

A Review: Method of Preparing Palm Oil Based Polyurethane

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Abstract—In this paper, a review on a methodology to prepared palm oil based polyurethane presented. Various methods have been attempted in the research for innovation to produce polyurethane palm oil based. Through the innovative use of palm oil in the production of polyurethane, it is expected to process an outcome that is environmentally friendly and cheaper in preparation process. Innovations that have been executed can also provide efficiency in the production of polyurethane

Keywords—polyurethane; glycerol; palm oil based

1. INTRODUCTION

A. Palm oil

Palm oil is one of the most widely used plants where it is produced from oil palm tree. Oil palm plantations abound in the tropical rainforests in Malaysia and Indonesia [1]–[3]. Palm oil is a triacylglycerol, which is consisting of fat and oils produced by the palm trees [1]–[5]. Triacylglycerol's structure include glycerol bonding with three fatty acids where in a liquid form known as oil, while in solid form known as fat [6]–[7]. Palm oil is a biological resource that provides the highest return on oil-based hydrocarbons and far more effective than any other commercial crop oil [8]–[9]. With good quality planting materials and agronomic practices, palm trees start producing fruit bunches as early as two and a half years after planting. Although the lifespan of oil palm plantations, referring to a specimen grown in the Botanical Gardens in Bogor, Indonesia, at least 120 years, this plant usually takes 25–30 years before through the process of replanting. This is because after this age, the palms become too high and difficult to harvest [10]. Continuous increased in petroleum prices, giving the user a paradigm shift towards using renewable raw materials for industrial and commercial goods. The use of palm oil and its products, which is renewable and biodegradable, making palm oil as an alternative raw material for the production of polyurethane polyol based on palm oil [11]–[12]. Furthermore, there is an increased awareness of social responsibility toward the environment to meet the demand for renewable resources and environmentally friendly products [8], [10], [13].

B. Polyurethane

Polyurethanes are versatile polymers as is flexible. Polyurethane can be used in the form of foam, elastomers, coatings, adhesives and sealants for because of the wide range of their properties [14]–[15]. Flexible and rigid foam have the largest polyurethane products market. The use of polyurethane in industries includes automotive, construction and insulation [3], [7], [14]. Polyurethanes are block copolymers containing segments of low molecular weight polyester or polyether bonded to a urethane linkages (–NHCO–O) which can react with isocyanate groups and hydroxyl groups [7], [16]–[17]. Most of the materials such as polyol and polyester used in the production of polyurethanes are derived from petrochemical-based resources such as crude oil and coal [18]–[19]. However, use of these types of materials is considered to be unsustainable and require high costs and results in depletion of natural resources [20]–[22]. Due to high demand, there is a need to find alternative sources to produce polyols for positive impact in the production of polyurethane [13], [20]–[23]. Another advantage of polyurethane foams is it can perform well in most areas of low-temperature insulations and is a low in cost of production [2], [7], [24]. Polyurethanes have become some of the most versatile polymers in the world since they were first developed in 1937; however polyurethane foam was developed in the 1960s, and was well known for its energy and sound absorbing capability as well as, low apparent density [7], [13], [23].

As a result of the reduction of petroleum resources, environmental factors also play an important role in industrial competitiveness, which requires the use of lower cost and reduce negative impacts on the environment. Based on these factors, one of which is capable of giving a good competition is the use of natural resources and of renewable sources produced from plants [7], [25]–[26]. Among the efforts that have been done is to develop bio-based polyurethane foam using vegetable oils such as castor oil, soybean oil, canola oil, rapeseed oil and palm oil [27], [28].

Up until this time, there has been a lot of research executed in the production of palm oil based polyurethane. The production of polyurethanes can diversify the use of palm oil in various fields. The use of palm oil is both bio-based and biodegradable. Palm oil also abundant in supply and low in cost [1], [8]. Basic polyurethane materials are polyol and isocyanate; so far only polyols can be synthesized from renewable resources such as oil, fat and starch [2]. Production of polyols from vegetable oil to replace petrochemical polyols start attracting the attention of researchers around the year 2004 due to the rising cost of petrochemical-based raw materials and partly to meet the needs of environmentally friendly green products [29]. Some of the most widely used vegetable oils to replace petrochemical polyurethane polyol are soy based polyol and palm oil based polyol [30].

2. PREPARATION PALM OIL BASED GLYCEROL

Glycerol is a simple polyol compound called glycerin or propane-1,2,3-triol. Glycerol is a chemical that has a variety of applications, such as in the pharmaceutical, cosmetics and food. Glycerol is produced through the process of saponification and transesterification [31]. There is also the method of producing glycerol by epoxidation of vegetable oils followed by oxirane ring opening [21], [32]. The glycerol can be used as the main chemical in the production of polyurethane, OH in which three glycerol molecules react with NCO groups in the molecule to form a bond isocyanate polyurethane polymer [6], [33].

Glycerol provided for the preparation of polyurethane can be obtained from several sources. There had been studies that use palm oil based glycerol generated from the plant [34]. In transesterification reaction, there are five types of catalyst that can be used to produced glycerol [31],[35] as shown in Table 1.

The process of transesterification of glycerol reported by Chuayjuljit et al. [2], mixing palm oil with Pentaerythritol, followed by mixed calcium oxide within temperature control from 200 °C to 245 °C. At 245 °C the temperature was maintained until a 1 part sample was soluble in 3 parts ethanol. The obtained product was allowed to cool at room temperature under nitrogen atmosphere.

Ho et al. [36] and Hayyan et al. [37] had used a basic transesterification process to produce glycerol in their study, using biodiesel synthesis. The study had been done by providing a pre-mixture of potassium methoxide through the process of mixing methanol with potassium hydroxide. The mixture was stirred at a constant speed for 2 hours, after which the mixture was cooled to ambient temperature. Finally, the mixture was left overnight to settle and form two layers. The top layer was biodiesel, while the bottom layer was the glycerol.

Arniza et al. [8], in their study had provided glycerol through the transesterification reaction of palm oil, epoxidation and ring-opening. In the transesterification reaction, palm oil and glycerol were added with the catalyst and then heated. In the process, n-hexana been used to dissolve the palm oil. Subsequently, the epoxidation reaction was initiated by heating the transesterified palm oil with premixed formic acid reagent. The last reaction was the ring-opening, where palm oil neutralized epoxidized transesterified was heated to 60 °C and added slowly with droplets of premixed ethylene complex glycol and boron trifluoride-ether.

Tanaka et al. [1] had been using palm oil in the preparation glycerolysis polyol. In this preparation, glycerol was added to the oil under temperature control. t-BuOH was added to act as a solvent to palm oil. Tetradecane was added to the mixture as an internal standard and NaOH acted as solvent in this reaction. After the reaction was complete, the acid hydrochloride was added for the neutralization process.

Saetae et al. [33], used the equipment consisting of a round flask equipped with a thermometer, stirrer and reflux condenser. Palm oil and glycerol were placed in a flask and added with litharge catalyst. This mixture was left at 240–250 °C for 2 hours.

Li et al. [38] had conducted a study on one-pot preparation of biopolyols with branched fatty acid ester chains and its effects on foam formation and properties. In this study, crude glycerol was added to the round bottom flask connected with a Liebig condenser and heated to 110 °C for 60 minutes under constant magnetic stirring using a heating mantle controlled temperature. Later, the temperature was increased to 150 °C in vacuum conditions to complete the sample.

Table 1: Types of catalyst for producing glycerol and examples of the catalyst

Types of catalyst	Example
Homogeneous base catalyst	NaOH KOH
Heterogeneous base catalyst	CaO MgO
Homogeneous acid catalyst	H ₂ SO ₄ HCl
Heterogeneous acid catalyst	ZrO ₂ TiO ₂ SnO ₂ Zeolite
Enzyme	Mucor miehei (Lipozym IM 60) C.antarctica(Novozym435) Bacillus subtilis

3. PURIFICATION PROCESS

After the process of extracting glycerol from palm oil, crude glycerol purification process needs to be done to obtain a cleaner glycerol with no dirt. Crude glycerol obtained after the production process, contains water, monoglycerides, diglycerides, salt, soap and some residual catalyst remaining ester [39]. The purity of crude glycerol obtained from vegetable oil transesterification depends on three parameters: (1) the type of catalyst used, (2) the amount of excess alcohol, and (3) the conversion achieved [40]–[41]. The purification process can guarantee that glycerol produced is of high value products [42]–[43]. There are conventional techniques for removing impurities from crude glycerol such as distillation and ion exchange [44].

Nanda et al. [42] made a study of the purification of glycerol through a study entitled Crude Glycerol Purification study using acidification. In their study, crude glycerol was mixed with acid at a particular pH and compounds would be stirred until well blended. The compounds would be given some time to allow for the formation of layers. The three layers obtained consisted of the middle layer which is the layer of glycerol. The glycerol layer was mixed with potassium hydroxide for the neutralization process. Next, glycerol will be evaporated at a temperature of 110 °C for 2 hours and filtrated to remove the precipitated salt.

N. Saifuddin et al. [44] through their research carried out purification process to reduce the content of acid and salt using assisted acidification microwave. Through this method, crude glycerol was transferred to a beaker and subjected to microwave irradiation using a microwave oven. After the irradiation, the solution was acidified by addition of H₂SO₄ in small portions at a time to bring the solution to the desired pH. The mixtures were allowed to stand at room temperature until the solution had phase separated into two layers, where the bottom aqueous layer was the glycerol and inorganic salts.

Y. Xiao et al. [45] prepared purified glycerol started with micro filtered (0.45 µm pore size) crude glycerol to remove all solid materials and after that crude glycerol was treated under vacuum conditions using a rotary evaporator at 50–90 °C for more than 2 hours. After cooled, deionized water was added and followed by NaOH until the pH was 11 and then the crude glycerol was kept stirred for 30 minutes at 50 °C to implement saponification. HCl was used to acidify the alkaline glycerol until the pH was 1, and kept stirred for another 30 min at 25 °C. The acidified solutions were vacuum evaporated at 90 °C for more than 2 hours and micro filtered. The glycerol was placed in a separation funnel for phase split overnight. The lower layer was neutralized with NaOH until the pH was 7 and micro filtered to eliminate salt, followed by vacuum evaporation of solvent at 90 °C for more than 2 hours. The neutral solutions were extracted by anhydrous ethanol in order to reduce residual salt. Finally, light solvents were evaporated out at 50–90 °C for more than 2 hours.

4. POLYURETHANE PREPARATION

Polyurethane foam is produced from a mixture of two types of compounds, namely Part A and Part B. Part A consists of a mixture of several other compounds such as polymericdiol or triol (glycerin normally used), blowing agents, silicone surfactant and catalysts. Part B only consists of polyisocyanate (diphenylmethanediisocyanate) [44]–[47]. When the two parts A and B are mixed through certain rules, it will produce the polymer chain.

Up to this date, there are many inventions in preparing polyurethane. Most studies in the preparation of polyurethane make modifications for substances in part A [30], [47]–[48]. Examples of materials used for the catalyst and the blowing agent are shown in Table 2.

Table 2: Example of materials used for the catalyst and the blowing agent in polyurethane preparations process

Part A			Author
Blowing agent	Surfactant	Catalyst	
Polyethyleneglycol Monoethylene glycol	–	–	[1]
Tegostab B-8404	Distilled water	–	[28]
N,N-dimethyl-cyclohexylamine Distilled water	Polymethylsiloxane	–	[2]
Stannous octoate			[33]
Water	DABCO DC5357	Polycat 5 Polycat 8	[38]
Dibutyltindilaurate	Tegostab B 8486	Niax Dabco LV33	[8]
Silicone oil		Dibutyltindilaurate	[50]
HFC M1 Water	Tegostab 8460	Dimethyl-cyclohexylamine	[4]
–	Tegostab® B-4900	Tegoamin® B75 Kosmos® 29	[51]
	TEGOSTAB B-8404	–	[38]
BYK A530	Scavenger Imsil 1240	–	[52]
1,1-dichloro-1-fluoroethane HCFC-141b	Silicone	Triethylenediamine Ethylene glycol	[13]
Water	Silicone oil AK8804	Dimethylcyclohexylamine	[53]
Water	Niax Silicone L-627,	DABCO T-9 Dimethyl-cyclohexylamine DABCO BL-11	[3]
–	Tegostab B8408	Tetramethylhexanediamine Pentamethyldiethylenetriamine	[54]

Mechanical properties and physical strength of polyurethane depending on the type of polyol used, diisocyanate, diisocyanate and index it [21], [52]. Part B contains a polyisocyanate (diphenylmethanediisocyanate). Isocyanates are an important family of low molecular weight chemicals. The most common examples are:

1. Toluene diisocyanate (TDI)
2. Methylenediphenyldiisocyanate (MDI)
3. Hexamethylenediisocyanate (HDI)

Other isocyanates used in industry are:

1. Polymethylenepolyphenylisocyanate (PAPI)
2. Isophoronediiisocyanate (IPDI)
3. Naphthalene diisocyanate (NDI)

Depending on the type of isocyanate and how it is used, isocyanates may be supplied in solid or liquid forms. TDI, HDI and IPDI are colourless to pale yellow liquids, while NDI is a white powder. MDI may sometimes be supplied in solid form as white or yellow flakes, but is usually in the form of a dark brown viscous liquid [55]–[56].

In the preparation of polyurethane, the use of two basic ingredients of isocyanate and glycerol without additives studied and characterized by researchers.

Saifuddin et al. [44] report the preparation of polyurethane performance in their study only using two main ingredients which are glycerol and polyisocyanate. These two main ingredients were mixed and stirred gently to form a gel. Polyurethane formed was left under microwave irradiation. After that, it would be left in the fume in two days for curing process.

Ang et al. [16] in the Synthesis of palm oil based polyester polyol for polyurethane adhesive production_ prepared by reacting a polyester polyol with a pMDI in NCO / OH ratio of 1.3 and glycerol was added as a cross-linker. The mixture was stirred at 180 rpm at room temperature for 3 minutes and then the product would be used on wood surfaces using a brush.

Next, there was innovation with the addition of additives such as blowing agent, catalyst and surfactant to streamline the invention of the resulting polyurethane.

Tanaka et al. [1] reported in their study, in the preparation of polyurethane, palm oil based glycerol was mixed with polyethylene glycol or diethylene glycol. Subsequently, mix dibutyltin dilaurate and water to produce a pre-mix compound. The MDI was added to the solution and stirred strong at room temperature.

Dzulkifli et al. [28] in the study reported in the preparation of polyurethane, they had prepared seven basic formula with different ratio of NCO–OH glycerol . In this study , they reported that the formation of polyurethane foam was the result of the exothermic reaction between Solutions A and Solution B. Solution A consisted of palm oil based glycerol , silicone surfactants , and distilled water while Solution B consisting of pMDI . The methods used in the preparation of polyurethane initiated with Solution A stirred for 2 minutes at a speed of 1500 rpm to form homogeneity. Then, Solution B was mixed and stirred at 1500 rpm for 45 seconds before being poured into the mold. It was left to cool at room temperature for at least 24 hours and removed from the mold. Thereafter, it was left again at room temperature for 24 hours before the analysis was conducted.

In a study to investigate the effect of surfactant content of the catalyst and the properties of the PU foams by Chuayjuljit et al. [2], they had provided a sample of sixteen different ratio catalysts , blowing agent and surfactant . Preparation of the polyurethane was started by providing a mixture of palm oil glycerol, distilled water, N,N-dimethyl-cyclohexylamine and polymethylsiloxane. Then pMDI was added and stirred at a speed of 1000 rpm using a high speed mixer for 1 minute. When it had reached a creamy consistency, the mixture was poured into an open mold. Once removed from the mold, the polyurethane would be left for 2 days at room temperature prior to analysis carried out.

Li et al. [38] reported in their study mixed glycerol , surfactants , catalysts and water. This mixture was stirred at high speed for 30 s to achieve homogeneous dispersion. Then, MDI polymer was added and stirred vigorously for 10 s. After that, the mixture was poured into a mould that had been coated with polytetrafluoroethylene and allowed to stand at ambient temperature. The samples were left overnight before being removed from the mold. After that, the samples were cut and left for one week before being analysed.

Arniza et al. [8], had reported a polyol-based polyurethane prepared using synthesized transesterified palm oil blended with petrochemical-based polyol in some ratio. The glycerol was blended with the amine catalyst, tin catalyst, surfactant and blowing agent and stirred continuously for a few seconds. This was followed by addition of isocyanate and stirred vigorously for 7 seconds. Then, the mixture was immediately poured into a plastic container. In this study, reactivity data such as time of foaming cream, the top of the cup, gel time, rise time and tack time were observed and recorded. After 5-10 min, the sample would be ready to be demolded from the foam containers and foam left for aging for 7 days.

Pinto [50], had prepared polyurethane by mixing a glycerol , distilled water , silicone oil and stirred vigorously for 1 minute using a mechanical stirrer . After that, the isocyanate was added and stirred for 15 seconds. Then the resulting mixture was left for 1 minute, for foam production process.

Septevani et al. [4] studied polyether glycerol replaced with palm kernel oil based polyester glycerol in rigid polyurethane foam. In this study, they provided polyurethane using the following method. Glycerol was mixed with a catalyst, surfactant and blowing agent to obtain a homogeneous compound. The mixture was then mixed with a pMDI. The mixture was put into an aluminum mold which was heated and left for 24 hours before being released.

Pillai et al. [7], had studied for rigid and flexible polyurethane bio -based materials. All compounds for part A was weighed and mixed in a beaker. Then, the mixture was added to the MDI. This mixture was then stirred vigorously for a few seconds and then poured into a cylindrical mold Teflon. The mold was already applied with the silicon release agent. The sample was cured for four days at 45 °C and after cured for one day at room temperature.

Badri et al. [22] conducted research in the preparation of these polyurethane. In the study, crude glycerol, pMDI, refined, bleached, and deodorized palm kernel oil, tegostabB8408, tetramethylhexanediamine, pentamethyldiethylenetriamine and water was stirred vigorously using a speed of 5000 rpm for 10 seconds at 25 °C. The mixture was poured into a mold and screwed tight. Empty fruit bunch was also added to the analysis as filler fibers on the sample of polyurethane.

She had continued his research as reported by Badri [54] in preparation of polyurethane by mixing dietanolamine, ethylene glycol and potassium acetate In this research, he reported about mixing dietanolamine, ethylene glycol and potassium acetate with a ratio of 90: 7: 3 to yield polyhydric compounds. This mixture was mixed with refined, bleached, and deodorized palm kernel oil at a certain temperature and at the same time nitrogen gas was flowed into the system. Then, MDI was poured into the mixture.

Haryono et al. [57] had reported that in preparing the rigid polyurethane foam, a mixture of palm oil based glycerol and additives were reacted directly with MDI, at room temperature. The additives used for preparation of rigid polyurethane foam were silicon glycol, dimethylcyclohexylamine, water as the blowing agent and ethylene glycol. Rigid polyurethane foam synthesis was performed in closed mold system.

Wong et al. [58] prepared polyurethane from palm kernel oil-based glycerol monoester through prepolymerization. The process of preparing started by dissolved palm kernel oil-based glycerol monoester in tetrahydrofuran. Dietanolamine was added to act as a chain extender and then the mixture was mixed with MDI under nitrogen gas atmosphere. The mixture was stirred vigorously at 200 rpm for one hour at room temperature before it was put to a translucent film about 50 microns teflon plate for analysis.

Daud et al. [59] made a study of palm oil based polyurethane as a solid polymer electrolyte. In this study, palm kernel oil-based glycerol monoester and MDI was dissolved in acetone separately at room temperature. This process was intended for the formation of urethane prepolymer. After that, LiCF_3SO_3 salt was added to the mixture. The mixture then poured into a mold.

After improvements made in the additives, there were also other inventions in the filling other material in the preparation of polyurethane or polyurethane will be acted as a filler material to another. This was done to increase the diversity of polyurethane.

Sari et al. [60] reported the preparation of polyurethane in their study on the development of lightweight concrete. In this study, polyurethane will be applied as a hardener in light weight concrete. Palm kernel oil-based glycerol and MDI are mixed and at a speed of 1000 rpm for 10 seconds. After that, the mixture poured into a mold. Polyurethane was formed through a range of processes and filtered for further processing, applications in light weight concrete.

Biomass characterization and mechanical properties of polyurethane were studied by Nur Azni et al. [61]. In their study, the ratio of glycerol and MDI mixture is 1: 1.1. The preparation of polyurethane foam, glycerol started with stirring at a speed of 2000 rpm. Thereafter, the MDI was added to the glycerol, followed by Henna and turmeric which were added according to the percentage ratio. Then the mixture was poured into the mold and heated at 80 °C for 2 hours for post curing process.

Tay et al. [12] had studied about thermal properties of polyurethane by adding of empty fruit bunches in the preparation of polyurethane. In the preparation process, glycerol and the catalysts were mixed well. The empty fruit bunches was added slowly over until the mixture blended. MDI was added and stirred strongly. The mixture poured into a mold and pressed by using hot press machine at 20 MPa for about 15 hours. Then, the mixture would be heated at a temperature of 120 °C for 2 hours and then allowed to cool before it was removed from the mold.

5. CONCLUSIONS

Polyurethane material is becoming more widely used. Many studies are conducted to obtain polyurethane by using natural resources and renewable sources. The application of palm oil as the main source for the preparing polyurethane materials because palm oil is cheap and easily available. Preparation of palm oil based polyurethane is also diversified to get results that can meet the characteristics of the material to be produced.

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