

Effect of Synthesis Oil Palm Mesocarp Fibre (PM) Biopolyol Incorporated with PM Waste Filler on Properties of Polyurethane Foam

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Abstract

Biopolyols have been synthesized from Oil Palm Mesocarp fibre (PM) as monomer feedstock to be crosslinked as polyurethane, PU foams (PMF). This study is conducted to determine the effects of PM as waste fibre filler on the performance of PU foam. A 'one-step method' technique is used to crosslink the monomer and disperses the PM waste filler with vigorous stirred and left to cure at room temperature in an open cylindrical mould. Increasing the PM waste filler percentage from 1% to 9% on PU foams namely as PMF₁ – PMF₉ respectively have shown dramatic enhancements in physical, thermal and mechanical properties over the neat PMF without compromising foaming kinetic, density, porosity, and processibility. The compressive strength of PMF slightly increased as the increments of the waste filler percentage content. TGA result indicated that PMFs displayed almost the same trend

in thermal stabilities and thermal degradation temperature. As comparison with PMF, the PMF₁ – PMF₉ were markedly increased the degradation temperature at three different decomposition stages as neat PMF. In addition, fourier transform infrared (FT-IR) analysis revealed that the incorporation with PM waste filler did not changed any chemical group of polyurethane.

Keywords: Biopolyols, Polyurethane Foams, Fibre Filler

I. Introduction

Recently, the lignocellulosic biomass (such as oil palm fruit waste) are considered to be one of the most important classes of renewable source and has high potential to synthesis and become a new polyol sources for polyurethane and can be replaced for commercial polyol in manufacturing polyurethane. The synthesis of polymeric materials from renewable resources has been and remained until this date as one of the greatest challenges for the scientific community. Nowadays, considering the economical and environment concern, together with an increasing dependence on petroleum resources, have reinforced the need of using sustainable renewable resources.

Polyurethane (PU) foams with versatility as an engineering materials find a wide range of applications due to its properties based on composition of their components. However, the main market for polyurethane foam is in polymeric foam, which are flexible and rigid (Hu and Li, 2014; Li, 2012). Flexible polyurethane foams are two predominant application forms of polyurethane with coatings, sealants, elastomers, and adhesives being other common forms of applications. Generally polyurethane foams are one of the major products from urethane material (Lee and Deng, 2014; Li, 2012). The characteristic of polyurethane foam can be changed via adjusting the composition of the raw materials or incorporation with fibre filler.

This paper describes the effect of the PM waste filler, (PW) on the properties of PU foams based on biopolyols obtained from liquefaction of oil palm mesocarp fibre.

II. Experimental

Raw materials. Oil palm mesocarp fibre (PM) was collected from Sindora Palm oil mills, Johor, Malaysia. PW grounded to particle size in the range 20-100 µm were selected for this study. These raw materials were then dried in an oven at 105°C for one night and kept in a desiccator at room temperature before using. 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. Crosslinker, methylene diphenyl diisocyanate (MDI), catalyst (dibutyltin dilaurate), surfactant (silicon oil), blowing agent (water, H₂O) was used as received.

Liquefaction oil palm mesocarp fibre (PM). Polyethylene glycol 400 (PEG400) was used as the main liquefaction solvent. First, oven dried PM (10g) and liquefaction solvent were mixed at 1/3 of weight ratio with 5% sulfuric acid as a catalyst. The mixture was placed in a 250 mL three-branch flask in oil bath equipped with

thermometer and magnetic stirrer 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 100 mL of methanol for 4 h. The liquefied solutions were then vacuum-filtered and evaporated at 70°C using rotary evaporator to remove the solvent. The obtained black liquid was namely as crude biopolyols (Kormin, Rus, and Azahari, 2017).

Filler preparation. Raw oil palm mesocarp fibre (PM) used in this study are supplied by Sindora Palm oil mills, Johor, Malaysia as shown in Fig. 1. Sodium Hydroxide (NaOH) used was supplied by Merck Sdn. Bhd. PM Fibre fillers were immersed in the alkaline solution of 10% NaOH concentration level for 24 hours, then the fibres were filtered out and washed with water to remove dirt layer and impurities on the fibre surface. The treated fibres then were dried at elevated temperature 100 °C for 24 hours.

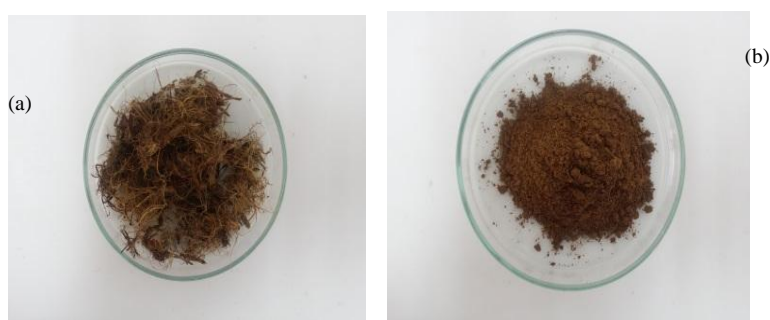


Fig. 1: Oil palm mesocarp fibre (a) Before (b) after grounded.

Foams Formulation and foam Preparation. As in our previous publication (Kormin et al., 2017; Kormin and Rus, 2017) polyurethane foams samples were prepared with ‘one-step method’. The foaming systems used in this work consisted of two components, A and B. Component A is a group of substances containing biopolyols, catalyst (dibutyltin dilaurate), blowing agent (distilled water) and silicon oil (surfactant), treated oil pal mesocarp fibre (filler) were mechanically stirred for 60s to ensure complete mixing. Component B is an isocyanate (MDI). The two components were mixed together using a mechanical stirrer at room temperature. Immediately, the mixtures were cast into an open cylindrical mould and leave to cure for 6 hours at room temperature. The properties of the foams were measured after curing at room conditions for 1 day.

Table 1: Foam formulations from liquefied PM biopolyols incorporated with PM waste fibre filler (PW)

Component	Part by weight (g)	
	PMF	PMF with PW
A		
Liquefied PM	10	10
Biopolyol		
PEG400	2.5	2.5
Dibutyltine	0.1	0.1
dilaurate		
Silicon oil	0.1	0.1
H ₂ O	0.2	0.2
PW	-	1, 3, 5, 7,9 (PMF ₁ , PMF ₃ , PMF ₅ , PMF ₇ , PMF ₉)
B		
MDI	20	20
(Crosslinker)		

Table 1 show the foam formulation for six experiments regarding the influence 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 in foaming processing. In the case of oil palm mesocarp filler reinforced foams; the inorganic material was added before the MDI.

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)(Abdel Hakim, Nassar, Emam, and Sultan, 2011; Lim, Kim, and Kim, 2008).

Density test and porosity measurement. Density (ρ) is the proportion of mass (m) to volume on particular of material. Density of PU foam was measured to identify the differences in density of PMF and PMF₍₁₋₉₎. In order to measure the density of the PU and its composites in small size (10 x 10 x 10 mm) were prepared to get an average value of the density for every portion. The densities PU foams were measured using Mettler Toledo Density Kit. It can be performed using Buoyancy Method according to European Standard EN 993-1 (Wang and Schuman, 2012). Whereas the open porosity ρ_A in volume percent is also calculated.

Thermal Gravimetric Analysis (TGA). The thermal properties of oil palm mesocarp fibre and its liquefaction product were measured by *Linseis* Thermogravimetry analyzer. First, 5-8 mg of the sample was placed in alumina crucible. Then the samples were heated from 40 to 600 °C at the heating rate of 10°C min⁻¹ under oxygen atmosphere and flow rate 0.3 µL (Rus, Normunira, and Hassan, 2014).

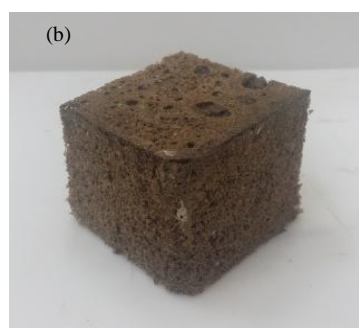
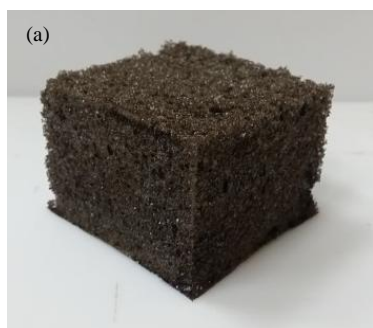
Compressive mechanical properties. Compression test of PU foams was conducted using Universal Testing Machine (UTM) of *Shimadzu-AGI* according to ASTM D1621-10 with the following dimensions; 51mm (length), 51mm (width) and 40mm (thickness) to determine the compressive properties of samples. The compression test was conducted starting with the setting parameter of zero distance of top block of samples surface by using touch screen controller of UTM. During the compression of samples, measurements were taken at a crosshead speed 50 mm/min with a maximum stroke strain of 70 % by thickness. A minimum of three specimens were tested and the average value along with standard deviation were calculated (Xue, Wen, and Sun, 2015; Zheng, Pan, Huang, and Chung, 2011).

Fourier Transform infrared (FT-IR) analysis. The Fourier transform infrared spectroscopy system that was employed in this work was Perkin Elmer spectrometer (Spectrum 100) Universal ATR Sampling Accessory. PU foams samples were cut into small cube (5x5x5 mm) and place in FT-IR sample holder. FT-IR spectra were recorded in the range of 400 to 4000 cm⁻¹ collecting 35 scans with 4 cm⁻¹ resolution, in the transmittance mode (Kormin and Rus, 2017).

III. Results and Discussion

Visual assessment of PU foam

The physical appearance and foam evaluation results of of PMF and (PMF₁, PMF₃, PMF₅, PMF₇ and PMF₉) are presented in the Figure 2. The result indicates that the PU foams obtained in this research were soft and flexible and the foam became darker in color with the addition of PM biopolyols. Viscous dark liquid is observed for PMF but reduced when PW is added in.



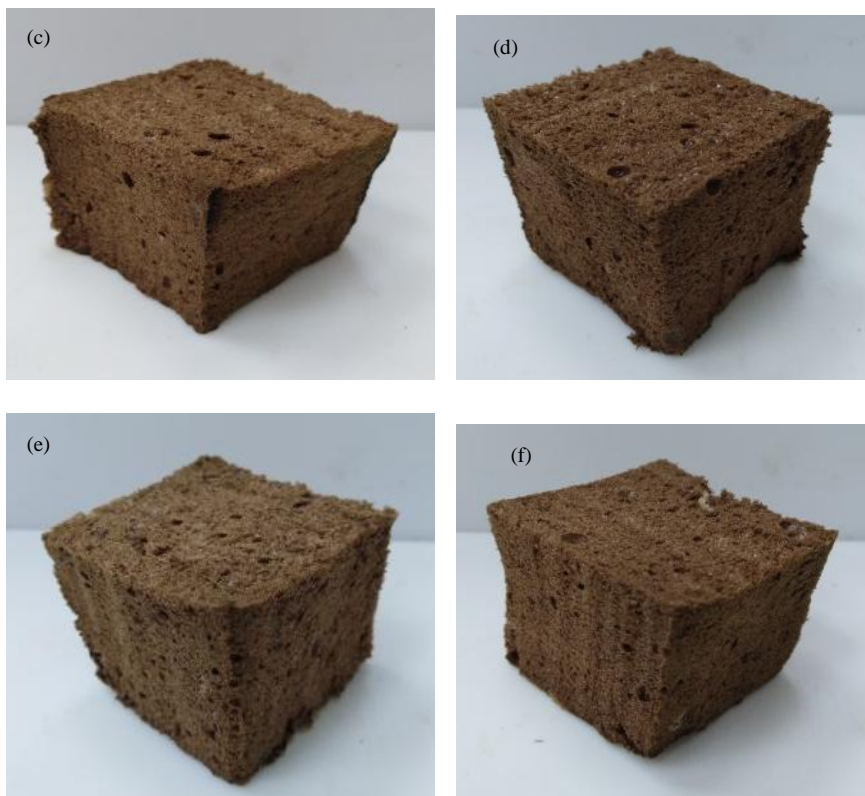


Fig. 2: Photographs of PU foam prepared from PM biopolyol with incorporation of PW (a) PMF (b) PMF₁ (c) PMF₃ (d) PMF₅ (e) PMF₇ (f) PMF₉.

Kinetics of foam formation

Figure 3 shows the foaming behavior (mix time, cream time, gelling time, free rise time and tack free time) of the samples prepared with different percentages of PW. Compared to PMF with PMF₁, PMF₃, PMF₅, PMF₇ and PMF₉, PMF had longer cream, tack-free, and free rise times, due to the lower reactivity of liquefied PM biopolyol caused by its relatively high hydroxyl number and low Mw (Xue et al., 2015). It was observed that the cream and gelling time decreased with increasing percentages of PW but PMF₁ is closer to PMF while sample PMF has the highest rise time.

The characteristic times measured for the filled systems are, in general, higher than those measured for the neat foams, but still in the range of foam formation conditions for preparing rigid polyurethanes foams. The differences are attributed again to the increasing viscosity of the reaction mixture whereby the PW filler attributed to the increased in concentration, which then complicates the processing step, slowing the polymer formation. It is found that the most affected time is the creaming, which is related with nucleation of gas bubbles and, from a macroscopic point of view, is evidenced by a change in color of the reacting mixture which adopts a creamy appearance due to the evolution of gas bubbles becoming big enough in size to scatter light. However, in the present case, this increase in the characteristic time is

considered an advantage, because it allows mixing filled mixtures for some extra seconds, thus achieving more uniform mixtures.

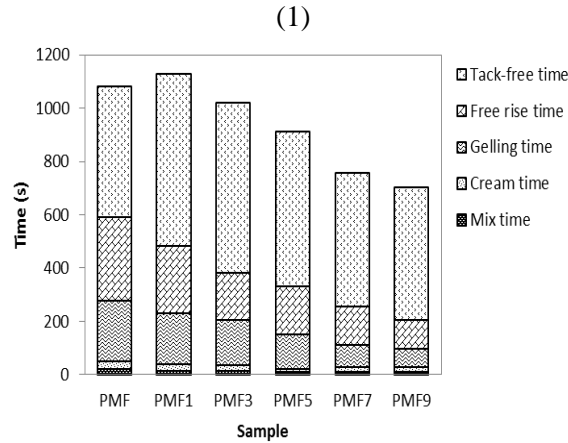


Fig. 3: Processing time of PU foam prepared from PM biopolyol with incorporation of PW.

Density and porosity

Density plays an important parameter for renewable polymer application in lightweight materials. It is well known that the higher the density, the higher the weight of renewable polymer obtained. Thus, density of PMF shows increase from 0.811 to 0.9972 with the increasing of PW filler loading from 1 % to 9 % as refer to Figure 4. The results shows increasing PW is eventually increased the density of foam. The density of the samples also depends on the type of polymer as well as the crosslinker used in the fabrication process.

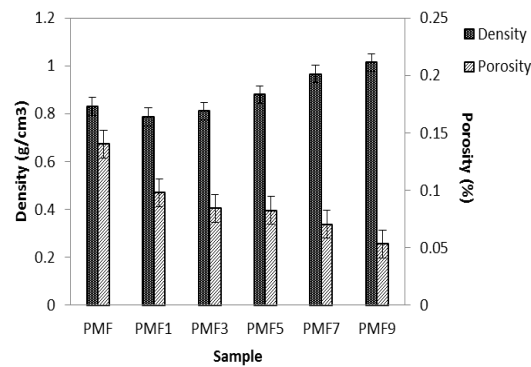


Fig. 4: Density and porosity of PU foam prepared from PM biopolyol with incorporation of PW.

Evidently, the porosity of PMF shows remarkable reduction from 0.147 to 0.050 with the increasing of PW from 1 % to 9 %. Porosity can be influence by density and the distribution of the pores of foam samples. Porosity of PMF₉ gives the smallest value due to the reduction pore size and cellular structure in the samples surfaces.

Thermal Gravimetric Analysis (TGA).

Figure 5 shows the thermal degradation of PMF and PMF₁, PMF₃, PMF₅, PMF₇ and PMF₉. Thermal degradation of the samples is similar in all stages of decomposition temperature. The first decomposition of PMF₁ revealed an increase of weight loss with increasing of PW loading. The shapes of the weight loss curve of all foams are most identical and the overall different in thermal stability has appeared to be small as referred to Figure 5(a) and Figure 5(b). The comparison between PMF and PMF₁ - PMF₉ exhibits smaller changes of the thermal degradation at all stages. This is due to bigger filler particle which leads to increase the thermal stability of the samples.

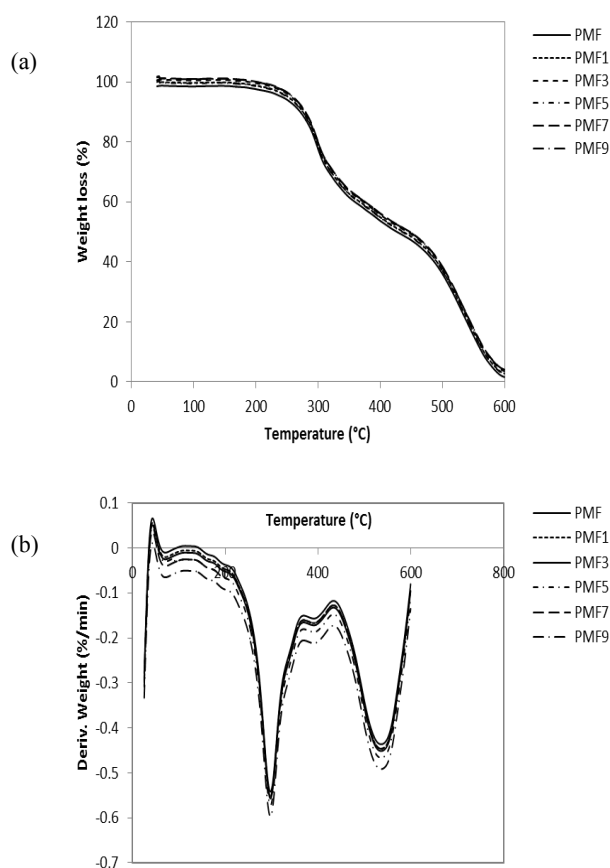


Fig. 5: Overlay thermogram of (a) thermogravimetry analysis (TGA); (b) differential thermogravimetry analysis (DTG) of PU foam prepared from PM biopolyol with incorporation of PW filler.

Decomposition of the urethane bonds start about 200-300 °C and polymer are known to be relatively thermally unstable. A polymer is thermally degraded through three basic mechanism which is the urethane bond dissociating into the component; alcohol and isocyanate, the breaking of urethane bond with the formation of primary amine, carbon dioxide and an olefin; and finally, the splitting of the urethane bond into secondary amine and carbon dioxide (Badri, Othman, and Ahmad, 2004; Gama et al., 2015).

The hard segment usually contains a high concentration of aromatic urethane groups of renewable polymer. The degradation starting at range 230-290 °C refer to the hard segment of renewable polymer composite. The second peak at about 380-430 °C was found to correlate with the amount of soft segment of renewable monomer decomposition. The range of 520-580 °C is referring to ash formation and decomposition of PM fibre filler at the range of above 600 °C.

Compressive mechanical properties.

The effects of PM fibre loading on compressive property are shown in Figure 6 with consistent trend of increased PW percentages loading contributed to higher compressive strength. Strong interface in between matrix and fillers as well as higher foam density of the samples are the main factor to be addressed. Another aspect could be attributed to the size, aspect ratio and morphology of PW fiber filler. Meanwhile, these result indicated that there was improvement due to fibre filler loading on compressive strength properties of PMF.

The mechanism work in absorbing energy for open-cell flexible of PMF is due to elastic buckling of cells. Furthermore, the absorption energy and static stiffness exhibited fluctuating values with increasing of percentages of PW. PMF₁₋₉ can absorb more energy than PMF because of the smaller cell size and higher density. Energy absorption of foam increased at densification region because fillers act as another medium to absorb energy when cells is collapse and the foam become a full solid material (Ribeiro Da Silva et al., 2013).

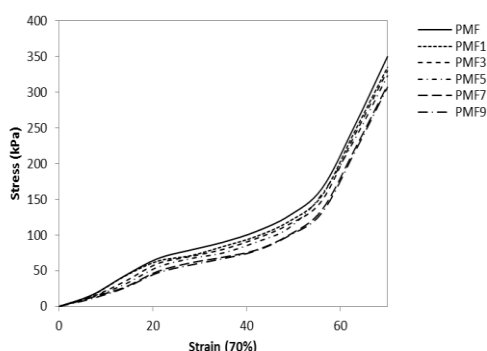


Fig. 6: Compressive stress-strain curves of PU foam prepared from PM biopolyol with incorporation of incorporation of PW filler.

Fourier Transform infrared (FT-IR) analysis.

Figure 7 show FTIR overlay spectra of PMF and PMF₁₋₉. All the foams have peaks that correspond to functionalities found in urethanes. The overlay spectra of all samples showed similar peaks at 3000-3400 cm⁻¹ represent the O-H groups either from cellulose or from unreacted liquefaction solvent. Strong absorption band characteristic of the N-H group is in the range of 3200-3330 cm⁻¹ (Kormin et al., 2017; Kormin and Rus, 2017).

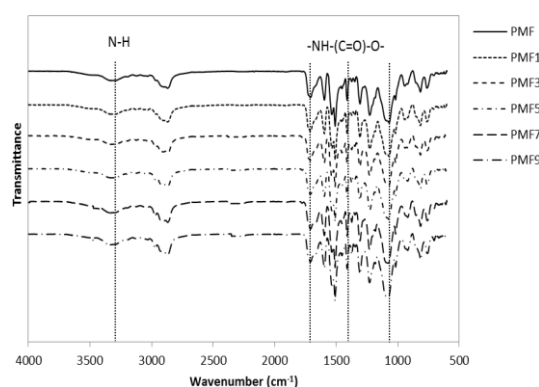


Fig. 7: FTIR spectra of PU foam prepared from PM biopolyol with incorporation of PM fibre.

The appearance of absorption peak of carbonyl groups near 1741 cm⁻¹ was broadened with increasing intensity of both PMF and PMF₁₋₉ which suggesting that more than one functional groups are formed within the carbonyl groups (C=O) family (Ferhan, Yan, and Sain, 2013; Kormin and Rus, 2017). The peak assignment and wavenumber of foams are shown in Table 2.

Table 2: FTIR characteristic peaks for polyurethane foams

Peak assignment	Wavenumber (cm ⁻¹)
N-H	3327
O-H	3000-3400
C-H	1680-1780
Aromatic ring	1590-1620
C-N	1190-1130
C=O	1741
C-N-H	1599
Isocyanurate ring	1422

IV. Conclusions

Oil palm mesocarp fibre foams (PMF) and oil palm mesocarp waste fibre (PW) filled foams based on liquefied oil palm mesocarp fibre biopolyol were

successfully prepared. Reinforced PU foams (PMF₁–PMF₉) presented promising characteristics than PMF, which was considered as an advantage, since filler addition increases the density and viscosity of the liquid biopolyol but more time is required for an adequate homogenization. TGA result revealed the thermal stabilities of PMF₁₋₉ were higher than that of PMF. TGA analysis indicated that thermal stability was almost unaffected by PW filler content. The addition of PW filler increased the mechanical strength; which associated with an increased density. Mechanical mixing of PU foams results in materials with higher chemical cross-links, density, and porosity. The addition of PW filler initiated the urethane structures and formation of carbodiimide groups was monitored using FTIR spectroscopy. The addition of PW signifies higher chemical cross-links in the system.

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