

Novel route of synthesis for cellulose fiber- based hybrid polyurethane

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Abstract. Polyurethanes, obtained by the reaction of a diisocyanate compound with bifunctional or multifunctional reagent such as diols or polyols, have been studied intensively and well developed. The wide range modifier such as chemical structures and molecular weight to build polyurethanes led to designs of materials that may easily meet the functional product demand and to the extraordinary spreading of these materials in market. Properties of the obtained polymer are related to the chemical structure of polyurethane backbone. A number polyurethanes prepared from biomass-based monomers have been reported. Cellulose fiber, as a biomass material is containing abundant hydroxyl, promising material as chain extender for building hybrid polyurethanes. In previous researches, cellulose fiber was used as filler in synthesis of polyurethane composites. This paper reported a novel route of hybrid polyurethane synthesis, which a cellulose fiber was used as chain extender. The experiment performed by reacting 4,4'-Methylenebis (cyclohexyl isocyanate) (HMDI) and polyethylene glycol with variation of molecular weight to obtained pre-polyurethane, continued by adding micro fiber cellulose (MFC) with variation of type and composition in the mixture. The experiment was evaluated by NMR, FTIR, SEM and STA measurement. NMR and FTIR confirmed the reaction of the hybrid polyurethane. STA showed hybrid polyurethane has good thermal stability. SEM showed good distribution and dispersion of sorghum-based MFC.

1. Introduction

Cellulose, the main structural component of plant that confers strength and stability to the plant cell wall, is widely used in commercial material due to its properties such as biodegradability. Cellulose that provided from fibers has many hydroxyl functional groups which makes it potential as a chain extender in polyurethanes polymerization, but there has not been any study that proved it. In last decade, some efforts have converted to several forms like, MFC, microcrystalline (MMC) with several end use application [1]. The aim of this study, is to determine the availability of Sorghum bicolor plant cellulose as a chain extender in polyurethane polymerization.

Sorghum bicolor is a plant with a high level of photosynthesis. It takes only 3 – 5 months for the sweet sorghum to mature, and the species can be planted in very dry areas. The top grain, leaves and stalks can be used for forage, and sugars can be extracted from stalks for use in syrup and fermenting ethanol [2]. According to a study conducted by Bakeer and his colleagues in 2013, sorghum containing 32.30% of fiber with high crystallinity [3]. Sorghum bicolor and sorghum bagasse are only different in name, but the same sweet sorghum plant [4]. According to those study, sorghum bicolor worthy to be utilized as chain extender because its fiber contain providing many hydroxyl groups.

Polyurethane (PU) chemistry has been studied intensively and is well developed. Typically, polyurethanes are obtained by the reaction of a diisocyanate with bifunctional or multifunctional

reagent such as diols or polyols. Material design is achieved by varying the chemical structures and molecular weights of both the polyol and the diisocyanate compounds as the polymer precursors. A number of polyurethanes prepared from biomass-based monomers have been reported. So far, these polymers were synthesized by using several stages, such as pre-polymerization followed by chain extension, and have relatively low molecular weights. Also the direct polymerization of relatively high molecular weight monomers is a promising approach to obtain high molecular weight polyurethanes [5]. A study in 2013 explains that a lignin based polyurethane thermoplastics have a high tensile strength shown by its young's modulus. The study shows that by utilizing lignin's rigid cell properties, one can synthesize a high tensile strength polyurethane [6]. This study proves that sorghum bicolor can be a chain extender in this hybrid polyurethane (HPU) synthesis and serves a novelty route of hybrid polyurethane synthesis. The hybrid polyurethanes are obtained by pre-polymerization reaction of polyethylene glycol as the soft segment with the molecular weight of 4000 and 6000 and high molecular diisocyanate, 4,4'-Methylenebis (cyclohexyl isocyanate) (HMDI) as the hard segment, followed by copolymerization reaction which cellulose as a chain extender.

Over the past few years, several materials used by the automotive industries have been using PU – incorporated materials. The mentioned materials are especially referred to the materials needed for body kits, tires, and interiors. However, PU – incorporated materials usually do not have the ability to degrade naturally.

2. Materials and Methods

2.1 Materials

Polyurethanes were synthesized from mixtures of Polyethylene glycol (PEG) Mw:4000 g/mole and 6000 g/mole obtained from Sigma – Aldrich as the soft segment with the composition 0.0025 moles (10g) and 4,4'-Methylenebis (Cyclohexyl isocyanate) (HMDI) obtained from Sigma – Aldrich as the hard segment with the composition 0.01 moles (2.45 mL), Dibutyltin dilaurate (DD) obtained from Sigma - Aldrich as the polymerization catalyst with the composition 2 drops (0.1 mL), dimethyl formamide (DMF) as the solvent, Sorghum bicolor plant cellulose obtained from Chandra Asih as the chain extender with the composition ranging from 0.5– 2.0 g, and cellulose obtained from Sigma – Aldrich as the chain extender with the composition ranging from 0.5 – 2.0g.

2.2 Cellulose Preparation

Sorghum was crushed by using a crushing machine and sieved to get uniform size (50 mesh). 50g of fiber were soaked with 0.25 M of NaOH solution overnight, then washed 4 times with distilled water until the pH of fiber became 7. After that, the fiber trough bleaching stage, in this stage, fiber was soaked by using 5% NaClO solution for 4 h and then it was washed with distilled water until the pH became 7. Next stage was acid hydrolysis stage with 25% wt H₂SO₄ solution for 2 h and washed

with distilled water. In all stages mentioned, fiber was immersed and stirred using hot plate magnetic stirrer. In the last step, cellulose obtained was dried by oven, at 60°C for 6 h.

2.3 Synthesis of Hybrid Polyurethane

The process started by preparation of schlenk tubes filled with DMF solvent and PEG was fluxed using vacuum suction machine and nitrogen gas three times. All of the flasks were then dipped into the oil bath and heated. The temperature is then raised to 75°C and stirring for 1h. After 1 h, HMDI were injected into the flasks in a nitrogen atmosphere. After that, 2 drops of Dibutyltin Dilaurate (DD) catalyst were added into each flask. Then stirring were conducted for 2 h at a constant temperature at 75°C [7].

After the solution became as white as milk, each of the schlenk tubes were filled by 0.5g chain extender (see each composition in Table 1 with the temperature raised to 80°C and stirring for 1h. The process was then terminated using 20 mL of water and was left intact for 24 h until a phase separation occurred, and the hybrid polyurethane will precipitate. After that, the precipitate will be separated using a filtration cloth and dried under room temperature for 3 days and will be continued with characterization afterwards.

2.4 Characterization

¹H-Nuclear Magnetic Resonance (¹H-NMR) and ¹³C-NMR was used to analyze the structure of hybrid polyurethanes. ¹H-NMR was used to identify the functional groups within the polyurethanes and to measure the amount of phenolic hydroxyl functional groups in the polyurethanes. Characterization procedure was conducted at DTMM FTUI using NMR Jeol 500MHz. Measurement condition are 23°C for the temperature and 6 Pa for the pressure (vacuum).

Fourier Transform – Infra Red (FTIR) to analyze and confirm the NMR data about the functional groups formed in the hybrid polyurethanes. Specifically, FTIR was used to identify the functional groups in the lignin. Characterization procedure was conducted at DTMM FTUI using FTIR PerkinElmer UATR Two Spectrum Two. The instrument has a limitation of range of wavelength from 450 – 4500 λ.

Simultaneous Thermal Analysis (STA) consisted of *Thermogravimetric Analysis (TGA)* and *Differential Scanning Chromatography (DSC)* to analyze physical changes such as Tg and Tm (thermal) and thermal stability. Characterization procedure was conducted at DTMM FTUI using STA PerkinElmer STA6000. The instrument has a limitation of rate of 5 min /°C and max temperature of 1000°C.

3. Results and Discussion

The reaction can be seen in Figure 1. The reaction was initiated by pre-polymerization

process of polyethylene glycol with a diisocyanate (HMDI). The isocyanate groups are reactive towards active hydrogen groups such as amine (-NH), hydroxyl (-OH), water, carboxylic acid (-COOH), urea, and amide. Isocyanate will attack hydroxyl group forming urethane group. In the pre-PU forming stage, urethane groups are formed by reacting HMDI and PEG with DD (Dibutyltin dilaurate) as a catalyst and DMF (dimethyl formamide) as a solvent in nitrogen atmosphere. The reaction followed by copolymerization, which cellulose as chain extender to obtain polyurethanes.

In this stage, the isocyanate group from HMDI reacted with the hydroxyl group from PEG forming a pre-polymer which is an interspersed polyurethane copolymer. The pre-polymer in this stage still has isocyanate (N=C=O) group which will be eliminated after the addition of cellulose in the second step. The reaction of pre-polymer and cellulose occurs in the second step. Isocyanate group left on the end of the pre-polymer's chain attacked hydroxyl group in the cellulose forming a urethane chain. The reaction shows two groups of hydroxyl; aliphatic hydroxyl, and phenolic hydroxyl. The reaction rate for isocyanate and aliphatic hydroxyl is higher than the reaction rate for isocyanate and phenolic hydroxyl. The result of this process is the hybrid PU.

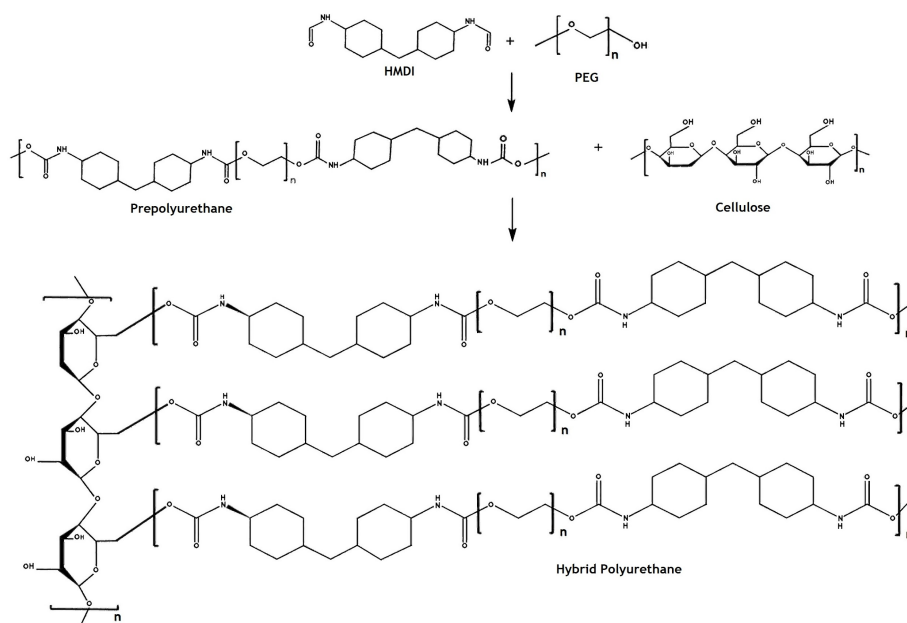


Figure 1. Purposed Synthesis Route of HPU

Figure 2 shows the FTIR spectra of each hybrid polyurethanes synthesized from PEG 4000 (a) and PEG 6000 (b) with addition of cellulose for each the macrodiol at the amount of 1.5 g for the top graph, 1 g for the middle graph, and 0.5 g for the bottom graph. The structure of the polymer was confirmed by FTIR spectrum. The presence of the amine bonds (NH₃) appears at 1280 – 1342 cm⁻¹, C-O Acyl bond at 1242 cm⁻¹, and secondary amine at 2887 cm⁻¹. Secondary amine indicating that isocyanate bonds (N=C=O) opened and made urethane group bond with hydrogen. Urethane group

bond in shows that hybrid polyurethane was obtained. According to the figure, fiber addition has influence on amount of polyurethane obtained, it is signed from high molecule vibration in 1242 cm^{-1} , 2887 cm^{-1} from polyurethane obtained and 1104 and 3361 cm^{-1} from cellulose.

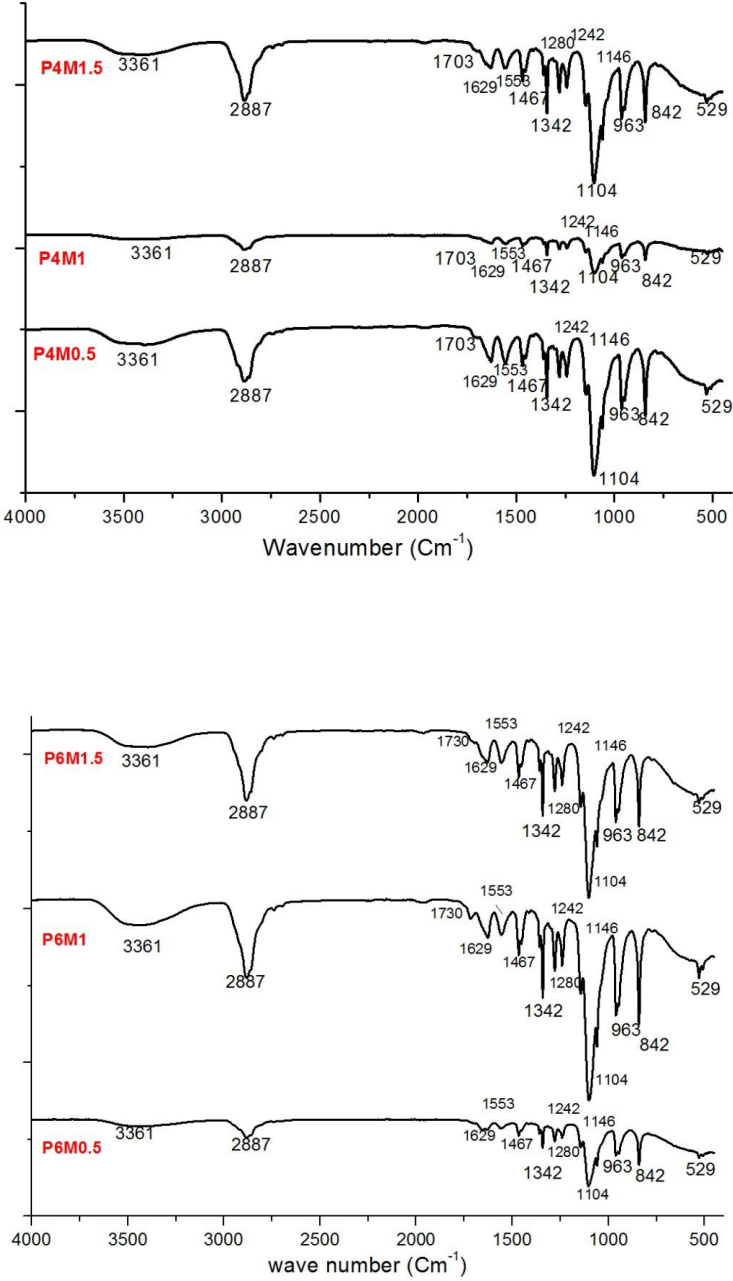


Figure 2. Top figure: FTIR Spectra of hybrid polyurethane (HPU) P4M05, P4M1, P4M15; Bottom figure: FTIR Spectra of HPU P6M05, P6M1, P6M15

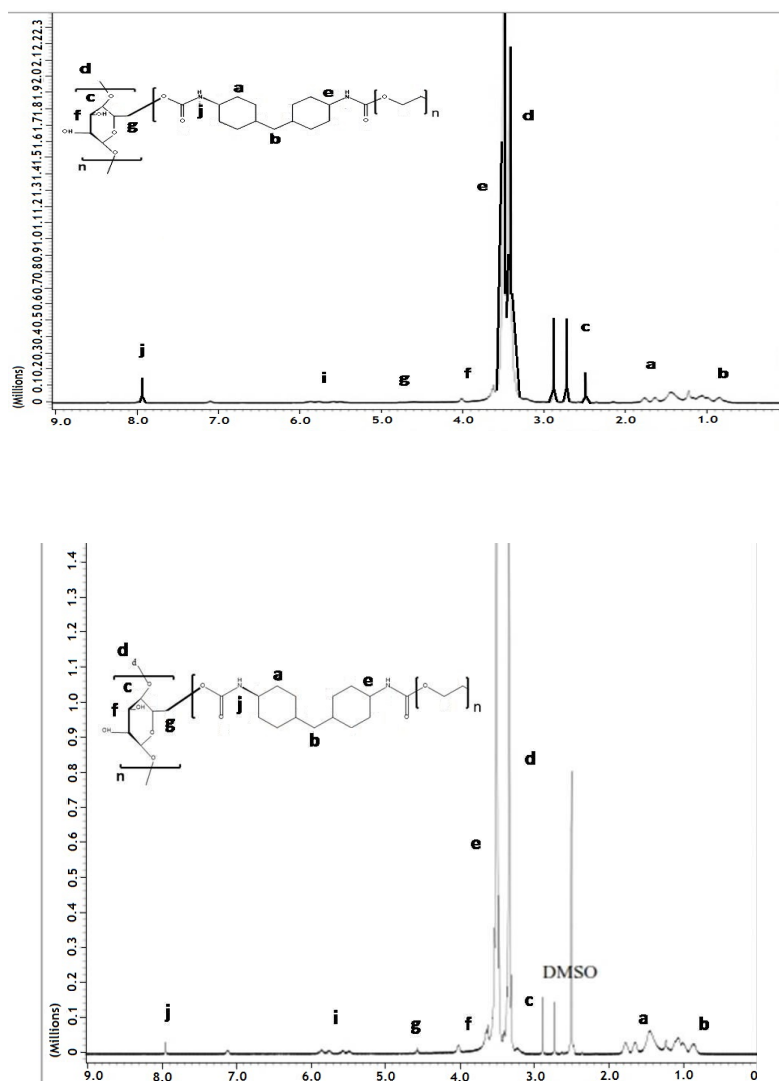


Figure 3. Top Figure: ^1H -NMR Spectra of P4M1; Bottom Figure: ^1H -NMR Spectra of P4S1

Characterization of the polymers was performed by ^1H - ^{13}C -NMR, and FTIR. A representative ^1H and ^{13}C -NMR spectrum for as one of the novel hybrid polyurethanes is shown in Figure 3. The urethane C=O group and amide groups appear in all of the samples, the former appears at about 0.865 until 1.075 ppm in ^1H -NMR and in 162.737 ppm in ^{13}C -NMR spectra. Meanwhile the chemical shift of the amide groups appear at about 8.2229 in spectrum for the NH.

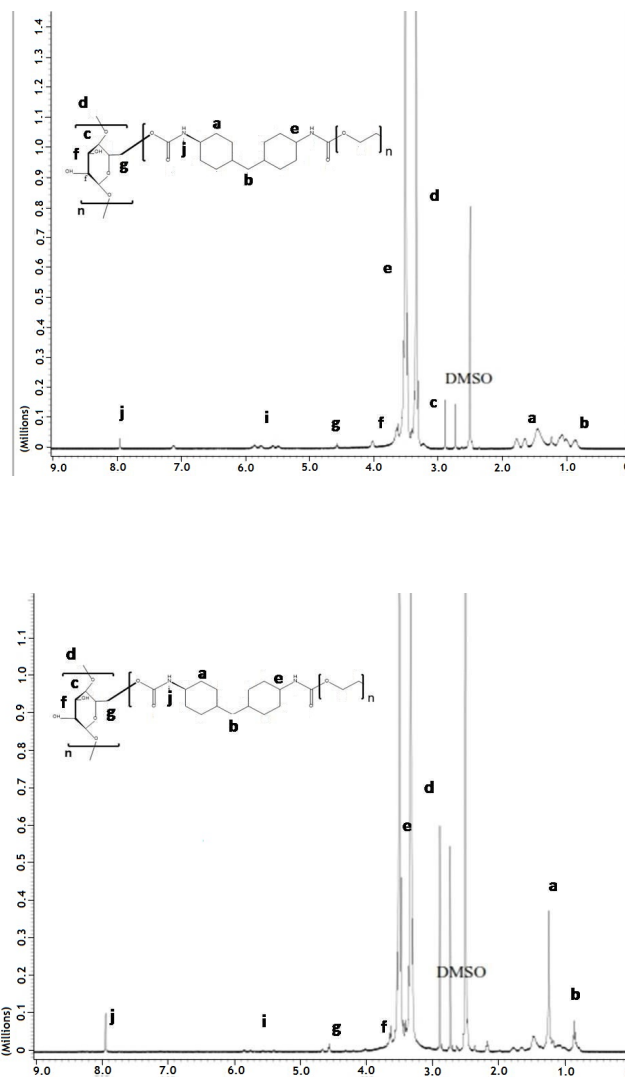


Figure 4. Top Figure: ¹H-NMR Spectra of P6M1; Bottom Figure: ¹H-NMR Spectra of P6S1

Based from the overall FTIR spectra from Figure 3 and 4, sample P4M1, P4S1, P6M1, P6S1 have a relatively similar absorbent bond. The structure of the hybrid polyurethane is also confirmed by FTIR spectrum, the presence of the amine bonds appears at 1342 and 1280 cm^{-1} , while the urethane group and the amide group appear at 1703 cm^{-1} and 1553 cm^{-1} , respectively. According to the FTIR spectra, compared with P4M1 (Hybrid Polyurethane based from PEG – 4000 and 1 gr of cellulose), P4S1 (Hybrid Polyurethane based from PEG – 4000 and 1 gr of sorghum) has higher peak of OH that appears at 3400 cm^{-1} .

From the Figure 3 and 4, it was proven that peak increases at the addition of sorghum as a chain extender (P4S1 and P6S1) because there were more formed products (main and side product). The main product is the hybrid polyurethane while the side product is the N-O₂ stretch in 1392 cm^{-1} which only occurred in the sample with the sorghum addition.

3.1 Thermal Behavior of Hybrid Polyurethane

The thermal characteristics on the hybrid PU material was done by utilizing *Differential Scanning Calorimetry* (DSC). The result obtained from DSC was shown as heat flow vs. temperature graph (Figure 5 left). The graph doesn't show any heat flow decreasing peak, however it shows the increase in glass transition (T_g) and melting temperature (T_m). The increase in T_g and T_m was caused by the higher concentration of O-H in sorghum than in cellulose so more urethane chain was formed in the sample. Figure 5 right shows that the differences of thermal characteristics of a material were caused by the differences in utilizing PEG as a soft segment.

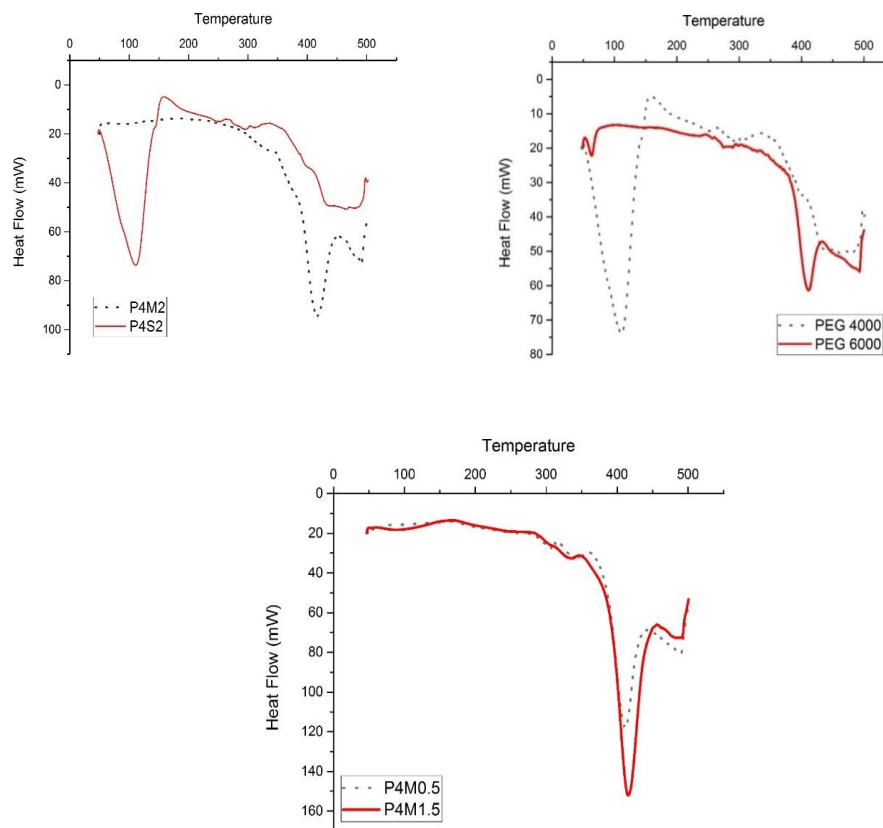


Figure 5. Left Figure: Sorghum and Cellulose Hybrid polyurethane P4M2, P4S2 DSC curve comparison; Right Figure: PEG 4000 and PEG 6000 DSC curve comparison; Bottom Figure: P4M0.5 and P4M1.5 DSC curve comparison.

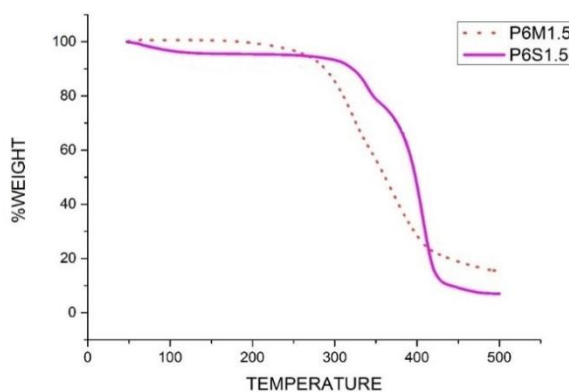
The higher the molecular weight, the higher the melting temperature because the PEG – 6000 has more polyol chain than PEG – 4000. This causes PEG – 6000 have more cross linking with sorghum in forming a PU. Figure 5, Bottom Figure shows that the addition of cellulose as a cross linker in polyurethane affects greatly the thermal characteristics of a material. The greater the amount of cellulose added to a material, the higher its melting temperature will be because there are more cross linking happened in the process in forming a PU.

Table 2. DSC curve analysis results on hybrid polyurethane

Sample	T _g (°C)	T _m (°C)
P4M2	76.49	415.32
P4S2	110.60	431.78
PEG 4000	111.22	410.30
PEG 6000	63.70	435.00
P4M0.5	59.07	410.05
P4M1.5	104.20	415.07

3.2 Thermal Stability Analysis

Thermogravimetric Analysis was utilized to analyze thermal stability. The result of the test was shown as a graph that shows the reducing of polyurethane mass against temperature increase as shown in Figure 6.

**Figure 6.** Polyurethane TGA Curve

According to the curve, it can be seen that, HPU cellulose obtained from sorghum bicolor addition (P6S1.5) has better thermal stability than HPU with pure cellulose addition (P6M1.5). It is predicted caused by the chemical strong bonds which come from the hydroxyl. The –OH functional group give a strong Van Der Walls intermolecular force on cellulose structure and provide the cellulose high mechanical and thermal stability. As this van der walls force increased from the –OH functional groups which has been bonded to the PU, it may arrange any ordered chain structure or strong attraction bonds with other functional groups which make it more difficult to break when the temperature is continuously increased. In this case, cellulose was obtained from sorghum predicted has more –OH functional than the pure cellulose, because cellulose from sorghum still containing hemicelluloses and lignin. This result was supported by Figure 7, where in the right of Figure 7 shows that there was bundles of cellulose obtained from sorghum in hybrid polyurethane sample, with diameter of cellulose about 16 μ m. While from the left Figure 7 it can be seen that surface of polyurethane with pure cellulose (P6M1.5) has no bundles like the right one does. It Indicates that the two type of cellulose has different size and diameter, so when it was mixed and reacted, the pure cellulose is able to be blended well with all of composition. While, cellulose form sorghum, with

larger diameter and tend to congregate, gave a stronger influence on the thermal stability. The bundle was hard to break when the sample was heated with high temperature.

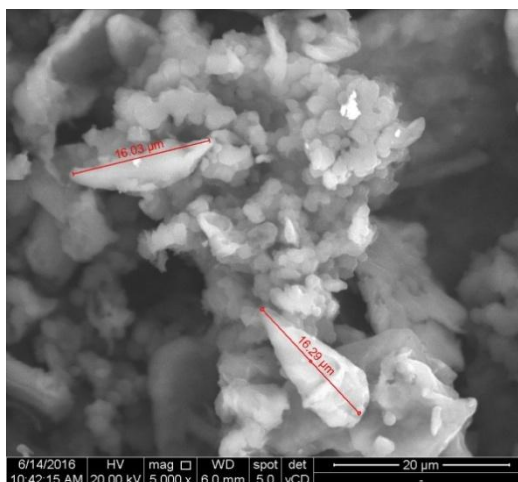


Figure 7. Left Figure: SEM Result of HPU with pure cellulose with 1000x magnifying; Right Figure: SEM Result of HPU with sorghum bicolor with 1000x magnifying.

4. Conclusion

The three composition of the base materials (PEG, HMDI, and Sorghum bicolor plant cellulose) have been successfully synthesized as hybrid polyurethane proven by the NMR and FTIR results in showing C=O, NH, amide, and C-O-H functional groups in all of the samples. Concentration variation of sorghum bicolor plant cellulose as a chain extender influences the thermal properties of the hybrid polyurethane proven by the DSC and TGA results in showing the glass transition and melting temperature comparison between 2 kinds of cellulose. Overall, the synthesis of hybrid polyurethane by using cellulose as the chain extender can be proven in this study.

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