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FABRICATION AND CHARACTERIZATION OF POLYURETHANE FOAM PREPARED FROM LIQUEFIED OIL PALM MESOCARP FIBRE WITH RENEWABLE MONOMER MADE FROM WASTE COOKING OIL

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ABSTRACT

This study aims performance characteristics of polyurethane foams prepared by the reaction of biopolyol prepared from liquefied oil palm mesocarp fibre and renewable monomer with methylene diphenyl diisocyanate. The effect of prepared oil palm mesocarp biopolyol with incorporation of renewable monomer of PU foam on the thermal stability, mechanical properties and was analyzed by thermo gravimetric analysis, tensile and compressive tests and Fourier transform infrared spectroscopy. The improved thermal properties were achieved at a composition of oil palm mesocarp fibre foams (PMF). Oil PMF foams showed mechanical strength as compared to renewable monomer foams. PU foam prepared from oil palm mesocarp biopolyol with incorporation of renewable monomer improved the foams strength. An infrared spectroscopy study demonstrated the formation of urethane linkage.

Keywords: polyurethane foam; oil palm mesocap fibre; biopolyol; renewable monomer.

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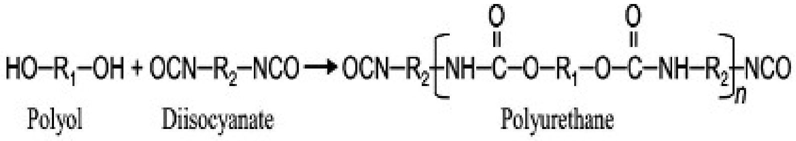
1. INTRODUCTION

Great interest towards biobased polymer in various applications is due to concerns over the depletion of petroleum resources, extensive research has been concentrating on developing bio-based polyols and PU products from renewable sources. The development of novel feedstocks for polyurethanes derived from renewable materials such as lignocellulosic biomass has become important because the use of polyurethane polymers is increasing at a rate of 1 million tonnes a year [2]. Polyurethanes (PUs) are usually obtained from reaction between polyol polyether or polyol polyester and polyisocyanate forming urethane linkages with a reactant consisting of at least two hydroxyl groups in the molecule, known as “polyol” [21, 24]. Polyurethanes are materials which have different properties by varying the ratio of their components. They diversify widely in composition and can be designed to possess either soft or stiff mechanical characteristics according to the intended end-use with the proper control of their molecular structure [9]. Polyurethanes are playing an important role in many industries because of their widely ranging mechanical properties and their ability to be relatively easily machined and formed as plastics, foams and elastomers. Polyurethanes also found as heat-insulating construction, flexible packaging, footwear, structural, synthetic, flotation and load bearing materials due to their ease of processing and unique combination of excellent thermal insulation and mechanical properties [4].

Polyurethane foam industries are polymers formed based on the condensation reaction of isocyanate groups with active hydrogen containing compounds. Isocyanates are compounds having more than one reactive isocyanate group per molecule (-N=C=O) as refer in Fig. 1. These groups will readily react with hydrogen atoms that are attached to atoms that are more electronegative than carbon. Commercial polyurethane products are usually formed by reacting liquid isocyanate components with liquid polyol resin component. In the polyurethanes foaming process, two major reactions take place in the process which is polymerization reaction to form the three dimensional network of polyurethane structure and gas producing reaction to expand the polyurethane structure from the polymerization reaction [21].



$$HO-R_1-OH + OCN-R_2-NCO \rightarrow OCN-R_2\left[NH-\overset{\overset{O}{\parallel}}{C}-O-R_1-O-\overset{\overset{O}{\parallel}}{C}-NH-R_2\right]_n NCO$$

Fig.1. Synthesis of polyurethane [21]

In this study, the liquefied PM biopolyol was directly used to prepare PU foams with MDI by one-shot method. The material component studied on our studied was divided into two components, A and B. Component A is a group of substances containing biopolyols, renewable polymer, catalyst blowing agent) and surfactant. Component B is an isocyanate (MDI). MDI is a molecule with two aromatic isocyanate groups of equal reactivity. It is used where high tensile strength, toughness and heat resistance is required and its lower volatility makes easier to handle [16].

The aim of this study is to investigate the effect PU foam made from 100% PM/PEG400 biopolyol (PMF), renewable monomer (RF) and PM biopolyol with incorporation of renewable monomer (PMRF) on the physical, thermal and mechanical of polyurethane based polymers. Small changes on the mass losses at high temperatures could be investigated by analysing TGA results. Compression and tensile experiments have shown the mechanical properties improvement. In order to verify the chemical group changing caused by the NCO/OH ratio variation, the investigation was carried out using FT-IR spectroscopy. It would be most advantageous to replace polyester or polyether polyols, as used in the production of polyurethane foam with more versatile, renewable, less costly and more environmentally friendly components.

2. METHODOLOGY

2.1. Raw Materials

Oil palm mesocarp fibre (PM) was obtained from Sindora Palm oil mills, Johor, Malaysia. The PM were ground into smaller sizes using heavy duty laboratory blender and sieved. The particles of mesh 20-100 µm were selected for this study. These raw materials were then dried in an oven at 100°C for one night and kept in a desiccator at room temperature before using. For the synthesis process, 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. For the PU foam fabrication process, crosslinker, methylene diphenyl diisocynate (MDI), catalyst (dibutyltine dilaurate), surfactant (silicon oil), blowing agent (water, H_2O) was used as received.

2.2. Liquefaction Oil Palm Mesocarp Fibre (PM)

Polyethylene glycol 400 (PEG400) was used as the main liquefaction solvent. First, 20 g oven dried PM fibre and liquefaction solvent were mixed at 1/3 of weight ratio with 5% sulfuric acid as a catalyst. The mixture was placed into 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 PM was 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. The residue was washed with methanol, dried at 100°C overnight in an oven and weighed [1-2].

2.3. Preparation of Renewable Polymer from the Waste Cooking Oil

Waste cooking oil was obtained from Small and Medium Industries (SMIs) and chemically manipulated at laboratory scale using less than 1L of waste cooking oil. It began with catalyst preparation to generate the epoxies from unsaturated fatty compound using in-house catalyst preparation at E1 Sustainable Polymer Engineering (AMMC), which comprises the acid-catalyst ring opening of the epoxides to form polyols. In order to produce renewable polymer foam, the reaction of renewable polymer with crosslinker is conducted [4-5].

2.4. Preparation of PU Foams Using Liquefied Product with Renewable Polymer

The foams were prepared by a 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, renewable polymer, catalyst (dibutyltin dilaurate), blowing agent (distilled water) and surfactant (silicon oil) in a mixing cup for 15-20 s using a mechanical stirrer. Component B is a methylene diphenyl diisocyanate (MDI).

Table 1. Designation and formulation of synthesized polyurethane (PU) foams

Sample	**A**						**B**
	Polyol (%)		**PEG400 (Solvent)/g**	**Dibutyltine Dilaurate (Catalyst)/g**	**Siliconce Oil (Surfactant)/g**	**Water (Blowing Agent)/g**	**MDI (Crosslinker)/g**
	Biopolyol	**Renewable Monomer (R)**					
PMF	100	-	2.5	0.1	0.1	0.2	20
RF	-	100	2.5	0.1	0.1	0.2	20
$\text{PMRF}_{80/20}$	80	20	2.5	0.1	0.1	0.2	20
$\text{PMRF}_{60/40}$	60	40	2.5	0.1	0.1	0.2	20
$\text{PMRF}_{40/60}$	40	60	2.5	0.1	0.1	0.2	20
$\text{PMRF}_{20/80}$	20	80	2.5	0.1	0.1	0.2	20

*PMF-oil palm mesocarp fibre foam, PMRF-oil palm mesocarp fibre/renewable polymer foam and RF-renewable polymer foam

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 [6]. Table 1 shows 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. Fig. 2 presents foaming reaction of PU foam preparation.

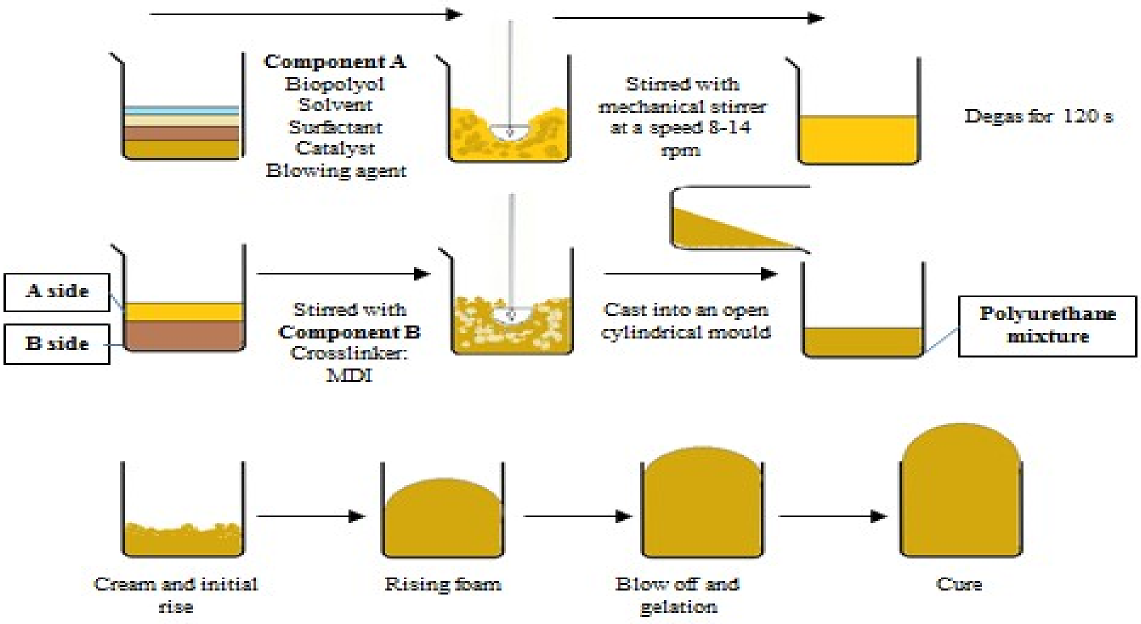


Fig.2. Foaming reaction of polyurethane foam

2.5. 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, RF and PMRF foam. In order to measure the density of the PU and its composites in small size (10 x 10 x 10 mm) for 4 cubes were prepared to get an average value of the density for every portion. The densities PU foam was measured using Mettler Toledo Density Kit. It can be performed using Buoyancy Method according to European Standard EN 993-1, which automatically determined the density read on the machine screen. Whereas, the open porosity ρ_A in volume percent is calculated as equation below

$$\text{Porosity}, P_A = \frac{(W_W - W_D)}{(W_W - W_S)} \times 100 \tag{1}$$

where W_W = Mass of an immersed and suspended specimen in air, W_D = Mass of air dried specimen and W_S = Mass of immerse and suspend specimen in liquid.

2.6. Thermal Gravimetric Analysis (TGA)

Thermal property measurement of PMF, RF and PMRF was performed using Linseis TGA for characterized the thermal properties of biopolymer foam according to ISO 11358. 10 mg of sample was prepared in alumina crucible and put in holder of TGA machine for thermal analysis. The setting for running the test was performed under oxygen atmosphere, temperature at 20 °C to 900 °C with heating rate of 10 °C/min and flow rate of 0.3 µL using alumina crucible. The weight loss and derivative weight loss of the samples were measured.

2.7. Tensile Test

The determination of tensile strength, elastic modulus and elongation at break of the foams are performed according to the ASTMD638–89 using Type IV specimen with dimensions: thickness = 4mm, width = 12.7mm, gage length = 64mm. Length of the specimen lies along the in-plane direction of the foam and specimens are prepared using a sharp knife to form a dog bone shape. Specimens are loaded quasi-statically until failure using a Universal Testing Machine (UTM) of Shimadzu-AGI test machine with 2.5kN load cell at a crosshead speed of 2 mm/min. Wedge type grips are employed to clamp specimen ends. Load-displacement data are recorded during the experiment using a data acquisition for further analyses of the tensile data. The tensile strengths were reported in a unit of kilopascal (kPa). The ultimate elongations were calculated by subtracting the original distances between the benchmarks from their total distances at the time of rupture.

2.8. Compressive Mechanical Properties

Compression test (strength and compressive modulus) were measured using Universal Testing Machine (UTM) of Shimadzu-AGI fitted with a 5kN load cell under compression mode. The specimens were cut in to rectangular shape according to ASTM D1621-10 with the following dimensions; 51mm (length), 51mm (width) and 40mm (thickness). The specimen was placed at the centre between both blocks inside the UTM compression machine. 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.

2.9. 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.

3. RESULTS AND DISCUSSION

3.1. Physical Characteristic

Density is an important parameter in conjunction with polymer applications for light-weight materials. It is well known that the higher the density, the higher the weight of PU foam obtained. The density of PU foam depends on the type of polymer as well as the crosslinker used in the fabrication process. Furthermore, the effect of the ratio and different condition will also affect the density value for each PU foam. This is evidently as refer to Table 2, which shows density and porosity for all samples (PMF, RF and PMRF). Density of liquefied PM biopolyol is lower than density of renewable monomer (R) due to the fact that biopolyol has shorter chain and lower molecule weight. The density results for PMF, RF and PMRF is expressed in grams per cubic meter (g/m^3) as shown in Fig. 3.

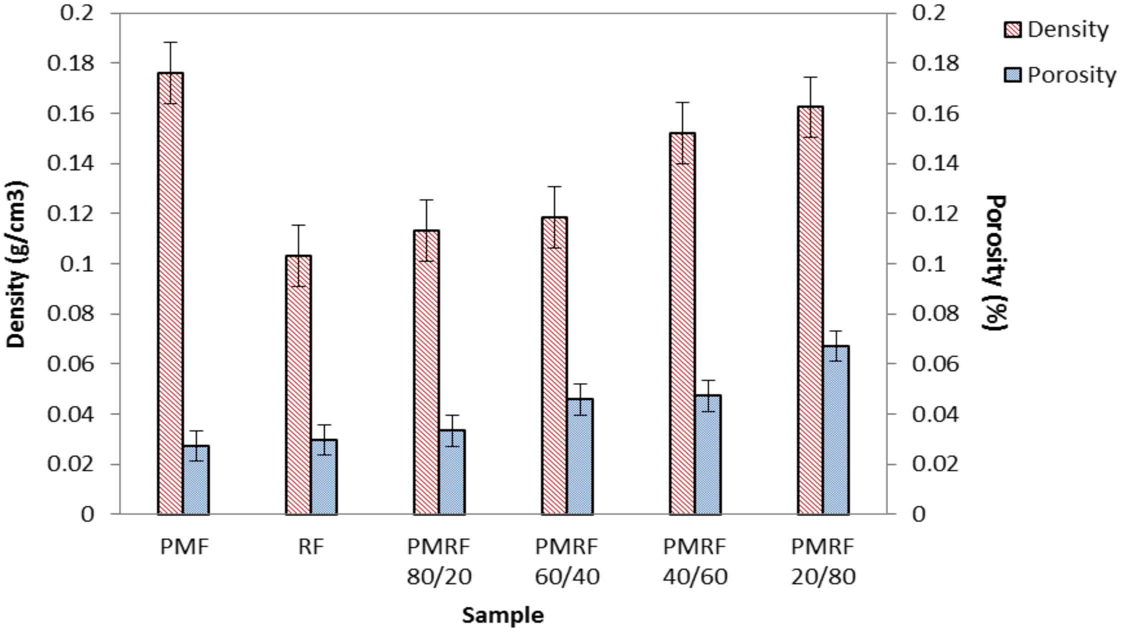


Fig.3. Density and porosity of of PMF, RF and PMRF foam samples

The obtained foam densities vary within the range of 0.1 to 0.2 g/cm^3, depending on the foam formulation. Formulation of foam with higher biopolyol content tends to produce higher density foams, due to the unreacted hydroxyl groups. Based on Table 2, the density of foam

$\mathrm{PMRF}_{80/20}$ until $\mathrm{PMRF}_{20/80}$ was slightly increased as compare with the PMF and RF. Among all the densities value, PMF shows the highest value 0.1761 g/cm^3, while the lowest densities value is 0.1133 g/cm^3 for $\mathrm{PMRF}_{80/20}$. As refer to average pores for all PU foam samples, the pores structure for PMF and PMRF were observed smaller (< 400µm, density value: 0.1-0.2 g/cm^3) than RF (> 400 µm, density value: > 0.1 g/cm^3) indicates that the smaller the pores structures resulting higher densities.

Low density foams are primarily used for insulation, packaging and cushioning application, and high density foams are primarily used for load bearing application such as structural part [7]. The density is related to foam contraction after the liberation of gases. At some point during foam development, the foam stop expanding, release gases and contracts, accumulating mass at the bottom of the block [8].

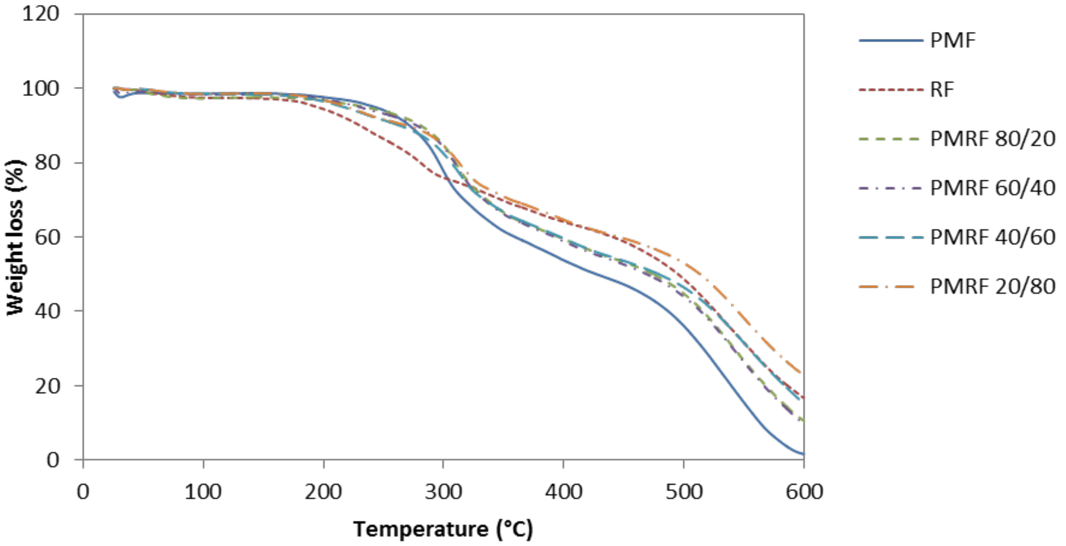
Table 2. Number, diameter and pore density per volume of of PMF, RF and PMRF foam samples

Samples	**Density (g/cm^3)**	**Porosity (%)**	**Number of Pore (n)**	**Average of Diameter Pore (µm)**	**Pore Density Per Volume, N*v* (10^6) cm^{-1}**
PMF	0.1761	0.0272	30	320	4.21
RF	0.1229	0.0298	20	401	2.42
$\mathrm{PMRF}_{80/20}$	0.1133	0.0332	24	396	3.21
$\mathrm{PMRF}_{60/40}$	0.1185	0.0457	22	379	2.78
$\mathrm{PMRF}_{40/60}$	0.1521	0.0472	26	357	3.58
$\mathrm{PMRF}_{20/80}$	0.1624	0.0670	28	330	4.17

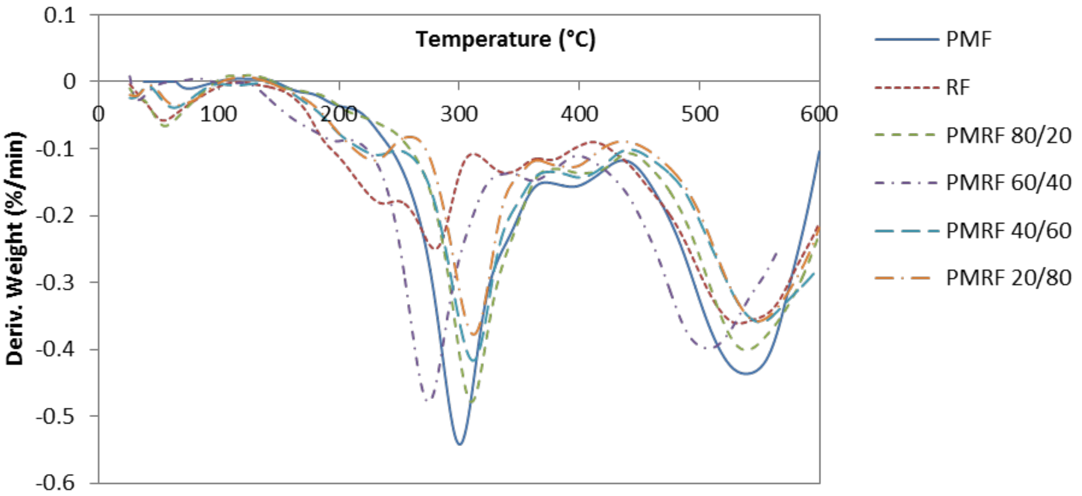
The porosity of a porous material is defined as the ratio of the volume of the voids in the material to its total volume. The porous material has its character to allow the sound waves to enter the materials through a multitude of small holes or openings of the surfaces. Table 2 represents average porosity value for PU foam data was replicates for 3 times for each samples by using the Equation (1). Table 2 shows the comparison of porosity for for all samples (PMF, RF and PMRF). PMF has the lowest percentage of porosity which is 0.0272 %. This shows that the pore of the sample is larger and it has absorbed most of the water during the density measurement, then followed by RF, $\mathrm{PMRF}_{80/20}$, $\mathrm{PMRF}_{60/40}$ and $\mathrm{PMRF}_{40/60}$ with 0.0298 %, 0.0332 %, 0.0457 % and 0.0472 % respectively. Meanwhile, the highest percentage of porosity is $\mathrm{PMRF}_{20/80}$ which is 0.0670 %. Evidently, the porosity was increased with the increasing ratio of renewable monomer (R). Overall, data for porosity for PMRF shows better in porosity value as compared to PMF and RF. However, the value for all PU foam samples in this study was observed fluctuated maybe due to due to the calculation, density influences and the distribution of the pores of the cubes of PU foam samples.

3.2. Thermogravimetric Analysis (TGA)

Fig. 4 presents the thermogravimetric (TG) and derivative weight loss (DTG) curves for PU foam prepared from PM biopolyol with incorporation of renewable monomer (R). Fig. 4(a) shows thermogravimetric (TG) of PMF, RF and PMRF respectively. Thermal degradation of PU foam is a complicated process involving the dissociation of the initial polyol and isocyanate components. Thermal decomposition can lead to the formation of water, amines, small transition components, and carbon monoxide and dioxide [9]. The weight loss of PMF, RF and PMRF which began at less than 100 °C indicated that the volatile matter in the samples is equivalent to 4.3 %. A sudden drop in the mass of the sample indicates thermal degradation of the materials. The first peak of renewable polymer degradation correlates with the hard segment while the second peak correlates with the degradation of the soft segment. This qualitative characterization of the degradation process was elaborated by the onset and maximum peak temperature of the first step, T_{1on} and T_{1max} along with the second step T_{2on} and T_{2max}. Detailed TGA data, the onset decomposition temperature (T_{onset}) and the maximum decomposition temperature (T_{max}) of renewable polymer foam are tabulated in Table 3.



(a)



(b)

Fig.4. Thermogram curve (a) thermogravimetry (TGA) (b) differential thermogravimetry (DTG) of PMF, RF and PMRF foam samples

The first decomposition temperature occurred at 232°C, 229°C for PMF and RF respectively. Second decomposition started at 314°C and 301°C. The weight loss of PMF and RF at first decomposition temperature is 23 % and 20%, weight loss at second decomposition temperature is 55% and 50% and weight loss at the third decomposition which is 22% and 23% respectively with char residue that does not change much until the temperature is ended at 600°C. The decomposition temperature was attributed to the crosslinker of isocyanate content in PMF, RF and PMRF at all stages. It has been suggested that the amount of weight loss at each degradation stage may be used as a quantitative measurement of the hard and soft content in renewable polymer of PMF, RF and PMRF.

Table 3. Thermal decomposition of PMF, RF and PMRF foam samples at 10°C/min

Samples	**PMF**	**RF**	**PMRF$_{80/20}$**	**PMRF$_{60/40}$**	**PMRF$_{40/60}$**	**PMRF$_{20/80}$**
First Decomposition (°C)	232	229	104	102	230	227
T_{1on} (°C)	93	86	93	87	91	85
T_{1max} (°C)	290	287	210	207	288	284
Weight loss (%)	29	31	7	9	28	30
Second Decomposition (°C)	314	301	226	219	312	299
T_{2on} (°C)	290	288	210	207	288	284
T_{2max} (°C)	395	386	307	302	393	385
Weight loss (%)	51	53	39	41	49	51
Third Decomposition (°C)	410	402	311	305	409	399
T_{3on} (°C)	395	383	307	302	393	385
T_{3max} (°C)	596	594	596	594	593	592
Weight loss (%)	18	20	35	37	17	19

Fig. 4(b) shows the curves of differential thermogravimetry (DTG) of PMF, RF and PMRF. It is evident that the decomposition mainly occurred in three successive stages above 100°C. The weight loss below 100°C was attributed to the evaporation of moisture content and the release of volatile components [10]. The initial decomposition started at 177.32°C and the rate of weight loss began to gradually increase to a maximum at about 302°C. This suggests that decomposition started at the urethane bond. Urethanes are known to be relatively thermally unstable materials, primarily due to the presence of urethane bond decomposition which occurs somewhere between 150 and 220°C depending on type of the substituents on the isocyanate and polyol side [8, 11]. The second stage, a shoulder in the DTG curve around 361.51°C, could result in the degradation of isocyanate which did not react with polyol or water. The third stage (415.53–565.18°C) largely attributed to the degradation of lignin and char residue from the second stage [10]. In conclusion, the amount of liquefaction solvent (PEG400) in the PM fibre has the ability of increasing thermal stability of PMF foams.

3.3. Tensile Strength

The mechanical properties of PMF, RF and PMRF foams concerning tensile strength, elastic modulus and ultimate elongation are shown in Fig. 5. The variability of tensile properties depends on the foam morphologies, including cell size, cell wall and foam density. As a general tendency, it was observed that as foam density increased and cell size decreased, tensile behavior enhanced. Among all, PMF foam containing 100% liquefied PM biopolyol has the highest tensile strength at 117 kPa. In contrast, $PMRF_{80/20}$ showed the lowest tensile strength at 85 kPa, the foam with the highest cell anisotropy foam and the highest cell size. The tensile strength of PMRF is lower than PMF and RF. Low tensile strength of PMRF occurred compared to PMF and RF primarily because the weakness of interfacial adhesion between the liquefied PM biopolyol with renewable monomer (R), in which probably attributed to hydrophilic nature of PM fibre that was not compatible with hydrophobic polymers of renewable monomer. With an increase of $PMRF_{80/20}$ ratio, the hard segment formed through the reaction between isocyanate and polyol or water included in liquefied PM biopolyol as well as the crosslink density increased [12-13]. The concentration of the hard segment affects the mechanical characteristics of PU and the higher concentration can increase the hardness of PU but decrease its flexibility. On the other hand, the output of CO_2 produced through the reaction between water and MDI was increased with higher $PMRF_{80/20}$ ratio, resulting in the growing void in the foam. When this became dominant in the mechanical property, the tensile strength PU foam would be decreased. This can be attributed to the decrease in flexibility and increase in rigidity of the foam with more hard segment content and higher crosslink density [13-14]. Moreover, SEM also can indicates that PU foam prepared from PM biopolyol with incorporation of renewable monomer (PMRF) may increase the cell size of the resultant foam somewhat. The literature indicates that the mechanical properties will not be strongly affected by such changes in cell size [15]. On the other hand, the degree of cell opening does play a role in determining mechanical properties.

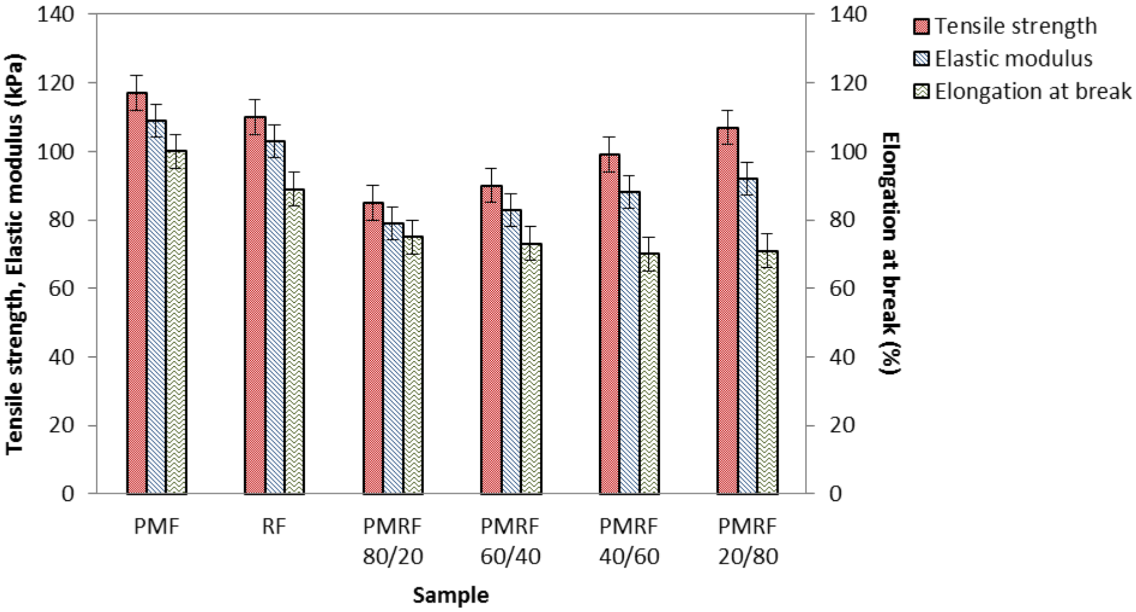


Fig.5. Tensile strength, elastic modulus and elongation at break of PMF, RF and PMRF foam samples

Compared with PMF, elongation at break of PU foam prepared from PM biopolyol with incorporation of renewable monomer (PMRF) were lower. In turn, much higher elongation values were obtained for PU foam with 100% liquefied PM biopolyol of lower hydroxyl value. In general, with an increase in $\mathrm{PMRF}_{80/20}$ ratio in PU formulations, the elongation at break values decreased. In the case of tensile strength values an inverse relationship can be seen. The increase in cross-linking density produces stiffer foams with reduced elongations at break and higher tensile strength values. Fig. 5 enables to identify an elongation at break decreasing by increasing the $\mathrm{PMRF}_{80/20}$ ratio. Reduction of elongation at break occurred because of the weakness of interfacial adhesion between the liquefied PM biopolyol with renewable monomer (R). Closer to the theoretical balance of NCO/OH, concerning stoichiometry, more brittle has become the obtained polymer. As known, the crosslinking density level is directly proportional to the material modulus [16]. Such low strength behavior can be related to the low crosslinking density, it means a “large” distance between urethane groups into the polymeric structure which allows the chains to deform, when submitted to a force and to recover the original shape by unloading the force, typical rubber-like or large strain material behavior. Moreover, the length of cross-linking was short due to structure of polyol which created low elongation at break point. The elongation at break point decreased as the proportion of $PMRF_{80/20}$ ratio is increased, which indicates that foam produced with high load of biopolyol will exhibit very poor tensile strength. RF and PMRF compared very well with PMF in terms of their elongation at break. Additionally, elongation of break is expected to scale with chemical crosslink density, all other things being equal since the elongation of a PU network is based on the extension of the soft segments and since crosslinking should limit soft segment extensibility. Therefore, that PMRF foam shows greater extensibility because of the lower chemical crosslink density. While the physical crosslinks associated with hard domain formation are more effective and complete phase separation in the PMRF foam and enhanced hydrogen bonding, the reversible nature of these hydrogen bonds ensures that soft segment mobility and elongation at break are not compromised [17].

The increased tensile at rupture, associated to the decreased elongation, results into an increasing of elastic modulus of the polymer, consequently an increasing of crosslinking density level. Previous research reported that elastic modulus increase as the PMRF ratio decrease. Generally, elastic modulus is closely related to the hard domain of the material. As the PM fibre content increases, the hard domain content increases, as does the tensile modulus of the blend. As PM fibre is partially crystallinity, there was possibility of increasing modulus attributed to crystalline. Incorporation of crystalline PM fibre in liquefied PM biopolyol shows an increasing in elastic modulus. Moreover, a simple visual analysis was needed to identify bubble formation into $PMRF_{80/20}$ ratio samples. These bubbles were probably composed by by-product polymerization, it means, CO_2 bubbles as effect of diisocyanate excess [16]. The mechanical results were damaged by the presence of bubbles, concerning the $PMRF_{80/20}$ ratio samples. To avoid such bubbles, the samples must be prepared at a controlled or inert atmosphere.

3.4. Compressive Strength

The stiffness of the oil palm mesocarp fibre foam (PMF), renewable polymer foam (RF) and PU foam prepared from PM biopolyol with incorporation of renewable monomer (PMRF) control the relationship between the forces applied to the surface which results in deformation. Hence, compression strength is one of the tests necessary to produce 70 % compression over the entire top surface of renewable polymer. PU foam is capable of absorbing load stress when forces are exerted due to the present of cellular structures. It can absorb load stress from constant imposed load. Compression test was carried out in the foam rise direction. Since this property depends on the cell shape and size, the thickness of the foam is the major part to be concern [18].

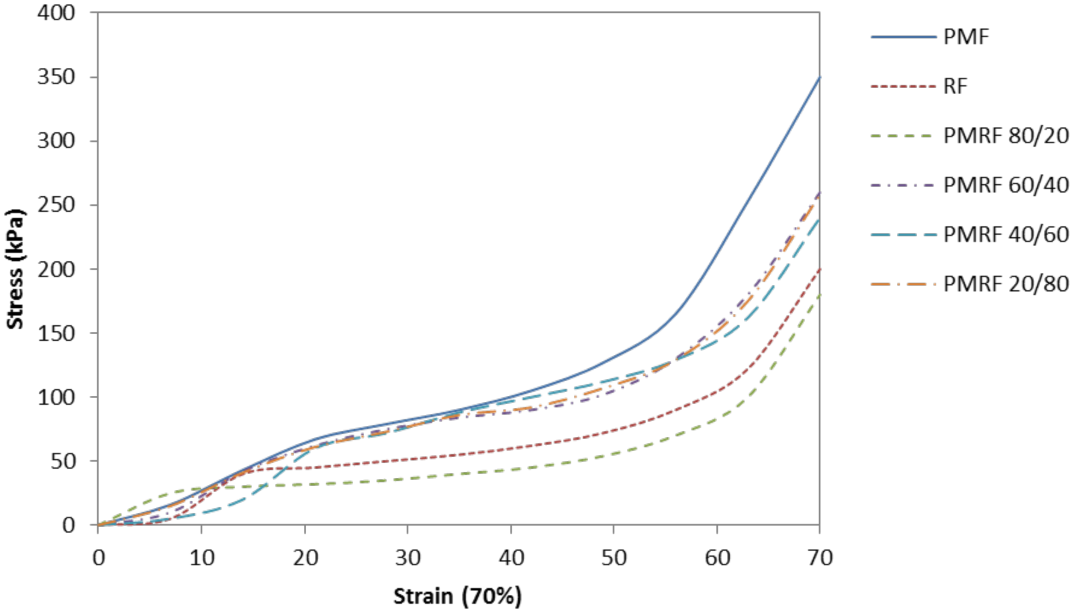


Fig.6. Compressive stress-strain curves of PMF, RF and PMRF foam samples

The results of stress versus stroke-strain of compressive strength of PMF, RF and PMRF are shown in Fig. 6 and tabulated in Table 4. There result appears to be a fairly broad plateau for compressive strength. PMF foam containing 100% liquefied PM biopolyol has the highest compression strength at 73 kPa. $\mathrm{PMRF}_{80/20}$ foam has the lowest compressive strength at 28 kPa among PMRF formulation. The compression strength of PMRF is lower than PMF and RF. This is due to the density of PMF and RF sample which is higher than PMRF samples and influenced the property of compressive strength with significant changes by using the compression moulding technique. The obtained results presented the lowering of the compressive strength of the materials with increasing content of the biopolyol.

The result shows that with the increase of the biopolyol content, both compressive strength and density were decreased. Incorporation the PM/PEG400 biopolyol with renewable monomer (R) reduced the compressive strength of the foam compared to PMF and RF, primarily because the biopolyol was less reactive (hydroxyl groups in biopolyol was less accessible) [19-20]. The biopolyol was not completely miscible with the renewable monomer and thereby the biopolyol was not uniformly dispersed in the foam. The introduction of biopolyol reduced the uniformity of the foam cellular structure and the deficiency in the cellular structure weakened the stability and strength of the structure. The mechanical properties of rigid polyurethane foam are closely correlated to the density, which the result of lower crosslink density in the polymer combined with the larger cell size and thus weaker cell walls observed with this formulation [21]. Moreover, when excessive biopolyol were added, the number of polyols and water in the formulation exceeded the number of isocyanate groups of the added MDI. Therefore, the remaining un-reacted components cannot form effective bonds and structure [22]. The increase in water content due to the increase in biopolyol in the formulation is expected to promote blowing or foaming, resulting in high porosity and hence decreased density and compressive strength. The higher liquefied PM biopolyol content, the lower economic costs for PU foams, but the mechanical properties were poor. Therefore, large amount of liquefied PM biopolyol incorporated with renewable monomer in the reaction would not be preferred.

Table 4. Compression properties of PMF, RF and PMRF foam samples

Samples	**Compressive Strength (kPa)**	**Compressive Modulus (kPa)**	**Energy Absorption (J)**	**Static Stiffness (kN/m)**	**Stress at Max (N/mm^2)**	**Strain at Max (%)**
PMF	24.525	35.761	0.55	0.002235	0.2311	71.51
RF	22.843	275.28	0.63	0.017205	0.1488	66.02
$PMRF_{80/20}$	26.943	263.13	0.68	0.016446	0.1495	68.49
$PMRF_{60/40}$	31.000	255.23	0.69	0.015952	0.2100	65.09
$PMRF_{40/60}$	31.418	253.74	0.72	0.015859	0.2081	67.15
$PMRF_{20/80}$	31.418	253.74	0.72	0.015859	0.2444	63.01

3.5. Visual Assessment

The physical appearance and foam evaluation results of PU foam prepared from PM biopolyol with incorporation of renewable monomer (R) are presented in the Table 5 along the results of the base formulation for easy comparison. Ideally, good quality foam is defined as not to have any parameter score below 3 in any foam formulation and an output value more than 3, but in reality maybe be very hard. Fig. 7 indicates that the PU foams obtain in this research was flexible type and the foam became darker in color with the addition of PM biopolyols except for renewable polymer foam (RF) which yellow in colour. The RF foam began to get orange coloured. In order to solve the base holes problem, mould begun to be sprayed with water prior to cast the foam. Viscous dark brownish liquid began to come out when PM biopolyol mix with renewable monomer for PMRF. This could mean that a poor mixing was applied after the can was filled with the gases, not resulting in homogenous liquid and consequently a poor reaction inside the mould [23]. Meanwhile, the foams $PMRF_{80/20}$ and $PMRF_{60/40}$ began to get a light brownish colour, whereas the $PMRF_{40/60}$ and $PMRF_{20/80}$ got dark brownish. The worse parameter common in every foam is the base holes. Excluding the base holes again, the foams yielded relatively good results. The PMF, RF and $PMRF_{60/40}$ foam had the best quality and the $PMRF_{80/20}$ was worst in terms of number of scores below 3, comparing to the all PU foam.

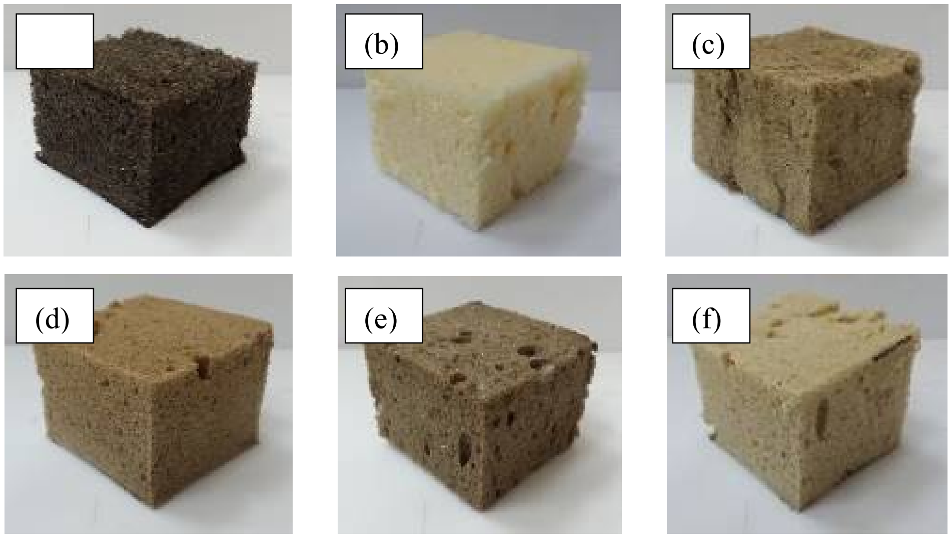


Fig.7. Photographs of PU foam prepared from PM biopolyol with incorporation of renewable monomer (R) (a) PMF (b) RF (c) $PMRF_{80/20}$ (d) $PMRF_{60/40}$ (e) $PMRF_{40/60}$ (f) $PMRF_{20/80}$

Table 5. Physical appearance and evaluation of quality of PMF, RF and PMRF foam samples

Physical Appearance	PMF	RF	PMRF$_{80/20}$	PMRF$_{60/40}$	PMRF$_{40/60}$	PMRF$_{20/80}$
Colour	Black	Yellow	Dark brown	Dark brown	Light brown	Light brown
Hand feeling	Rough	Smooth	Rough	Rough	Smooth	Rough
Shrinkage mould	4	4	3	4	3	4
Gas bubbles	3	4	3	4	3	3
Cell structure	4	3	2	3	3	3
Void and pinholes	3	4	3	3	4	3
Base holes	1	1	0	2	1	1
Cell collapse	4	4	3	4	3	4
Curing streaks	4	4	4	4	3	4

*1-2: Low quality and 3-5: Good quality

3.6. Fourier Transform Infrared (FT-IR) Analysis

The polyurethane polymer structure was studied by analyzing its functional groups using FT-IR. The reaction between biopolyol, monomer, additives and MDI forms a polymer with urethane backbone (NHC(O)O). The FT-IR absorption spectrums of the six foams are shown in Fig. 8. All the foams have peaks that correspond to functionalities found in urethanes and ureas. In the spectra, the residual or unreacted isocyanate group (NCO) can be identified at a band of 2250 cm^{-1}. A broad peak around 3000 to 3400 cm^{-1} represents the O-H groups either from cellulose or from unreacted liquefaction solvent. The N–H stretching in the urethane linkage which is in the PU hard segment region is identified at 3320 to 3370 cm^{-1} [24]. The peak around 2870 cm^{-1} represents the C-H symmetric stretching in aliphatic methyl. The appearance of absorption peak at 1710 to 1740 cm^{-1} (C=O), 1500 to 1590 cm^{-1} (N-H) and 1000 to 1200 cm^{-1} (C-O) indicate the existence of the urethane linkage as expected. All six foams showed a peak at 1420 cm^{-1} (N-H) that indicative of an isocyanurate rings (resulting from reactions between isocyanate and urethane groups), conjugated and unconjugated C-O stretching at 1000 to 1020 cm^{-1} respectively and C-H deformation of aromatic groups in the range of 600 to 800 cm^{-1} are also noted in the spectra [19, 24-25]. Dibutyltine dilaurate (catalysts) are used to have some activity at promoting isocyanurate formation. Besides that, it is also used to promote the gelling (urethane linkage) and blowing (urea linkage) reactions in the formation of PU foams. The FT-IR results showed that the liquefied PM biopolyols reacted with isocyanate (MDI) resulted small residual NCO peak and produced a mixture of urea and urethane linkages, consistent with typical polyurethane (PU) foam.

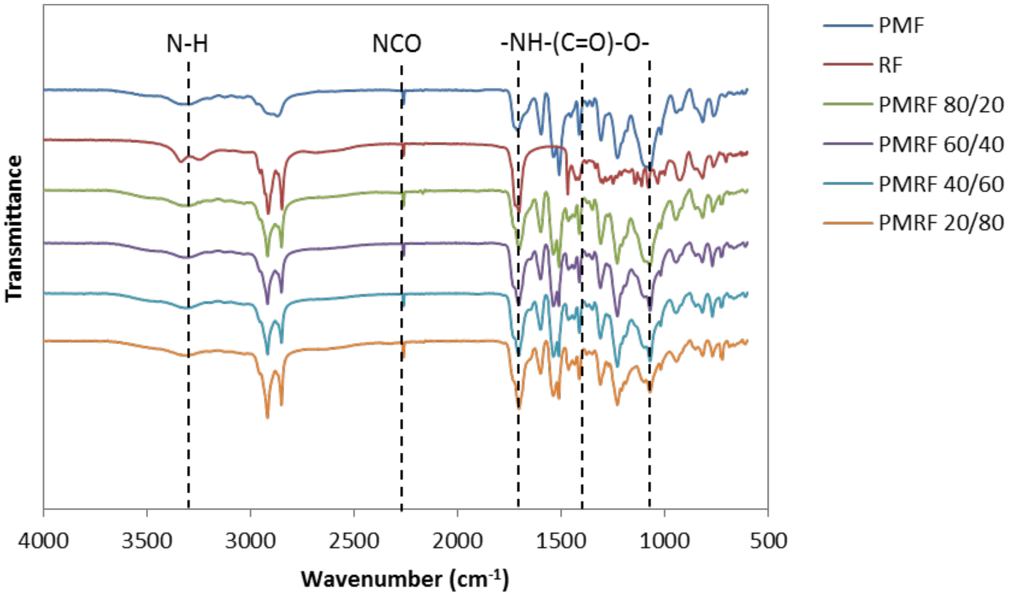


Fig.8. FTIR spectra of PMF, RF and PMRF foam samples

4. CONCLUSION

The oil palm mesocarp fibre (PM) biopolyol from solvolysis liquefaction was found to have a reasonably high hydroxyl value and was therefore considered a good source of biopoyols. The biopolyols were crosslinked with methylene diphenyl diisocyanate (MDI) to form polyurethane (PU) foams. The prepared biopolyol was also reacted with polyethylene glycol (PEG400), distilled water as blowing agent, silicone oil as surfactant, and dibutyltine dilaurate as catalyst allows one to make foams with specific average cell size and foam density that can fit different applications. The effects of prepared PMF, RF and PMRF on the foam kinetics, thermal stability, morphology and mechanical properties of the PU foams were investigated. The PMF foam with high hydroxyl values made from 100% liquefied PM biopolyol had a higher density, tensile strength and compression strength than RF and PMRF. Lignin derivatives in PMF contributed to the denser foams. A significant difference was found in the thermal stability of PMF foam and those made from renewable monomer, RF and PMRF. The thermogravimetry analysis showed that all the PU foams had approximately the same degradation temperatures of about 200°C to 550°C. FTIR result reveals the formation of urethane linkage in the PU foams.

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