activation process was carried out at 800˚C for 1 hour in a tubular furnace under nitrogen atmosphere. The activated product was then cooled to room temperature and washed with 0.1M HCl solution and deionized water repeatedly until the pH of the filtrate water became 7. Finally, the activated carbon was dehydrated in oven overnight at 105˚C to remove moisture before being used to purify WCO [5].

Sample of WCO was obtained from a restaurant located in Kuala Terengganu, Malaysia. The WCO was first filtered using filter paper to remove any suspended materials. 100 mL of filtered WCO then heated at95-125°C/0.5 g of coconut husk activated carbon adsorbent was added to WCO and left for 24 hours. Next, the adsorbed WCO was stirred at 500 rpm and 110˚C for 1 hour. Adsorbed WCO was then filtered by using filter paper and analyzed using FTIR and %FFA [5].

DEA, MEG and PA were mixed homogenously with a ratio of 90:7:3 to form polyhydric compound. The solution was then stirred to mix well and kept overnight. Transesterification reaction was carried out by mixing adsorbed WCO-based polyol with polyhydric solution with a ratio of 80:20 respectively. The solution mixture was heated and continuously stirred at 185-195˚C with 200 rpm for 20 minutes to yield polyol. The polyol was then analyzed for FTIR spectroscopy, %FFA, acid value, hydroxyl value, iodine value and viscosity.

Resin was prepared in a plastic cup under elevated temperature. The resin was blended using an overhead mechanical stirrer at condition of 200 rpm rotor speed for 1 minute. MDI was added to the resin at a ratio of 1:1 at condition of 1000 rpm rotor speed for 10 second. The effect of amount of DEA as catalyst and glycerol as crosslinking agent on reaction behaviour of PU in terms of cream time, gel time, rise time and tack-free time of the foam was recorded. The rigid PU foam was then characterized for FTIR, densityand compressive strength [9].

2.3. Characterizations
Fourier transformed infrared (FTIR) spectroscopy analysis was carried out by using Perkin Elmer FTIR Spectrum BX spectrophotometer to identify functional groups presence in WCO, polyol and PU. The samples were scanned in the range of 650-4000 cm⁻¹ wavenumbers. Free fatty acid percentage
(%FFA) was characterized using ASTM D5555–95 standard method to measure amount of free fatty acids contained in WCO and polyol. Acid value was calculated from %FFA to measure mass of KOH in milligrams required to neutralize one gram of chemical substance in polyol. Hydroxyl value was analyzed using Lubrizol Test Procedure TP-AATM-111A-02 to measure the content of free hydroxyl groups in WCO and polyol. Iodine value was analyzed using Lubrizol Test Procedure TP-AATM-112-01 to determine the amount of unsaturation in fatty acids. Viscosity of WCO and polyol was determined by using Brookfield viscometer in the range of 10 to 100 000 mPa·s (cP) using ASTM standard method D4878-08. Compressive strength test for rigid PU foam was conducted on a Universal Testing Machine Model Instron. The specimen was cut into cubes of 50 mm × 50 mm × 50 mm in dimensions. The foam rise direction was marked and 50 mm/min crosshead speed was applied. The maximum stress and load of the foam was recorded.

3. Results and discussion

3.1. Synthesis of waste cooking oil-based polyol

The properties of WCO and WCO-based polyol are summarized in Table 1. Adsorption process using coconut husk activated carbon had reduced %FFA and acid value in WCO sample. Transesterification reaction had been used to convert the purified WCO into polyol. Transesterification or alcoholysis is generally defined as a chemical reaction involving the displacement of alcohol from an ester by another. The viscosity of polyol produced was found to be 155 mPa·s which is quite high. Viscosity was measured to determine the resistance of polyol to uniformly continuous flow without other forces. High viscosity polyol is not favoured due to low stirring efficiency during PU processing.

| Properties             | Raw WCO | Adsorbed WCO | WCO-based polyol |
|------------------------|---------|--------------|------------------|
| Free Fatty Acid (%)    | 4.4     | 1.4          | 1.5              |
| Acid Value (mgKOH/g)   | 8.756   | 2.786        | 2.985            |
| Viscosity (mPa.s)      | 106     | 97.8         | 155              |
| Colour                 | Dark brown | Light brown | Colourless       |
| Hydroxyl value         | -       | -            | 46.3             |

The structure of WCO-based polyol was confirmed by FTIR spectrometer. The polyol consisted of chains of fatty acid with carboxylic acid group. As shown in figure 1, the presence of peaks at 3303.13 cm⁻¹ and 1743.81 cm⁻¹ of hydroxyl group and carbonyl stretching of ester group, respectively, confirmed the formation of polyester polyls. C-H stretching peaks can be seen at 2922.48 cm⁻¹ and 2853.29 cm⁻¹, C-O stretching and O-H bending near 1377.27-1237.44 cm⁻¹ and 1457.04-1395.60 cm⁻¹, respectively, and C-O-H bending peak was found at 1457.04-1395.60 cm⁻¹[9].
3.2. Synthesis of waste cooking oil-based polyurethane foam

Two main factors affecting the foam formation, which are amount of catalyst and glycerol were studied using various compositions. Table 2 shows the compositions used to prepare rigid PU foam in three different amount of DEA as catalyst. The function of DEA is to increase the rate of reaction involved in the foaming system. Cream time and rise time is defined as the rate of expansion, principally an exothermic effect, while the gel time and tack-free time could be used to determine the gelation rate taken to form rigid PU foam. The different composition of catalyst used could affect the cream time, gel time, rise time and tack-free time involved in the formation of rigid PU foam. From the result obtained, composition C showed faster expansion rate during foaming compare to A and B. The cream time, rise time, gel time taken were 4, 58 and 24 seconds, respectively. Composition C gave the optimum PU foam formation. The high amount of catalyst provided fast cream time, rise time and gel time of the PU foam [10]. Figure 2 shows the effect of catalyst on the reaction times of PU foam formation.

| Raw Material   | Composition |
|----------------|-------------|
| Polyester polyol | A  B  C  | 90 90 90 |
| Glycerol       | 60 60 60   |
| H₂O            | 54 54 54   |
| DEA            | 20 30 40   |
| MDI            | 21 22 23   |

Table 2. Composition of PU foam formation with different amount of DEA as catalyst.

Figure 1. FTIR spectra of waste cooking oil and waste cooking oil-based polyol.
Glycerol acts as a crosslinking agent in PU foam formation. Three compositions; A, B and C, as shown in Table 3 were prepared to observe the effect of amount of glycerol. The amount of glycerol in composition C provided fast cream time for the PU foam to expand which was 4 seconds rather than 40 and 50. The time taken for the components in the resin to get cross-linked to each other was faster due to the high composition of glycerol used. Figure 3 shows the effect of glycerol on reaction times during PU foam formation.

Table 3. Composition of PU foam formation with different amount of glycerol.

| Raw Material   | Composition | A  | B  | C  |
|---------------|-------------|----|----|----|
| Polyester polyol | 90          | 90 | 90 |    |
| Glycerol      | 40          | 50 | 60 |    |
| H2O           | 54          | 54 | 54 |    |
| DEA           | 40          | 40 | 40 |    |
| MDI           | 21          | 22 | 23 |    |
Figure 3. Effect of glycerol on reaction times during PU foam formation.

The composition of 90 polyester polyol: 60 glycerol: 54 H₂O: 40 DEA: 23 MDI was found as the optimum formulation for rigid PU foam production, thus used to be characterized further, chemically and physically. Analysis by FTIR, as shown in Figure 4, proves the successful formation of polyurethane can be proven by the presence of amide (NH) at 3720.90 cm⁻¹, urethane carbonyl (C=O) at 1741.52 cm⁻¹, C-N-H at 1512.36 cm⁻¹, C-O-C at 1231.16 cm⁻¹ and the absence of hydroxyl (OH) absorption peak at around 3000 cm⁻¹. The stretching vibration of –NH₂ (amide) was located at 3294.19 cm⁻¹ overlapped with the OH peak as in PU from WCO based polyol structure. The synchronous reflection of asymmetric and symmetric of CH₂ bridges from the linkage of the urethane with DEA appeared at peak 2924.90 and 2854.37 cm⁻¹. At peak 1636.94 cm⁻¹, the absorption peak of N=C=O of urethane overlapped with ester linkage of the DEA was assigned.
Figure 4. FTIR spectra of waste cooking oil-based polyol and polyurethane.

The rigid PU foam samples were cut into cubes of 1 cm × 1 cm × 1 cm in dimensions to obtain the volume of the foams. The mass of the cube foam was weighed using an analytical balance. The volume is 1 cm³ while the average mass of the cubes is found to be 0.2084 g. The density of the rigid PU foam was determined by using a simple mathematical equation, mass (kg)/volume (m³). Thus, the density of the rigid PU foam is 2.084×10⁻⁴ kg/m³.

The compressive strength test of the rigid PU foam was carried out on a Universal Testing Machine Model Instron. The maximum stress of the foam was observed to be 0.03 MPa, considered the strength and elongation capability during the compressive strength test. The foam can receive a maximum load of 0.09 kN. The strength showed was affected by the segment content in the PU matrix [11].

4. Conclusion
In conclusion, WCO has great potential in replacing petroleum and vegetable oils as starting raw material for rigid PU foam. The use of the WCO also appears to be feasible and eco-friendly besides helping to reduce environmental problems. Pretreatment of WCO through adsorption process using coconut husk activated carbon as the adsorbent successfully removed the suspended materials and improved the colour and odour, which is important in producing commercial product. Viscosity of the WCO was decreased to 97.8 mPa s after adsorption. Transesterification reaction was used to synthesize polyol from the adsorbed WCO in order to add O-H group in the structure. FTIR proved the WCO-based polyol was successfully synthesized as shown by the presence of O-H absorption peak. The rigid PU foam-based polyol has been successfully synthesized as shown by the presence of urethane linkage in FTIR spectra. The effect of DEA as a catalyst and glycerol as a crosslinking agent on the PU foam formation was studied in terms of cream time, rise time, gel time and tack-free time during the foaming process. The composition of 90polyol: 60 glycerol: 54 H₂O: 40 DEA: 23 MDI foundas the optimum composition for rigid PU foam production. The compressive strength test revealed the maximum stress and load of the PU foam which was found to be 0.03 MPa and 0.09 kN. Thus, the properties shown by the rigid WCO-based PU foam is suitable to be used as alternative material for house construction such as thermal insulation panels.
5. References

[1] Li Y, Luo X and Hu S 2015 *Bio-Based Polyols and Polyurethanes* (Springer International Publishing)

[2] Zienieswksa M, Leszcynski M K, Kuranska M, Prociak A, Szczepkowski L, Krzyowska M and Ryszkowska J 2015 Biobased polyurethane foams modified with natural fillers *Ind. Crops Prod.* 74 887

[3] Arniza M Z , Hoong S S, Idris Z, Yeong S K, Hassan H A, Din A K and Choo Y M 2015 Synthesis of Transesterified Palm Olein-Based Polyol and Rigid Polyurethanes from this Polyol *Am. Oil Chem. Soc.* 92 243

[4] Tahir S M, Salleh W N W, Hadid N S N and Enderus N F 2016 Synthesis of Waste Cooking Oil-Based Polyol Using Sugarcane Bagasse Activated Carbon and Transesterification Reaction for Rigid Polyurethane Foam *Mater. Sci. Forum* 846 690

[5] Wannahari R, Nordin M F M 2014 The recovery of used palm cooking oil using bagasse as adsorbent *Am. J. Eng. Appl. Sci.* 5 59-62

[6] Sipaut C S @ Nasri M, Sundang M, Saalah S, Hoon T C, Ibrahim M N M , Rahman I A and Abdullah A A 2012 The effect of different peroxide on ldpe foam properties in the presence of polyfunctional monomers *Cellular Polym.* 31 19

[7] Rus A Z M, Salim N S M and Sapiee N H 2015 Recycling of Cooking Oil Waste into Reactive Polyurethane for Blending with Thermoplastic Polyethylene *Int. J. Polym. Sci.* 2015

[8] Gupta V K, Jain R and Shrivastava M 2010 Adsorptive removal of dyes from aqueous solution onto carbon nanotubes: a review. *J. Colloid Interface Sci.* 347 309

[9] Badri K H, MohdDawi L I and Abd Aziz N A 2013 Rigid polyurethane foam from glycolysed polyethylene terephthalate dissolved in palm-based polyol *Sains Malaysiana* 42 449-457

[10] Dworakowska S, Bogdał D, Zaccheria F and Ravasio N 2014 The role of catalysis in the synthesis of polyurethane foams based on renewable raw materials *Catalysis Today* 223 148-156

[11] Prociak A, Rojek P and Pawlik H 2012 Flexible polyurethane foams modified with natural oil based polyols *Journal of Cellular Plastics* 48 489

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