

## Thermal properties of biopolyol from oil palm fruit fibre (OPFF) using solvolysis liquefaction technique

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**Abstract.** Liquefaction is known to be an effective method for converting biomass into a biopolyol. The biomass liquefaction of oil palm fruit waste (PFW) in the presence of liquefaction solvent/polyhydric alcohol (PA): polyethylene glycol 400 (PEG400) using sulfuric acid as catalyst was studied. For all experiments, the liquefaction was conducted at 150 °C and atmospheric pressure. The mass ratio of OPFF to liquefaction solvents used in all the experiments was, 1/3. Thermogravimetric analyses (TGA) were used to analyze their biopolyol and residue behaviors. It was found that thermal stability of oil palm mesocarp fibre (PM), oil palm shell (PS) and oil palm kernel (PK) fibre exhibited the first degradation of hard segment at (232, 104, 230 °C) and the second degradation of soft segment at (314, 226, 412 °C) as compared to PM, PS and PK residue which (229, 102, 227 °C) of hard segment and (310, 219, 299 °C) of segment, respectively. This behavior of thermal degradation of the hard segment and soft segment of biopolyol was changes after undergo solvolysis liquefaction process. The result analysis showed that the resulting biopolyol and its residue was suitable monomer for polyurethane (PU) synthesis for the production of PU foams.

### 1. Introduction

The oil palm is replanted every 25 to 30 years. Malaysia is one of the largest producer and manufacturer of palm oil products. 5 million tons of trunks and 1.1 million tons of fronds are being disposed annually during replantation. Moreover, in the production process of palm oil and palm kernel oil in factories, 7 million tons of mesocarp, 4.1 million tons of shell, 1 million of palm kernel and 13.4 million tons of empty fruit bunches (EFB) are produced every years [1] [2]. This palm oil waste generates large amount of palm oil by-products, which can be recycled into biopolyol. If this biopolyol is put into good use, in this case as a main material in bio-polymer compound, then it will largely reduce the cost of high performance composite [2] [3]. At the same time, it will also reduce the amount of waste generated by the palm oil industry thus achieving a global aim of sustainable development. Not only it reduces the waste, it also preserves the nature by eliminating the need to harvest natural aggregates from natural sources.

Biopolyol has been widely used as a raw material for polyurethane production which has many applications in daily life such as foam synthesis, thermoset, thermoplastic and coating materials [4] [5]. As the limiting amount of polyol derived from petroleum and the demand of polyol is increasing, effort is needed to find out alternative raw materials in particular potential feedstock comes from agricultural waste.



However, there are limited studies focused on the use of oil palm fruit waste as material for synthesis of biopolyol. Oil palm fruit waste is very potential raw material for synthesis of biopolyol as it contains lignocellulose hence through solvolysis liquefaction process will produce biopolyol.

Thermogravimetric analysis (TGA) is an analytical technique that measures the weight of a small polymer sample as a function of time or temperature and hence gives a quantitative description of the thermal stability of material and the amount of the corresponding residue. The derivative weight loss curve known as differential thermogravimetric analysis (DTG) shown on the TGA themogram can be used to understand the onset decomposition temperature, the temperature at which the rate maximum of decomposition and decomposition temperature as well as the number of step involved in the thermal degradation of flexible polyurethane foam [5] [6]. TGA is useful to determine thermal stability and degradation behavior of a polymer or composite. The purpose of this research is to study the influence of independent variables (different types of biomass) on thermogravimetric analysis through liquefaction process of biopolyol.

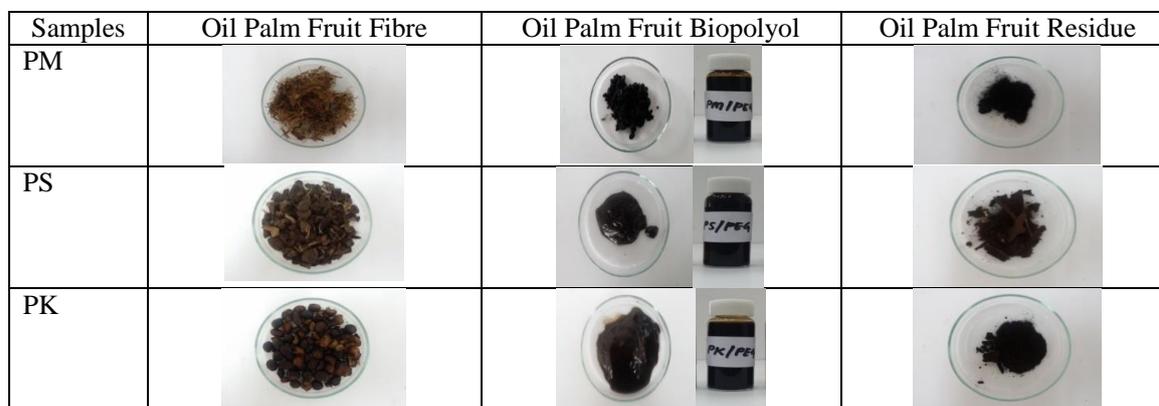
## 2. Methodology

### 2.1. Materials

Materials used in this research were 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. Polyhydric alcohol (PA) such as polyethylene glycol 400 (PEG400) were used as liquefaction solvents and 98% percentage of sulfuric acid was used as the catalyst. All chemicals were purchased from Sigma-Aldrich.

### 2.2. Liquefaction of oil palm fruit fibre (OPFF) in PEG solution under conventional glass flask

Oil palm fruit fibre (OPFF) was liquefied at different liquefaction condition. Polyethylene glycol 400 (PEG400) was used as the main liquefaction solvent. First, oven dried oil palm fruit waste (20g) and liquefaction reagent were mixed 1:3 weight ratio with 5% sulfuric acid as a catalyst. Then the mixture was placed into a 250 mL three-branch flask equipped with thermometer and magnetic stirrer. Liquefaction temperature and time was 150 °C and 120 min (2 hours), respectively. The liquefaction was carried out in an oil bath. After that, the liquefied oil palm wastes were dissolved in 100 mL of methanol for 4 h. The liquefied solutions were then vacuum-filtered through filter paper. The filtrated liquid was evaporated at 70 °C using rotary evaporator to remove methanol, the obtained black liquid was designated crude biopolyols [7] [8]. Figure1 show the photograph of oil palm fruit fibre before and after solvolysis liquefaction process.



**Figure 1.** Photograph of oil palm fruit fibre before and after solvolysis liquefaction process.

### 2.3. Characteristics of polyol

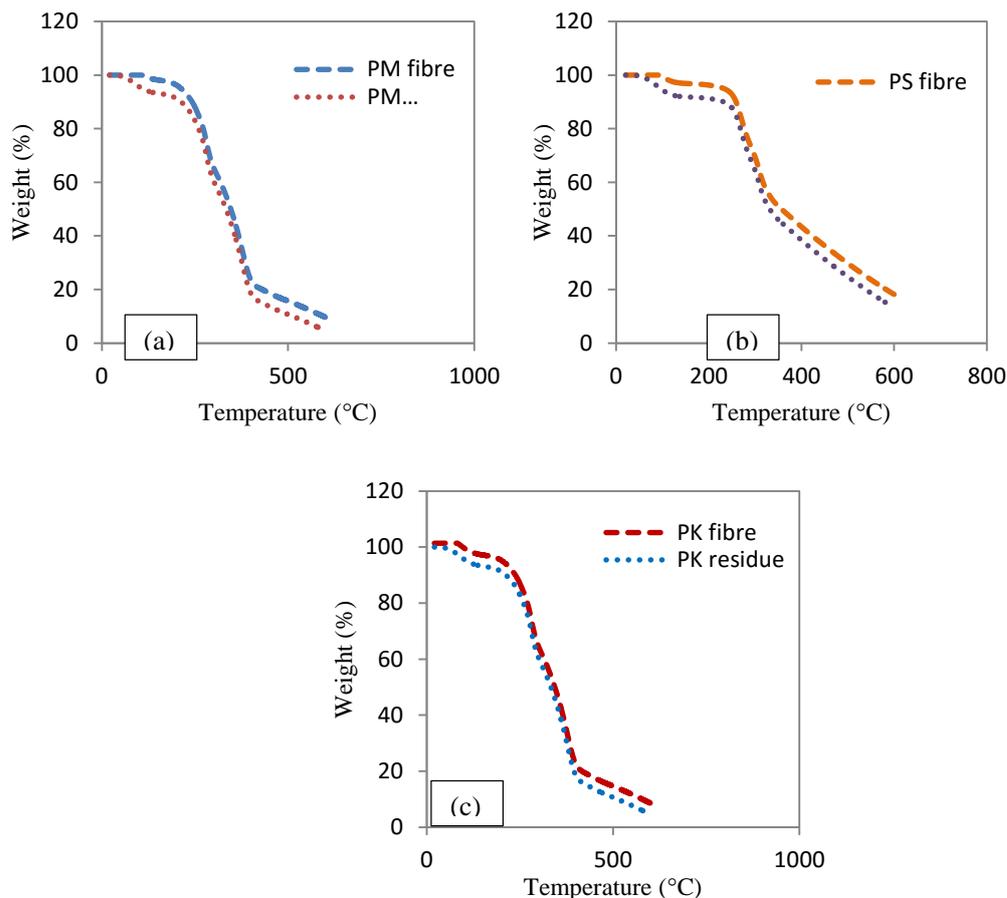
#### Thermal Gravimetric Analysis (TGA)

TGA measurement was performed using *Linseis* TGA for characterized the thermal properties of biopolymer foam. The TGA for flexible and rigid biopolymer foam was measured weight loss and derivative weight loss curve was heated in the thermal gravimetric furnace from 20oC to 900oC at the heating rate of 10oC/min under oxygen atmosphere, flow rate 0.3  $\mu$ L and using alumina crucible.

### 3. Result and discussion

#### Thermogravimetric analysis (TGA)

Figure 2 presents the thermogravimetric (TG) curves for oil palm fruite fibres (PFF) and its residue. The first point degradation correlates with the hard segment while the second peak correlates with the degradation of the soft segment. Qualitative characterization of the degradation process is elaborate by the onset and maximum peak temperature of the first step  $T_{1on}$  and  $T_{1max}$  along with the same for second step  $T_{2on}$  and  $T_{2max}$ . Detail TGA data, the onset decomposition temperature ( $T_{onset}$ ) and the maximum decomposition temperature ( $T_{max}$ ) for PFF and its residue are tabulated in Table 1.



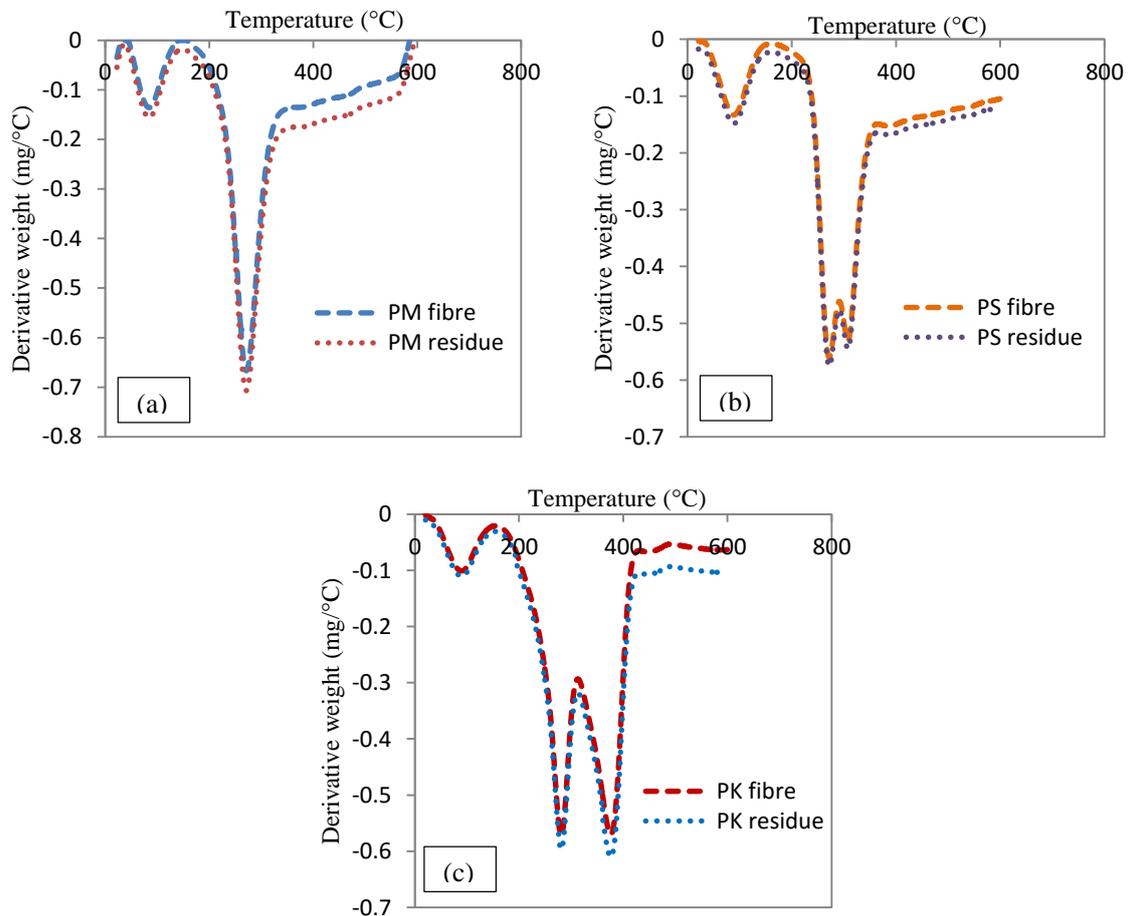
**Figure 2.** Thermogram weight loss of oil palm fruit fibre before and after liquefaction. (a) PM (b) PS (c) PK. Reaction condition: Oil palm fruit fibre/liquefaction solvent ratio, 1/3; temperature, 150 °C; reaction time, 120 min; biomass loading, 20g; acid loading, 5%.

**Table 1.** Thermal decomposition of PFF and PFF residue.

Samples	PM fibre	PM residue	PS fibre	PS residue	PK fibre	PK residue
<b>First Decomposition ( °C)</b>	232	229	104	102	230	227
T <sub>1on</sub> ( °C)	93	86	93	87	91	85
T <sub>1max</sub> ( °C)	290	287	210	207	288	284
Weight loss (%)	29	31	7	9	28	30
<b>Second Decomposition ( °C)</b>	314	301	226	219	312	299
T <sub>2on</sub> ( °C)	290	288	210	207	288	284
T <sub>2max</sub> ( °C)	395	386	307	302	393	385
Weight loss (%)	51	53	39	41	49	51
<b>Third Decomposition ( °C)</b>	410	402	311	305	409	399
T <sub>3on</sub> ( °C)	395	383	307	302	393	385
T <sub>3max</sub> ( °C)	596	594	596	594	593	592
Weight loss (%)	18	20	35	37	17	19

The weight loss of the first stage, which occurred from about 50 to 300 °C, was due to the volatilization of methanol and water. It is clear that the decomposition of fibre characterized by a very small weight loss at around 100 °C attributed to the release of residual water. The previous researchers was investigated the first peak of thermal degradation of biomass which is palm kernel shell, empty fruit bunch and palm mesocarp fiber due to moisture drying stage. The thermal decomposition observed below 200 °C corresponded to the moisture evolution of the water linked to the hydroxyl and carbonyl groups of the fiber [6]. With increasing temperature during the TGA process, the decomposition lignin and other contents that are difficult to decompose caused the weight loss of fibres and residue at the second stage (300–400 °C). the third stage of PFF and its residue largely attributed to the degradation of lignin and char residue from the second stage [9] [10]. When the TGA temperature reached the third stage of decomposition, the weight loss curve of biopolyols remained constant with a residual weight of approximately 10%, which consisted mainly of coke and ash. The dramatic difference between the TGA curves of fibre and its residue suggested that extensive reactions occurred among the components of fiber during the liquefaction process of biopolyols. In the process of liquefaction when using H<sub>2</sub>SO<sub>4</sub> as a catalyst and PEG400, it was possible that the cellulose in the insoluble residues was changed into cellulose sulphate, which has the characteristic of thermal durability. Moreover, due to liquefaction, more active OH groups on PFF were possibly exposed in the polyols prepared with PEG400. Thus, the insoluble residues created from liquefaction process could act as a more efficient cross-linking agent [11].

From Figure 3(a), the DTG curve of PM fibre and PM residue degraded throughout the temperature range of 50–400 °C and resulted in large mass losses, with one smaller peak at 100 °C followed by a significantly large degradation maximum at 300 °C. Figure 3(b) show the DTG graphs of PS fibre and PS residue with smaller peak at 98 °C followed by two large maximum peak at 280 °C and 350 °C respectively. Figure 3(c) shows the DTG curve for PK fibre and PK residue. It was found that one smaller peak at 100 °C and two large peak of degradation maximum at 250 °C and 380 °C. From the curves of differential thermogravimetry (DTG), it is evident that the decomposition mainly occurred in three successive stages above 50 °C. The first peak appeared at the temperature range less than 100 °C was attributed to the evaporation of moisture content and the beginning of weight loss of volatile components in the DTG evaluation profile of the samples [11] [12]. The thermal characteristic of PFF significantly changes after liquefaction process are shown in Figure 2 and Figure 3.



**Figure 3.** Thermogram DTG of oil palm fruit fibre before and after liquefaction. (a) PM (b) PS (c) PK. Reaction condition: Oil palm fruit fibre/liquefaction solvent ratio, 1/3; temperature, 150 °C; reaction time, 120 min; biomass loading, 20g; acid loading, 5%.

#### 4. Conclusion

The biopolyol based from oil palm fruits fibre (PFF) could be used as one of the raw material for preparation of polyurethane (PU) foam. The thermal degradation of PM fibre and residue exhibited the highest hard segment and soft segment as compared to PS fibre and PK fibre. The thermal degradation of oil palm fruit fibre is consistent after liquefaction process at the first degradation, second degradation and third degradation. This is due to thermal stability of samples at the hard segment has a great influence on the thermal stability of soft segment.

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