International Journal of Engineering & Technology, 7 (3.14) (2018) 366-374

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET

Research paper



Liquefaction of Oil Palm Fruit Waste and Its Application for The Development of Polyurethane Foams

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Abstract

This research utilizes solvolysis liquefaction of oil palm fruit waste (PW) biomass for production of polyurethane (PU) foam. Three part of PW: oil palm mesocarp fibre (PM), oil palm shell (PS) and oil palm kernel (PK) was treated using liquefaction solvent with sulfuric acid. Effects of different liquefaction condition such as effect of raw material/liquefaction solvent ratio, reaction time, liquefaction temperature, catalyst amount and liquefaction solvent on liquefaction yield have been determined. Analytical methods used were SEM and DSC analysis. Result showed that more than 70% of the PW were converted into biopolyols within optimum reaction condition of 120 minutes at 150°C with raw material/liquefaction solvent ratio of 1/3 using PEG400. In liquefaction process, hemicellulose, cellulose and lignin are degraded which results in changes of acid and hydroxyl value. Biopolyols of PM/PEG400 ratios was yielded highest biopolyol which is used to continue the experiment. Foaming kinetic indicate a slight increase from initial mix time to gelling time. Moisture content and water absorption are strongly affected the mechanical properties of PU foam. There is no T_g observed in PMF in DSC analysis. Oil palm fruit waste showed great potential for PU foams fabrication.

Keywords: *Solvolysis liquefaction; biomass; biopolyols; renewable polymer; polyurethane; foams.*

1. Introduction

Fossil fuels product are an emergent problem, as consequences of their less biodegradability. Engineers and researchers are motivated to increase desire in substitute petroleum based fossil fuel product for utilization of lignocellulosic biomass waste with an aid for economic development. Furthermore, the use of biomass as a substitute for fossil fuels can reduce the carbon content in the atmosphere as carbon dioxide is absorbed by plant via photosynthesis during growth [1].

Malaysia is one of the country which exporting and producing palm oil in the world. Indiscriminate disposal of palm byproduct will cause serious ecological and environmental issues. The wastes, for example, oil palm mesocarp fiber (PM), oil palm shell (PS),oil palm kernel (PK), empty fruit bunches (EFB), palm oil mill effluent (POME), oil palm trunks (PT), oil palm leaves (PL) and oil palm fronds (OPF) are produced after the palm oil processing, oil palm fruits harvesting or during oil palm trees replantation [2]. Therefore, thermochemical conversion incorporates several of possible techniques, for example, liquefaction, pyrolysis, and gasification to produce fuels and chemical from biomass. In the fields of materials and bioenergy, the solvolysis liquefaction of oil palm waste to produce liquefied biopolyol has received consideration due to its potential for lower energy utilization and good efficiency compared with other thermochemical conversions, for example, gasification or pyrolysis [3]. During the liquefaction processes, biomass waste is decomposed and degraded into smaller molecules by liquefaction solvent thru solvolysis liquefaction reactions. Some polyurethanes foams and polyesters have been prepared from the liquefied polyol product [4].

Biopolyols that produce from the process of biomass liquefaction have incredible potential and high hydroxyl functionalities in the fabrication of polyurethanes (PU) foams [5]. PU foams formation is obtained from the liquefied oil palm mesocarp fibre biopolyol, renewable polymer and isocyanate reaction, which are derived when polymerization reactions occur to all polymeric materials. This polymer is addressed as polyurethane PU foams are various engineering materials which find an extensive variety of applications. Generally, PU foams are one of the major productions from urethane polymer structure. In this study, the forming process of liquefied oil palm mesocarp biopolyol with renewable polymer foam include three basic stages, as an instance, bubble growth bubble initiation and cell opening. The bubble begin was initially brought by physically bending air into the mixture. The bubble growth happens once the gas subtle and expands the gas phase as a result of increasing of forming temperature. The gas could begin from the component such as solvent, catalyst, blowing agents and surfactant. The heat produced throughout the reactions attributed to exothermic process play a very important role in expansion to form a cellular structure [6]. The bubble kept on growing and it will start to open the cell to produce polymer foam.

The potential of synthesis liquefied PW biopolyol and renewable polymer reduces the dependence of the chemical from petroleum oil resources. It can be determined the huge economic and social advantages will have accomplished if efforts are put into the study on synthesis of agricultural biomass waste and waste cooking oil. Therefore, the objectives of this research was to utilizing solvolysis liquefaction conversion technology of oil palm fruit waste

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biomass and waste cooking oil for the production of polyurethane foam.

2. Methodology

2.1. Raw Materials

Oil palm fruit wastes (PW) which contain oil palm mesocarp fibre (PM), oil palm shell (PS) and oil palm kernel (PK) was obtained from Sindora Palm oil mills, Johor, Malaysia. The PW were ground into smaller sizes using heavy duty laboratory blender, sieved. The particles of mesh 20-100 µm were selected for this study. These raw materials were then dried at 100°C in an oven and kept in a air tight container at room temperature before using. Polyethylene glycol 400 (PEG400), ethylene glycol (EG) and glycerol were used as liquefaction solvents and 98% percentage of sulfuric acid was used as catalyst. Phthalic anhydride, imidazol, phthalation reagent, sodium hydroxide and dioxane were used to determined acid and hydroxyl value of biopolyol. Crosslinker, methylene diphenyl diisocynate (MDI), catalyst (dibutyltine dilaurate), surfactant (sulicont oil), blowing agent (water) was used as received. All chemicals were purchased from Sigma-Aldrich.

2.2. Liquefaction Oil Palm Fruits Waste (LPW)

Polyhydric alcohol: Polyethylene glycol 400 (PEG400), ethylene glycol (EG) and glycerol was used as liquefaction solvent. At first, dried PW and liquefaction solvent were mixed at 1/2, 1/3 and 1/4 of weight ratio with 5% sulfuric acid as a catalyst. The mixture was placed into a 250 mL four-branch flask in oil bath equipped with magnetic stirrer and thermometer at 150°C for 120 min (2 hours). Then, the flask mixture was immersed in a cold-water bath to stop the reaction process. The liquefied PW were dissolved in 200 mL of methanol for 6 h. The liquefied solutions were then vacuum-filtered and evaporated at 80°C using rotary evaporator to remove the solvent. The residue was washed and rinsed with methanol, dried at 100°C overnight in an oven and weighed [4]. In order to measure the percent of liquefied PW residue residue (R) was calculated as follow equation:

$$\text{Residue content, } R\ (\%) = (Wr / Wo) \times 100\ \% \quad (1)$$

$$\text{Liquefaction yield } (\%) = 100 - R\ (\%) \quad (2)$$

where R is the residue percentage; Wo is the weight of oven-dried biomass (g); Wr is the weight of biomass residue (g) after liquefaction.

2.3. Acid Value and Hydroxyl Value of Liquefied Oil Palm (LPW)

A mixture of 7 g LPW, 70 ml dioxane and 30 ml water was titrated with 1 M sodium hydroxide (NaOH) solution to the equivalence point [7]. The acid value was calculated as follow equation:

$$\text{Acid value (mg KOH/g)} = \frac{(C-B)N \times 56.1}{W} \quad (3)$$

where C is the titration volume (mL) of the sodium hydroxide solution at the equivalence point (mL); B is the volume of the blank solution (mL); N is the equivalent concentration of KOH solution used, and W is the weight of biomass sample (g).

The measurement of hydroxyl number was conducted as follows: a mixture of 1 g LPW sample and 25 mL of a phthalation reagent was heated at 110ºC for 20 min. 50 mL of dioxane and 25 mL of water were added and titrated with 1 M sodium hydroxide solution to the equivalence point. The phthalation reagent consisted of a mixture of 24.2 g imidazole, 150 g phtlatic anhydride and 1000 g dioxane [7]. The hydroxyl number of sample was calculated as follow equation:

$$\text{Hydroxyl value (mg KOH/g)} = \frac{(B-A)N \times 56.1}{W + Acid\ value} \quad (4)$$

where B is the volume of the blank solution: A is the volume (mL) of the NaOH solution after the phthalation liquefied of reaction sample; N is the normality of the NaOH solution; W is the weight of biomass sample (g).

2.4. Viscosity of Liquefied Oil Palm Fruits Waste (LPW)

Viscosity is a property of the fluid which opposes the relative motion between the two surfaces of the fluid in a fluid that are moving at different velocities. The viscosity of LPW was determined according to ASTM D 4878-08 using A&D viscometer, equipped with a temperature probe, small sample adapter and temperature control unit. Viscosity was determined at 25 ± 0.5 °C using rotational speeds.

2.5. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) observations of liquefaction residue were examined by using SEM of JEOL-JSM6380LA operates at 15 kV at 30 µm magnifier under high vacuum. Samples were sputter coated with thin layer of gold to avoid electrostatic charging during scanning.

2.6. Preparation of Renewable Monomer

Waste cooking oil (WO) was obtained from Small and Medium Industries (SMIs) and synthesized chemically at laboratory scale using less than 1L of waste cooking oil. WO collected from the food sector was recycled five times during fried the tapioca crisp. It began with preparation of catalyst to generate the epoxies from unsaturated fatty compound using in-house catalyst preparation at Sustainable Polymer Engineering, E1 (SPEN-AMMC) that contain the acid-catalyst ring opening of the epoxides to produce polyols. In order to produce renewable polymer foam, the reaction of renewable monomer with crosslinker is conducted [8-10].

2.7. Preparation of PU Foams

The route of production polymer foam was formulated at Sustainable Polymer Engineering, E1 (SPEN-AMMC) laboratory. The foams were prepared by a two-step method. The foaming process used in this work is consist of two components, A and B. Component A is a substances containing liquefied PM biopolyols, renewable monomer, epoxy, catalyst (dibutyltin dilaurate), blowing agent (water) and surfactant (silicon oil) in a mould. Component B is a methylene diphenyl diisocyanate (MDI). The two components were mixed vigorously using a mechanical stirrer at room temperature for about 1 minute and allowed to rise, a bubble was initiated due to the physical blending of air with the mixture of polymer foam. Immediately, the mixtures were cast into a mould and cure at room temperature for 6 hours. As the temperature increased during the forming process, the bubble raised was caused by the gas diffusion and the expansion of gas phase. The process was called exothermic as heat was generated during the reaction. When one or more bubbles ruptured, a closed cell opened which is called cell opening of the pore. The properties of the foams were determined after curing at room conditions for 1 days [5]. Table 1 shows the six formulation regarding the effect of the reaction conditions on the cell structure, such as the mass ratio of the polyol to crosslinker (1:2), and the amount of solvent, catalyst, surfactant and blowing agent.

Table 1: Foam formulations from liquefied PM biopolyols and renewable polymer.

No.	Sample	A						B
		Polyol (%)		PEG400 (Solvent)/g	Dibutyltine dilaurate (Catalyst)/g	Siliconce Surfactant/g	Blowing agent (H_2O)/g	Crosslink (MDI)/g
		Biopolyol	Renewable monomer					
1	PMF	100	-	2.5	0.1	0.1	0.2	20
2	RF	-	100	2.5	0.1	0.1	0.2	20
3	$PMRF_{80/20}$	80	20	2.5	0.1	0.1	0.2	20
4	$PMRF_{60/40}$	60	40	2.5	0.1	0.1	0.2	20
5	$PMRF_{40/60}$	40	60	2.5	0.1	0.1	0.2	20
6	$PMRF_{20/80}$	20	80	2.5	0.1	0.1	0.2	20

*PMF – oil palm mesocarp fiber foam
RF – renewable monomer foam
PMRF – oil palm mesocarp fiber/renewable monomer foam

2.8. Foaming kinetics

The following process parameters were observed and characterized: mix time (time elapsed from the start of the process until the start of volume expansion); Cream time (time at which the mixture changed from an apparently free flowing liquid to the beginning of the foaming of the mixture); rise time (time elapsed from the start of volume expansion until the foam reaches its maximum height); and tack free time (time elapsed from the moment the foam ceases to have a sticky texture and becomes hard and the surface of the foam stops being tacky to the touch) [11].

2.9. Moisture Content and Water Absorption

Empty pan on the PMB 53 were place in Moisture Analyzer. Press (tare) to zero the weight. Sample pan will fill with the foam. Filled pan were place the on the analyzer. Lower the lid of the weighing chamber and press the start button to begin the test. The moisture content of samples was calculated using following equation.

$$\text{Moisture content (\%)} = \frac{(Initial\ mass - Dry\ mass)}{(Initial\ mass)} \times 100\ \% \quad (5)$$

The samples of 45 x 10 mm (diameter x height) were soaked in 1000 ml beaker glass of water and kept for 6 days in room temperature. The samples were removed from beaker containing water and weighed. The sample mass change resulting from the water uptake (expressed as a gram/volume percentage) was calculated according to following equation:

$$\text{Water absorption (\%)} = \frac{(Wet\ mass - Dry\ mass)}{(Volume\ of\ foam)} \times 100\ \% \quad (6)$$

2.10. Differential Scanning Calorimetry (DSC)

Polyurethane foam thermal behaviour can be investigated and studied using DSC to identify the endothermic and exothermic activity of materials. The glass transition (T_g) and the cure reaction of foam samples which were conducted using TA Q2000 DSC calorimeter. In order to measure the T_g, 5 to10 mg of foam sample was placed into an aluminum sample pan and sealed with a lid by Tzero sample press. The temperature of DSC was programmed first from the room temperature to 250 °C and back to 0 °C at 20 °C/min to remove moisture content. Dynamic scans were conducted with heating rates, 10 °C/min. in a scanning temperature range from 25 to 200 °C [11]. The onset temperature (T_o) was determined from the DSC thermogram by drawing a tangent line from the inflection point to the baseline and recording the temperature at the intersection of these two lines.

3. Results and Discussion

3.1. Optimization of Liquefaction Process

3.1.1. Effect of Raw Material in the Liquefaction Solvent of Oil Palm Fruit Waste

Figure 1(a) shows the effect of raw materials/liquefaction solvent ratio on residue content and viscosity. The amount of residue was decreases by changing the ratio of PW/PEG400 from 1/2 to 1/5 which reducing in PW composition ratio from 50% to 20% of PM, PS and PK. The decreased for all composition ratio on PM, PS and PK to PEG400 revealed the reduction of residue content 31 to 17%, 33 to 19% and 32 to 18% respectively. The decreasing residue content obtained from 1/2 to 1/5 ratio due to recondensation reactions because of the high raw material of biopolyol [12]. Generally, lower residue content obtained in this research might be clarified by the utilization of liquefaction solvent and different lignocellulosic biomass [13]. High residue content (31, 32 and 33% for PM, PK and PS, respectively) at high raw material concentration (50%) due to the insufficient amount of liquefaction solvent which reducing the potential to liquefied and degrade the composition components to direct recondensation reactions. The raw material with lower concentration (20%), the residue content decreased (17, 18 and 19%) showing that the amount of liquefaction solvent was sufficient and recondensation occur in low reactions. Thus, moderate raw material concentration (33%), i.e. raw material/liquefaction solvent ratio 1/3 with less chemical is preferable for this work. The viscosity of PW/PEG400 ratio of PM/PEG400 slightly increased from 400 to 540 Pa.s, PS/PEG400 reached 610 to 650 Pa.s, while PK/PEG400 ratio increased from 550 to 580 Pa.s when the ratio decreases from 1/2 to 1/5.

Figure 1(b) shows the acid value and OH number was considerably increase from 0.5 to 0.2 for PW with PEG400 at 150°C. The acid values were slightly increased from 14 to 18.2 mg $KOH.g^{-1}$, 11 to 17.5mg $KOH.g^{-1}$ and 12 to 16.5 mg $KOH.g^{-1}$ for PM/PEG400, PK/PEG400 and PS/PEG400, respectively. Moreover, PS/PEG400 with 425 to 495 mg $KOH.g^{-1}$ ratio contributed to higher hydroxyl values than PM/PEG400 with 425 to 485 mg $KOH.g^{-1}$ and PK/PEG400 with 430-484 mg $KOH.g^{-1}$ ratios. The increase in the PEG400 content in the mixture, the acid value and hydroxyl value of the polyols increased. The increase in acid number are often in all probability attributed either to the oxidation of the carbonhydrates and lignin or to the increase of acidic substances during the liquefaction process. Moreover, the increase in hydroxyl number can be due to the cleavage of ether or ester linkages between the lignin units [14]. High amount of solvent produced to higher acid number and hydroxyl values. This demonstrates that the liquefaction solvent in the mixture can give the hydroxyl group of the polyols. A loss of hydroxyl groups also occurred during the liquefaction reaction. Alcoholysis reaction of oil palm fruit waste also occur during the liquefaction reaction process. The increased of acid value could be attributed to the increase of the liquefaction solvent with 5% H_2SO_4, and also to the increase of acidic substances produced with the decomposition of oil palm components and the oxidation of alcohols as the liquefaction continued [15].

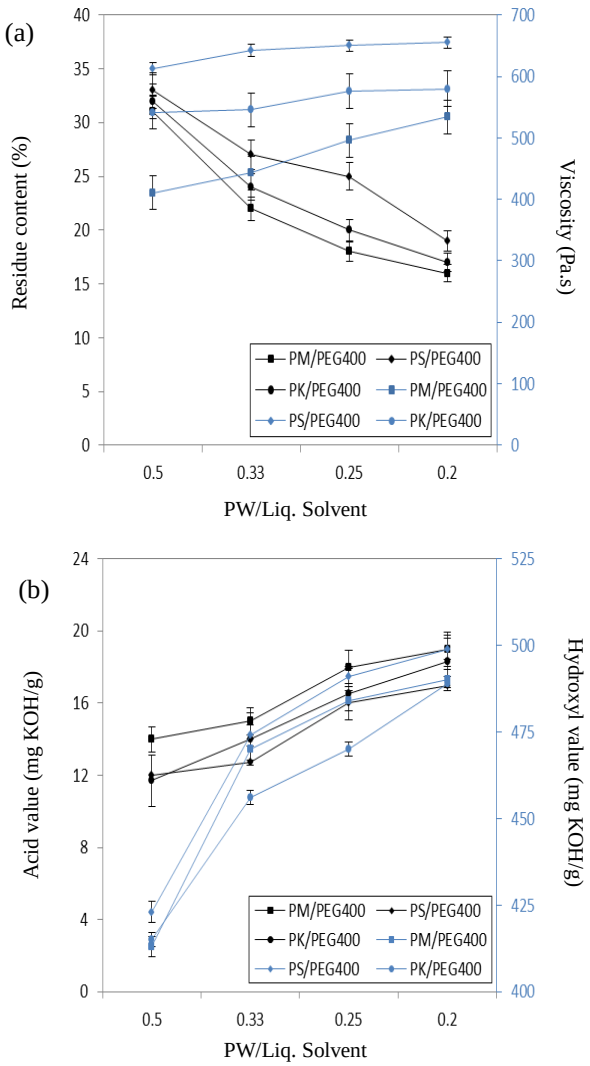


Fig. 1: Effect of raw material/liquefaction solvent ratio on (a) residue content and viscosity (b) acid value and hydroxyl value. Reaction condition: Oil palm mesocarp fibre/liquefaction solvent ratio, 1/2 to 1/5; temperature, 150 °C; reaction time, 120 min; liquefaction solvent, PEG400; acid concentration, 5 %.

3.1.2. Effect of Reaction Time of Oil Palm Fruit Waste

In order to study the efficiency of liquefaction solvent (PEG400) on the liquefaction of oil palm mesocarp fiber (PM), oil palm shell (PS) and oil palm kernel (PK), a series of experiments were performed at different reaction time and the results are presented in Figure 2. It is clear from the figure that all part of oil palm fruit fiber (PW) having similar liquefaction trend, which decreased gradually after 30 min. Increasing in the liquefaction time to 60 minutes resulting the residue content of PM/PEG400 (39%), PS/PEG400 (42%) and PK/PEG400 (48%). At 90 minutes, the residue content for PM/PEG400, PK/PEG400 and PS/PEG400 remained almost unchanged.

Degradation and re-polymerization coexist in the liquefaction of oil palm fruit waste. Degradation reduce the residue percent and makes the oil palm fruit wastes decompose. In contrast, re-polymerization increases the residue percent and produces insoluble material. Degradation gets the superiority, resulting decreased of residue content percentage at the early stage of the liquefaction [16]. Re-polymerization is improved steadily as a result of increase in the concentration of small molecules in the reaction process. Small molecules are re-polymerized into the insoluble macromolecule [16]. Accordingly, the residue content percentage reduced slowly at the end of the liquefaction. The viscosity as a function of reaction time is shown in Figure 2(a). The viscosity of PM/PEG400, PK/PEG400 and PS/PEG400 increased at the initial stages, and then increased gradually after 30 min. This can be attributed to the decomposition reaction was a major reaction during the first 30 min.

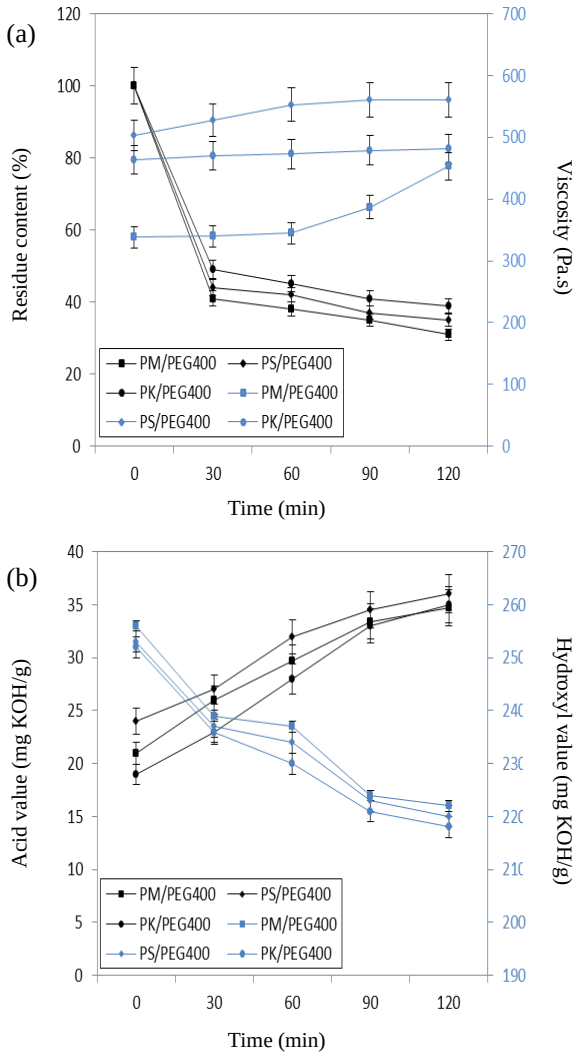


Fig. 2: Effect of reaction time on (a) residue content and viscosity (b) acid value and hydroxyl value. Reaction condition: Oil palm fruit waste/liquefaction solvent ratio, 1/3; temperature, 150°C; reaction time, 120 min; liquefaction solvent, PEG400; acid concentration, 5%.

Based on the result in Figure 2(b), the hydroxyl number of biopolyol decreased as the reaction time increased. It probably due to various dehydration, oxidation, or recondensation reactions between liquefaction solvent and liquefied products which occur during liquefaction [17-18]. The hydroxyl number of PM/PEG400 biopolyols decreased from 255 to 221 mg KOH/g as liquefaction time increased from 0 to 120 min. The hydroxyl number of PS/PEG400 reached 253 to 220 mg KOH/g from 0 to 120 min. The hydroxyl number of PK/PEG400 ratio decreased from 251 to 218 mg KOH/g when the reaction time increase from 0 to 120 min. The acid number of PM/PEG400, PK/PEG400 and PS/PEG400 biopolyols slightly increased as the liquefaction time increased. This could attributed to the fact that acidic substances can be produced during the decomposition of biomass [17].

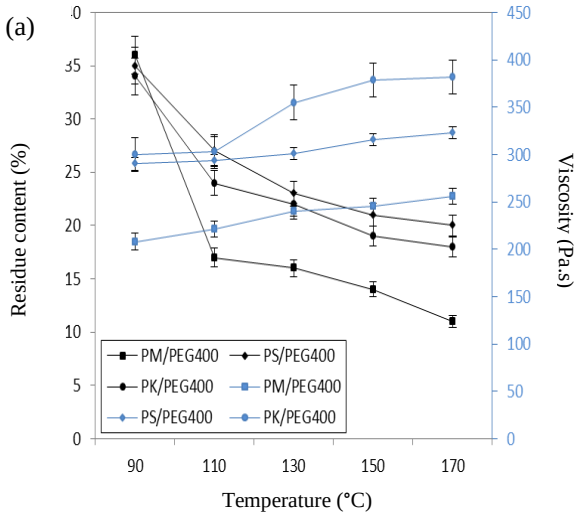
3.1.3. Effect of Temperature of Oil Palm Fruit Waste

Figure 3(a) clearly shows the residue content for PM/PEG400, PK/PEG400 and PS/PEG400 decreased when the liquefaction temperature increased from 90 to 170°C. Additionally increased in the liquefaction temperature to 170°C was resulted in very slight decreased in the amount of residue content. This indicates that re-condensation reactions are non-existent at high liquefaction tem-

peratures (> 150°C). It shows that 150°C can be considered as the most suitable temperature for this reaction [12]. It is also proved that PM/PEG400 gives lower residue content than PS/PEG400 and PK/PEG400 at all liquefaction temperatures. The residue content for PM/PEG400, PK/PEG400 and PS/PEG400 decreased from 36 to 12%, 34 to 18% and 35 to 22% when the temperature increased from 90 to 170°C. This result affirms that PM/PEG400 is more susceptible to liquefaction than PK/PEG400 and PS/PEG400 as shown in Figure 3(a).

Meanwhile, the viscosity of PK/PEG400, PS/PEG400, PM/PEG400 increased from 305 to 375 Pa.s, 301 to 310 Pa.s and 205 to 250 Pa.s as reaction temperature increased from 90 to 170°C. For the most part, the reaction temperature enhanced re-condensation reactions between the liquefied biopolyol during the liquefaction, resulting in compounds of higher viscosity with higher molecular weight. Additionally, the evaporation of volatile compounds at higher reaction temperatures also contribute to the increase of viscosity [19].

The resulting hydroxyl and acid numbers of biopolyols with reaction temperature are shown in Figure 3(b). The PM/PEG400, PS/PEG400, PK/PEG400 acid number decreased from 34 to 24 mg KOH/g, 33 to 23 mg KOH/g and 35 to 20 mg KOH/g respectively from 90 to 170°C. The decrease in the acid number at higher temperatures can be attributed to impurities in the biopolyol, as in which the existence residues of fatty acid which react with hydroxyl groups in the compounds. Therefore, it can prompt the utilization of acidic compounds at high temperature [13]. These can be predominant at this liquefaction condition, leading to a decrease in the acid number of biopolyol. The hydroxyl number of PM/PEG400, PS/PEG400, PK/PEG400 decreased approximately from 380 to 130 mg KOH/g, 360 to 120 mg KOH/g and 370 to 110 mg KOH/g respectively from 90 to 170°C. When the temperature increase, resulting decrease in the hydroxyl number. This can be attributed to a decrease in the components containing hydroxyl groups via thermal oxidative reactions and condensation or dehydration reactions of the liquefaction solvents that occur between liquefaction components [20].



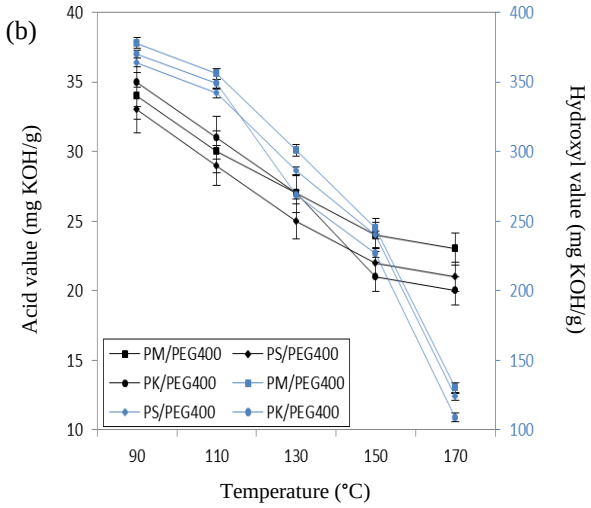


Fig. 3: Effect of temperature on (a) residue content and viscosity (b) acid value and hydroxyl value. Reaction condition: Oil palm fruit waste/liquefaction solvent ratio, 1/3; temperature, 90-170°C; reaction time, 120 min; liquefaction solvent, PEG400; acid concentration, 5%.

3.1.4. Effect of Catalyst of Oil Palm Fruit Waste

In this experiment, sulfuric acid concentrations in the range 1 to 5% (w/w) were used. Figure 4(a) shows that the residue content decreases with the increase of acid concentration. When the concentration of sulfuric acid rose from 1 to 5%, the PM/PEG400, PK/PEG400 and PS/PEG400 biopolyol showed decreases of residue content. Increasing the acid concentration to 5% (w/w) resulting decrease in residue content of PS/PEG400 from 47 to 24%. The residue content of PM/PEG400 shows dramatically decreased from 45 to 21% as the sulfuric acid concentration increased from 1 to 5%. The PK/PEG400 residue content also decreased from 40 to 21%, as acid concentration increased from 1 to 5%. Sulfuric acid as catalyst with high concentration has very high oxidizability and secondary reaction may occur in the liquefaction process. Sulfuric acid concentration from 3 to 5% was found to reduce the risk of significant condensation reactions that might occur between liquefied components [20].

Figure 4(a) represents the change of biopolyol viscosity as a function of catalyst concentration. The biopolyol viscosity of oil palm fruit waste increased slightly as sulfuric acid concentration increased from 1 to 5%. The viscosity of PM/PEG400, PS/PEG400 and PK/PEG400 biopolyols increased from 310 to 400 Pa.s, 320 to 400 Pa.s and 300 to 400 Pa.s respectively as acid concentration increased from 1 to 5%. With the increasing amount of acid concentration resulting the viscosity of biopolyols increased. This is because of the fact that the higher acid concentration resulted in the higher re-condensation occur in the liquefied components.

The effects of sulfuric acid concentration on the acid and hydroxyl number of biopolyols are shown in Figure 4(b). The acid number of PM/PEG400 increased from 28 to 55 mg KOH/g as the acid concentration increased. The acid number of PS/PEG400 and PK/PEG400 also increased from 19 to 52 mg KOH/g and 18 to 48 mg KOH/g respectively as the acid concentration increased from 1 to 5%. The hydroxyl number of PM/PEG400, PS/PEG400 and PK/PEG400 biopolyols decreased from 350 to 300 mg KOH/g, 340 to 230 mg KOH/g and 260 to 220 mg KOH/g, respectively as acid concentration increased from 1 to 5%. Considering the oil palm fruit waste fiber conversion, 5% sulfuric acid of catalyst concentration is the suitable for liquefaction.

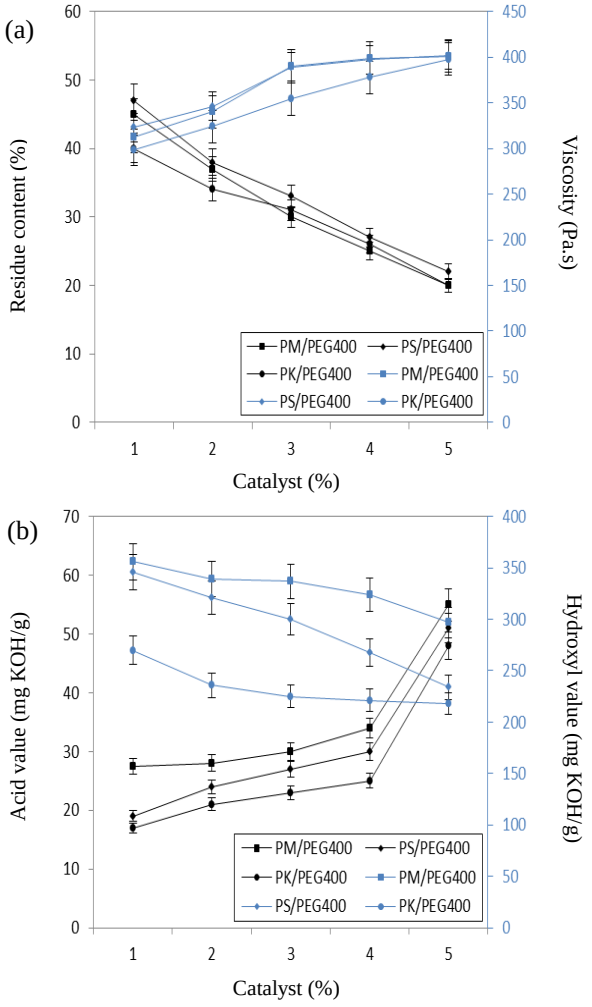


Fig. 4: Effect of catalyst on (a) residue content and viscosity (b) acid value and hydroxyl value. Reaction condition: Oil palm fruit waste/liquefaction solvent ratio, 1/3; temperature, 150°C; reaction time, 120 min; liquefaction solvent, PEG400; acid concentration, 5%.

3.1.5. Effect of Liquefaction Solvent of Oil Palm Fruit Waste

Figure 5(a) shows the residue content and viscosity for liquefied PW biopolyol using different liquefaction solvent (Glycerol, EG and PEG400) at 150 °C. Among the three liquefaction solvent, PEG400 gives the highest liquefaction yield compared to EG and glycerol. PM/PEG400 biopolyol shows the highest yield about 62 % followed by PK/PEG400, PS/PEG400 biopolyol with liquefaction yield of 61 % and 53 % respectively. A similar trend is also observed for liquefied PS and liquefied PK biopolyol, where the highest is for PEG400 and the lowest is for glycerol. PS/Glycerol shows the lowest conversion yield with 50 %. Present study play important role in determining the conversion rate of solvolysis liquefaction process. PEG400, EG and glycerol are polar solvent. The efficiency of these three solvent in solvolysis liquefaction of PW fiber can be sequence as: PEG400 > EG > glycerol. PEG400, EG and glycerol are polar protic solvents which favor the S_N1 reaction [21]. These results suggest that high polarity protic solvents are suitable for solvolysis of PW fibres in order to obtain high conversion yield.

Figure 5(a) also represents the effect of liquefaction solvent of oil palm fruit waste on viscosity. The biopolyol viscosity of liquefied PW/PEG400 biopolyol gives the highest liquefaction yield compared to the liquefied PW/EG and PW/glycerol biopolyol. The viscosity increased as the acid concentration increased. This is because of the PEG400 gives higher efficiency and high polar solvent than the rest of the solvent, resulting to higher viscosity of biopolyol.

Based on the result in Figure 5(b), when the molecular weight of PEG400 increased, acid number of liquefied PW biopolyol decreased but the biomass conversion of each liquefied PW biopolyol was different, respectively. The hydroxyl number of liquefied PW biopolyol decreased as PEG400 were used. This was due to PEG has less hydroxyl groups per unit weight than EG and glycerol. Based on the results, the utilization of PEG400 in the liquefaction compositions improves the biomass conversion.

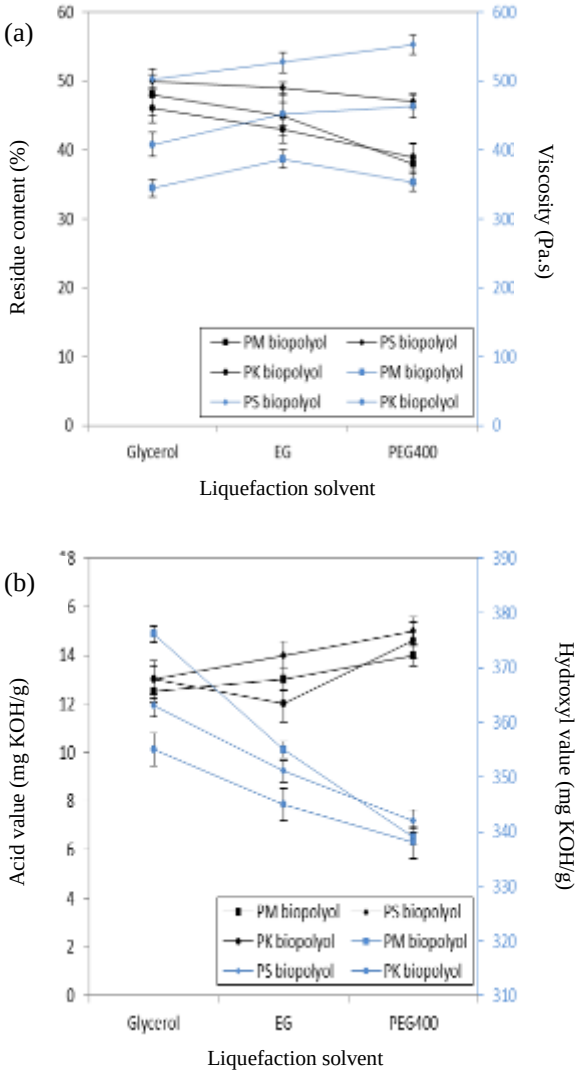


Fig. 5: Effect of liquefaction solvent on (a) residue content and viscosity (b) acid value and hydroxyl value. Reaction condition: Oil palm fruit waste/liquefaction solvent ratio, 1/3; temperature, 150 °C; reaction time, 120 min; liquefaction solvent, Glycerol, EG, PEG400; acid concentration, 5%.

3.2 SEM applied to Liquefaction of PW

The optimum liquefaction condition was obtained at liquefied PW biopolyol was chosen from the previous experiment. The PW particles that remained after liquefaction were analyzed using SEM and compared between different parts of PW. Figure 6 shows the SEM images of the liquefied residue for PM/PEG400, PS/PEG400 and PK/PEG400 prior to the reaction after the liquefaction reaction process. The micrographs reveal a substantial difference in composition and size. The PW residue appears in irregular shape, powdery particles of fiber fragments that occur at the end of the liquefaction processes. It consisted by small particles, intact fibers part and torn fibers. The PM/PEG400 residue surface has longer fibrous appearance than PS/PEG400 with contains fiber and smaller particles composition materials. Meanwhile, PK/PEG400 has more compact structure. When the reaction process occurs, the damaged fibers and small particles would experience dissolution first, leaving behind just only the most resistant and undamaged parts of fiber. There is a small difference between

PM/PEG400, PS/PEG400 and PK/PEG400. In the images with x100 magnification is that the PM fiber particles are really much smaller after carry out the reaction with a PEG400 of liquefaction solvent. The degree of depolymerization of PM/PEG400 was substantially higher than with PS/PEG400 and PK/PEG400.

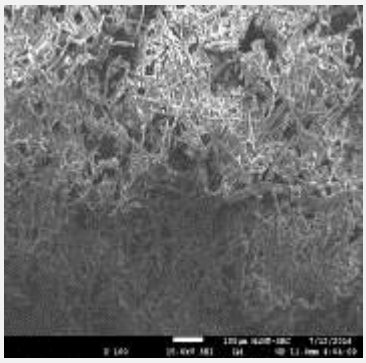
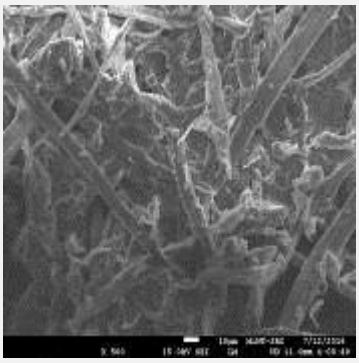
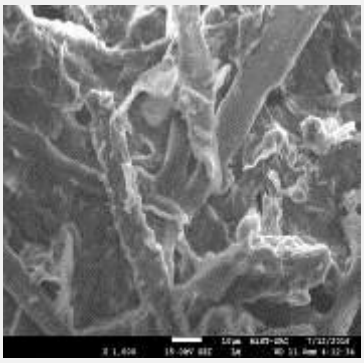
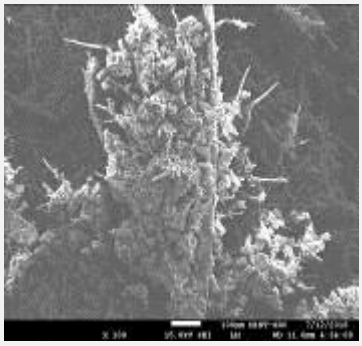
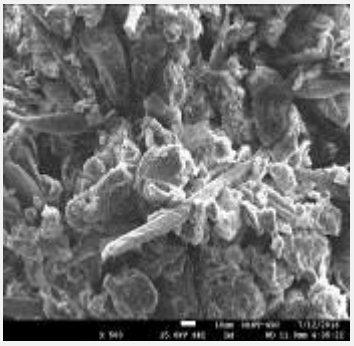
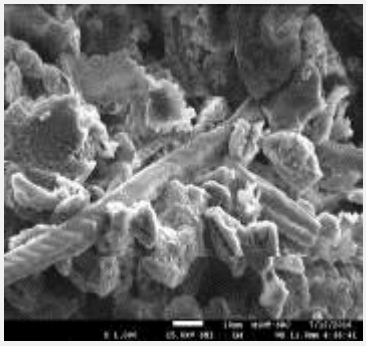
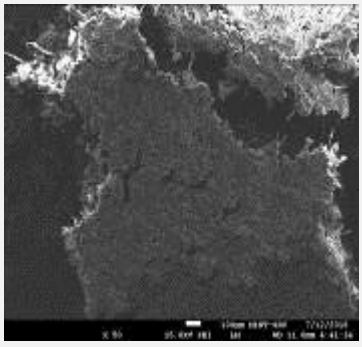
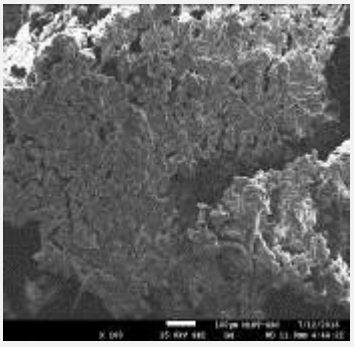
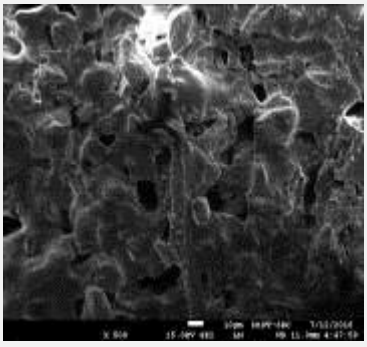
Samples	Magnification		
	X100	X500	X1000
(a) PM/PEG400			
(b) PS/PEG400			
(c) PK/PEG400			

Fig. 6: SEM images of the liquefied residue for PW (a) liquefied PM/PEG400, (b) liquefied PS/PEG400, (c) liquefied PK/PEG400, Reaction condition: Oil palm mesocarp fiber/liquefaction solvent ratio, 1/3; temperature, 150°C; reaction time, 120 min; acid concentration, 5%; liquefaction solvent, PEG400

3.3. Moisture Content and Water Adsorption

Figure 7 represents moisture content and water absorption value for PMF, RF and PMRF foam. The data was replicates for 3 times for each samples by using the equation (5) for moisture content and equation (6) for water absorption. The moisture content and water absorption varies within the range of 2 to 6 % and 20 to 40 %, respectively. Based on Figure 7, RF shows the highest value at 5.11 % compared to PMF with 4.13 %. Then, moisture content decreased dramatically from $PMRF_{80/20}$ to $PMRF_{20/80}$ from 4.19 to 2.98 %. Figure 7 reveals that water absorption of $PMRF_{80/20}$ shows the highest value at 35.2 %, while PMF shows the lowest value at 30.1 %. High moisture content and water absoprtion of PU foam will eventually leads to tremendous drawback in mechanical properties. PEG400 as solvent in the composition is a highly hydrophilic polymer. Therefore, maintaining low moisture content in the PU foam is more difficult, while renewable monomer is hydrophobic polymer. The foam rise because the moisture content in the liquefied PM biopolyol act as blowing agent by reaction with the isocyanate to form carbon dioxide. If there is excess moisture, the reaction will be very exothermic and the mixture will turn into black color [23]. The foam will rise very fast because more carbon dioxide is being created and this will easily cause the foam to collapse. Also, the low water absorption, which allows for an easy drying of the product and prevent the growth of bacteria and fungi [24].

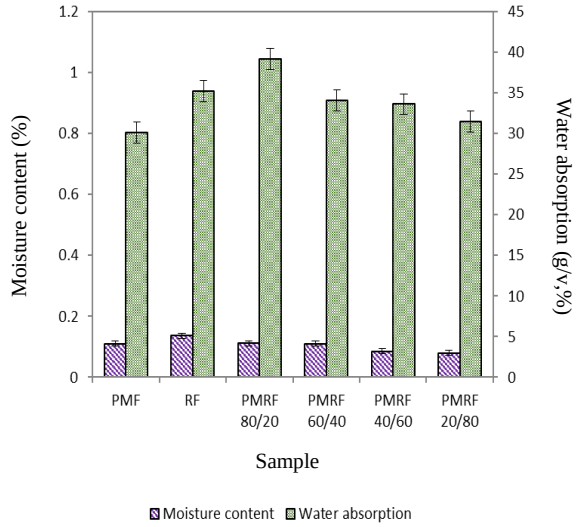


Fig. 7: Moisture content and water absorption of PMF, RF and PMRF foam samples

3.4. Kinetic Profile of Foam Formation

Figure 8 shows the processing times of PMF, RF and PMRF. The PMF shows the longest processing time followed by EF, RF, PMRF and PMEF. The results indicate a slight increase from initial mix time to gelling time for the foams, which is related to the molecular weight of liquefied PM biopolyol, renewable monomer and their viscosity. The initial reactivity of PMF (mix, cream and gelling time) was faster with PMRF it took a longer time to completely cure the foams, as evidenced by the long tack free time. PMRF exhibit fastest processing time due to (1) incompatible mixtures and the reaction mixtures are heterogeneous; (2) the incorporation of renewable monomer will increase the concentration of the composition resulting reduction of diffusion across the interfaces; (3) higher reactivity of the polyols towards isocyanate. Primary hydroxyl groups are more reactive toward isocyanate than the secondary hydroxyl groups due to reduced steric hindrance [21]. The results which showed reduced mix time and higher extent of rising due to the increased presence of primary hydroxyl groups. For this reason, foaming additives such as surfactants should carry high surface activity to act as a nucleation supporter and good emulsifying ability for the raw materials and blowing agents [22].

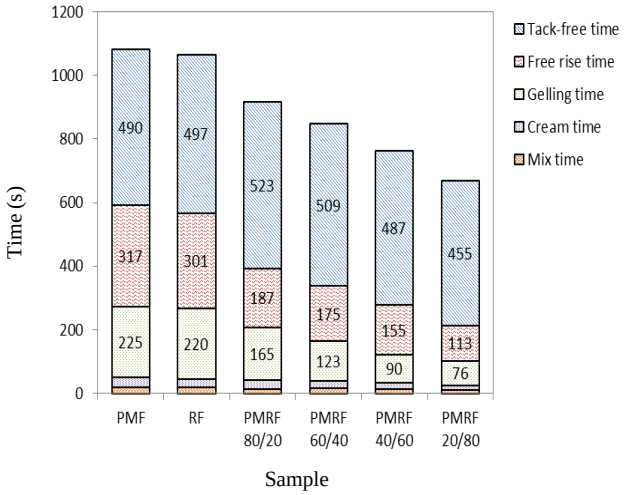


Fig. 8: Processing time of PMF, RF and PMRF foam samples.

3.5. Differential Scanning Calorimetry (DSC)

DSC is a technique to determine the glass transition temperature (T_g) of polymeric materials. DSC thermogram curve of PMF, RF and PMRF are shown in Figure 9. Table 2 shows the specific glass transition temperature (T_g), onset cure temperature (T_{on}), peak cure temperature (T_p) of each sample. The different sample show endothermic cure peaks similar to each other.

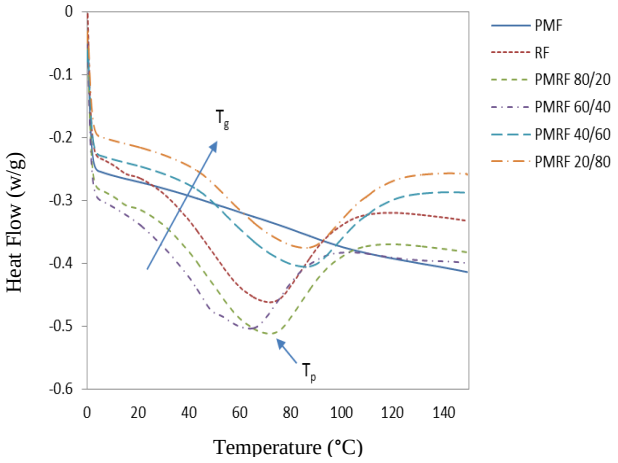


Fig. 9: DSC thermogram curve of PMF, RF and PMRF foam samples

Table 2: DSC curves analysis of PMF, RF and PMRF foam samples

Sample	T_g (°C)	T_{on} (°C)	T_p (°C)	ΔH (J/g)
PMF	-	-	-	-
RF	37.5	53.1	68.9	- 21.34
$PMRF_{80/20}$	38.6	52.3	71.8	- 30.86
$PMRF_{60/40}$	54.9	51.7	64.5	- 4.227
$PMRF_{40/60}$	56.1	54.5	59.5	- 2.358
$PMRF_{20/80}$	61.8	59.8	86.1	- 9.476

The T_g varied significantly ranging from 20 to 120 °C. In PMF, the T_g were not observed, whereas RF, $PMRF_{80/20}$, $PMRF_{60/40}$, $PMRF_{20/80}$, and $PMRF_{20/80}$ showed T_g at 37.7, 38.6, 54.9, 56.1 and 61.8 °C, respectively. According to the result obtained, there is no T_g observed in PMF which can be attributed to their large crosslink density which restricted the molecule movement. Distinct T_g were observed in the range of scanned temperature. The T_g range of the PMRF was larger than the PMF and RF due to the difference of crosslink density. Structurally, liquefied PM biopolyol and renewable monomer have a low molecular weight between crosslinks, which could lead to high T_g of the soft domains. Moreover, an increase in phase mixing could also result in high T_g's and especially broader T_g.

4. Conclusion

Oil palm fruit waste (PW) has been successfully liquefied in the presence of polyhydric alchohol as liquefaction solvent. Among three part of liquefied oil palm fruit waste (PW) tested, PM/PEG400 ratios was the effective and produce highest of liquefaction. It found that, the optimum liquefaction reaction conditions were (material/liquefying solvent ratio, 1/3: reaction time, 120 min: temperature, 150°C and catalyst concentration, 5%). Acid value, hydroxyl value and viscosity are similar to those commercial petrochemical polyols. Polyurethane (PU) foam was successfully prepared by mixing liquefied PM biopolyol, renewable monomer, catalyst and crosslinker (MDI). Foaming kinetic resulted increasing in time from initial mix time to gelling time. Moisture content and water absorption decreased from $PMRF_{80/20}$ to $PMRF_{20/80}$ foam samples. There is no T_g observed in PMF in DSC analysis. Meanwhile, T_g value increased from $PMRF_{80/20}$ to $PMRF_{20/80}$ foam samples. The research shows the liquefied PM biopolyol and renewable monomer have potential for the fabrication of polyurethane (PU) foams.

Acknowledgement

The author would like to thanks Sustainable Polymer Engineering, Block E1, Advanced Manufacturing and Materials Center (SPEN-AMMC), Universiti Tun Hussein Onn Malaysia (UTHM), Johor for supporting this research under GPPS U774, IGSP U678 and A136.

References

[1] H. Mazaheri, K. T. Lee, S. Bhatia, and A. R. Mohamed, "Subcritical water liquefaction of oil palm fruit press fiber in the presence of sodium hydroxide: An optimisation study using response surface methodology," Bioresource Technology, 101(23), 9335–9341, 2010.

[2] M. F. Awalludin, O. Sulaiman, R. Hashim, and W. N. A. W. Nadhari, "An overview of the oil palm industry in Malaysia and its waste utilization through thermochemical conversion, specifically via liquefaction," Renewable and Sustainable Energy Reviews, 50, 1469–1484, 2015.

[3] S. E. Hosseini, M. A. Wahid, and A. Ganjehkaviri, "An overview of renewable hydrogen production from thermochemical process of oil palm solid waste in Malaysia," Energy Conversion and Management, 94, 415–429, 2015.

[4] S. Kormin and A. Z. M. Rus, "Preparation and characterization of biopolyol from liquefied oil palm fruit waste: Part 1," Materials Science Forum, 882, 108–112, 2017.

[5] J. Xu, J. Jiang, C. Y. Hse, and T. F. Shupe, "Preparation of polyurethane foams using fractionated products in liquefied wood," Journal of Applied Polymer Science, 131(7), 1–7, 2014.

[6] N. Mahmood, Z. Yuan, J. Schmidt, and C. (Charles) Xu, "Depolymerization of lignins and their applications for the preparation of polyols and rigid polyurethane foams: A review," Renewable and Sustainable Energy Reviews, 60, 317–329, 2016.

[7] S. Kormin and A. Z. M. Rus, "Preparation and characterization of biopolyol from liquefied oil palm fruit waste: Part 2," Materials Science Forum, 882, 113–118, 2017.

[8] A. Z. M. Rus, N. Normunira, and M. Hassan, "Thermal characteristic of biopolymer foam using hot compression technique," Proceedings of the Malaysia University Conference Engineering Technology, 2014, pp. 1-6.

[9] N. Q. A. Adnan and A. Z. M. Rus, "Sound absorption of laminated biopolymer foam and epoxy foam," Key Engineering Materials, 594–595, 291–295, 2013.

[10] A. Z. M. Rus, S. Shafizah, and A. P. Samples, "Acoustic behavior of polymer foam composite of shorea leprosula after UV-irradiation exposure," International journal of Mechanical, Aerospace, Industrial and Mechatronics, 9(1), 188–192, 2015.

[11] A. A. Abdel Hakim, M. Nassar, A. Emam, and M. Sultan, "Preparation and characterization of rigid polyurethane foam prepared from sugar-cane bagasse polyol," Materials Chemistry and Physics, 129(1–2), 301–307, 2011.

[12] R. Briones, L. Serrano, R. Llano-ponte, and J. Labidi, "Polyols obtained from solvolysis liquefaction of biodiesel production solid residues," Chemical Engineering Journal, 175, 169–175, 2011.

[13] M. S. Shengjun Hu, "Production and characterization of bio-based polyols and polyurethanes from biodiesel-derived crude glycerol and lignocellulosic biomass," PhD thesis, Ohio State University.

[14] M. S. Fidan and M. H. Alma, "Preparation and characterization of biodegradable rigid polyurethane foams from the liquified eucalyptus and pine woods," Wood Research, 59(1), 97–108, 2014.

[15] J. Xie, X. Zhai, C. Y. Hse, T. F. Shupe, and H. Pan, "Polyols from microwave liquefied bagasse and its application to rigid polyurethane foam," Materials, 8(12), 8496–8509, 2015.

[16] H. Wang and H. Z. Chen, "A novel method of utilizing the biomass resource: Rapid liquefaction of wheat straw and preparation of biodegradable polyurethane foam (PUF)," Journal of the Chinese Institute of Chemical Engineers, 38(2), 95–102, 2007.

[17] J. Xie, J. Qi, C. Hse, and T. F. Shupe, "Optimization for microwave-assisted direct liquefaction of bamboo residue in glycerol/methanol mixtures," Journal of Forestry Research, 26(1), 261–265, 2015.

[18] B. L. Xue, J. L. Wen, and R. C. Sun, "Producing lignin-based polyols through microwave-assisted liquefaction for rigid polyurethane foam production," Materials, 8(2), 586–599, 2015.

[19] R. Briones, L. Serrano, R. Llano-Ponte, and J. Labidi, "Polyols obtained from solvolysis liquefaction of biodiesel production solid residues," Chemical Engineering Journal, 175(1), 169–175, 2011.

[20] S. Hu, C. Wan, and Y. Li, "Production and characterization of biopolyols and polyurethane foams from crude glycerol based liquefaction of soybean straw," Bioresource Technology, 103(1), 227–233, 2012.

[21] R. Roslan, S. Zakaria, C. H. Chia, R. Boehm, and M. P. Laborie, "Physico-mechanical properties of resol phenolic adhesives derived from liquefaction of oil palm empty fruit bunch fibres," Industrial Crops and Products, 62, 119–124, 2014.

[22] H. Lim, S. H. Kim, and B. K. Kim, "Effects of silicon surfactant in rigid polyurethane foams," Express Polymer Letters, 2(3), 194–200, 2008.

[23] N. Saifuddin, O. Chun Wen, L. Wei Zhan, K. Xin Ning, "Palm oil based polyols for polyurethane foams application," Proceedings of the International Conference on Advances in Renewable Energy Technologies, 2010, pp. 6-7.

[24] M. Zieleniewska, M. K. Leszczyński, M. Kurańska A. Prociak, L. Szczepkowski, M. Krzyzowska, and J. Ryszkowska, "Preparation and characterisation of rigid polyurethane foams using a rapeseed oil-based polyol," Industrial Crops and Products, 74, 887–897, 2015.