

Characterization of Fluoroacrylate Palm Oil Polyurethane (FPOPU) with Different Synthesis Methods Using Fourier-Transform Infra-Red (FTIR)

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Abstract. In this study, fluoroacrylate palm oil polyurethane (FPOPU) was synthesized with different synthesis methods. FPOPU was synthesized stepwise starting with the synthesis of acrylated epoxidized palm oil (AEPO) by a reaction of acrylic acid (AA) and triethylamine (TEA) as the catalyst. Then, palm oil polyurethane (POPU) was formed by the reaction of AEPO with isophorone diisocyanate (IPDI) and hydroxyethyl acrylate (HEA) as an end cap agent. POPU was further added with 1,6 hexanediol diacrylate (HDDA), trimethylolpropane triacrylate (TMPTA), and heptafluorodecyl methyl-metacrylate (HDFDMA) monomers to form FPOPU. FPOPU synthesis methods were studied by manipulating the sequence of chemicals added, temperature, and mixing time of POPU. The FPOPU mixture was finally cast onto a silicone mold with 1 mm thickness and cured under UV radiation at 120 seconds. Based on the analysis, pre-mixed IPDI with HEA at 60°C for 15 min followed by the addition of AEPO at 60°C and further mixed for 3 hours (Method 2) shows the complete formation of the urethane chain. It is proven by the existence of NH peak at 3500 cm⁻¹ and the disappearance of NCO peak at the range of 2200-2500 cm⁻¹ indicating the NCO functional group has completely reacted with OH group in AEPO. The addition of fluorination also can be proved by the existence of CF stretching at 1012 cm⁻¹. This study provides information regarding comparison between the synthesis method of FPOPU.

Introduction

Synthetic and bio-based polyurethane (PU) are two categories of polyurethane that can be differentiated. Synthetic polyurethane is traditionally produced by the reaction of polymeric diols or amines with multifunctional isocyanates to form urethane or urea linkage [1]. It is also possible that other pertinent catalysts and additives are incorporated into the production of PU. PU can be formed into any shape with various properties of different hardness and densities such as rigid film layer or spongy foam-like structure depending on the quantity and types of polyols, isocyanates (i.e aromatic, aliphatic, cycloaliphatic, and polycyclic), and additives used [2]. Based on previous research, aromatic diisocyanates create more rigid PUs than aliphatic diisocyanates [3], [4]. Short chain polyols also produce more rigid crosslinked products [4]. However, long chain polyols will produce soft elastomeric polyurethane. In general, polyols with two or more hydroxyl groups are frequently used in the production of PU.

Recently, bio-based polyurethane has attracted the attention of researchers due to the abundance of potential raw material supplies [5]. Additionally, bio-based polyurethane may reduce the reliance on petroleum resources. To produce bio-based polyurethane, a variety of vegetable oils, including soybean, castor, and jatropha oil, are employed as raw materials. When combined with isocyanates in a poly addition reaction, these vegetable oils can be employed to create a single urethane chain [6]. Malaysian Palm Oil Council reported that Malaysia has exported 18.47 million metric tonnes of palm oil compared to Indonesia which 29.52 million metric tonnes in 2019, making Malaysia the second-largest producer of palm oil worldwide [7]. The huge availability has brought researchers' attention in further developing the product from palm oil. Based on current research findings, the long palm

oil fatty acid can be functionalized by epoxidation and acrylation process to provide polyol acrylate structure; which offers great potential as the foundation of polyurethane synthesis [8]. There have been several studies conducted on synthesized of bio-based polyurethane from functionalized palm oil with the addition of other functionalized monomers with ultraviolet (UV) radiation curing [9], [10].

Photo-radical polymerization (UV curing) is a great substitute for conventional heat-radical polymerization (heat curing) [10]. This is because UV curing method uses lower energy and solventless as compared to the traditional heat curing method. In addition, UV curing may avoid slow curing rates and volatile organic compound (VOC) issues due to solvent addition, making it an environmentally benign procedure [11]. The important substances of UV curing method are oligomers, photoinitiators, and monomers. These substances are used as reactive diluents to change the viscosity of the curing solutions and impart specific properties to the cured films, such as increased chemical resistance, hardness, flexibility, durability, and substrate adhesion.

The synthesis of POPU oligomer has been well established nowadays, in which AEPO as starting material was added with isocyanate first followed by the addition of acrylate monomers such as HEA. The POPU oligomer was further added with various types of monomers and photoinitiator to form a functionalized palm oil based polyurethane [8]. Various studies were also conducted on the effect of different type of isocyanate (ie HMDI and TDI) on the properties of palm oil based polyurethane [12]. However, the study on different synthesis methods of POPU oligomer and functionalized POPU polymers are not well discussed. The different synthesis method of an oligomer can lead to different polymer structure configuration which significantly affects the properties of the resulting polymers. Thus, this article aims to present the differences in method synthesis of fluoroacrylate palm oil polyurethane (FPOPU) polymer in a comprehensive spectroscopic investigation.

Methodology

Materials. Epoxidized palm oil (EPO) was used as the main material in this study obtained from PolyGreen Sdn. Bhd. Anhydrous acrylic acid (99%), triethylamine (TEA) (99%), hydroquinone in solid crystal form (99%), isophorone diisocyanate (IPDI) (98%), 2- hydroxyethyl acrylate (HEA) (96%), and dibutyltin dilaurate (DBTL) (95%). trimethylolpropane triacrylate (TMPTA) (99%), 1,6-hexanediol diacrylate (HDDA) (80%), benzophenone (99%), and heptafluorodecylmethylacrylate (HFDMA) (97%) were bought from Sigma Aldrich Chemical Co. Inc, USA. All the chemicals were used without further purification.

Synthesis of Acrylated Epoxidised Palm Oil (AEPO). Firstly, a three-neck round bottom flask equipped with a condenser, dropping funnel, and thermometer was prepared. Epoxidized palm oil was added to the flask and mixed with 1% of hydroquinone and 1% TEA. Then, an acrylic acid at 1:4 ratio to EPO was added dropwise. The mixture was stirred for about 15 hours at a constant temperature of 110°C. Then, the mixture was quenched with petroleum ether overnight and further washed with distilled water. The mixture was dried using a rotary evaporator at 90°C until constant weight was obtained.

Synthesis of Palm oil Based Polyurethane (POPU). Method 1. IPDI and HEA were added into the flask with mole ratio of 1:1 (NCO: OH). Then, AEPO with the same mole ratio as IPDI was added. 0.5wt% hydroquinone, and 1wt% of DBTL were added to the mixture. No heat was applied, and the mixture was stirred for 15 minutes.

Method 2. IPDI and HEA were added into the flask with mole ratio of 1:1 (NCO: OH). 0.5wt% hydroquinone and 1wt% of DBTL were added to the flask. The mixture was stirred for 15 minutes at 60°C. Then, AEPO was added with mole ratio of 1:1 (NCO: OH). The mixture was stirred for 3 hours, and the temperature was constant for 60°C.

Method 3. AEPO and IPDI, were added into the flask with mole ratio of 1:1 (NCO: OH). 0.5wt% hydroquinone and 1wt% of DBTL were added. The mixture was stirred for 3 hours at 60°C. Lastly, 1 mol of HEA was added and stirred for another 1 hour to terminate the reaction.

Synthesis of Fluoroacrylate-Palm Oil Polyurethane (FPOPU). 60wt% POPU was added into the flask. 30wt% TMPTA, 10wt% HDDA, and 2phr HDFDMA monomer were added. Then, 4% benzophenone was added, and the mixture was stirred until miscible. The sample was cast onto 10 cm × 2 cm × 1 mm silicon mould and cured under UV light by using TX-UV200 for 2 min. The thickness of the film was constant at 1 mm.

Characterization

Observation. The observation was done by eye monitoring the sample condition such as changes in colour and viscosity during and at the end of sample synthesis. A picture of the POPU sample for each method was also taken at the end of the reaction process.




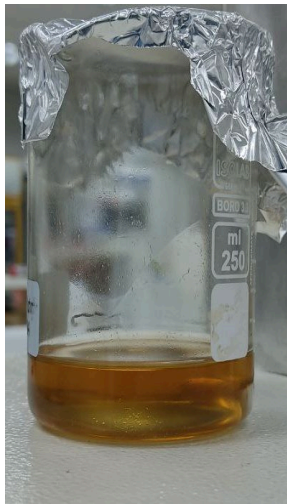
Fourier-Transform Infrared (FTIR) Analysis. The attenuated total reflection (ATR) mode of the FTIR spectrometer was used to produce infrared spectra. The model of the instrument is PERKIN ELMER, Spectrum 100. The sample did not require further preparation and was directly analysed. The sample was put into an ATR cell. Each sample was scanned ranging from 700 cm⁻¹ to 4000 cm⁻¹. FTIR was used to confirm the functional group present in the sample.

Results and Discussion

Observation. Table 1 shows the physical appearance of FPOPU sample with different synthesis methods. From the result, it was found that Method 1 forms a thick liquid viscosity and a clear yellowish sample. While Method 2 forms thick liquid viscosity and a clear brownish liquid appearance. In contra, Method 3 forms a less viscous and clear brownish liquid sample. From these observations, it was found that Method 1 has the lightest color among the three methods. This phenomenon could be due to the low mixing time and no heat applied during the synthesis. Thus, the color is inherent to the pure AEPO color. Method 2 and 3 appear to be darker as the reaction undergoes a longer period with a continuous heating process. The heat energy supplied during the reaction initiated to better reaction and complete formation of urethane linkage which could be assumed to be the darker observation of the final sample. Besides the color, the viscosity of Method 3 is lower than Method 2 due to the length of the urethane polymer chain formation. A longer chain of polymer tends to have thicker consistency [13].

Fourier-Transform Infrared (FTIR) Analysis. Fig. 1 shows the FTIR spectra of FPOPU with different POPU synthesis methods. Based on Figure 1, uncured sample of Method 1 shows clearly strong band of CH₃ and CH₂ stretching at 2930 cm⁻¹ and 2870 cm⁻¹ respectively. In addition, the C=O (carboxylic group), NH, and C=C group at 1727 cm⁻¹, 3546 cm⁻¹ and 1645 cm⁻¹ also present, respectively. After curing, it can be seen the obvious change to the spectrum as C=C group at 1642.32 cm⁻¹ peak is absence indicating the incomplete consumption of acrylate functional group with isocyanate during curing process [14]. It can also observe the appearance of small NH group peaks at 3546 cm⁻¹ suggesting that AEPO has reacted with isocyanates and shows that urethane linkage has formed [15]. C-F peak also present at 1011 cm⁻¹ that showed linkage between HDFDMA [16]. However, the existence of free isocyanate group at 2341 cm⁻¹ suggested that the reaction was incomplete [14]. Method 1 was designed based on prepolymer method [17]. The sequence of chemicals addition was based on reaction of short chain monomers before reaction with bulk AEPO. Advantages on this method is it requires no heating which is beneficial for large scale production.

Table 1. Appearance, viscosity, and colour for methods 1,2,3 and AEPO

Method	AEPO	1	2	3
POPU Image				
viscosity	Less viscous liquid	Thick liquid	Thick liquid	Less viscous liquid
colour	Clear yellowish	Clear yellowish	Clear brownish liquid	Clear brownish liquid

Method 2 was conducted by applying heat and longer mixing time during synthesis process as compared to Method 1. Based on Figure 1, the FTIR spectrum of uncured Method 2 sample shows broad N-H peak at 3558cm^{-1} , C=C peak also at 1645cm^{-1} , and CF stretching at 1024cm^{-1} . Besides, it can also confirm there is no NCO functional group peak present at the 2200 to 2300cm^{-1} indicating complete urethane linkage formation [18]. After curing, the C=C peak at 1654cm^{-1} was disappeared from the spectrum. The existence of CF stretching at 1025cm^{-1} indicating the successful addition of HDFDMA [19]. Absence of NCO peaks suggested that AEPO has reacted completely with IPDI, and isocyanate group are fully occupied. The disappearance of C=C peak indicates that the acrylate group have completely reacted each other. The reaction can be referred in Fig. 2.

In Method 3, AEPO was reacted with IPDI first and then terminated with addition of HEA. The time of reaction are 4 hours with presence of heat. Based on Figure 1, Before curing, weak N-H peak at 3542cm^{-1} , C=C peak at 1656cm^{-1} were present. In addition, it can be confirmed that no free isocyanates group existed at the range of 2200 to 2300cm^{-1} [20]. After curing, the C=C functional group at 1630cm^{-1} was disappeared from the spectrum [21]. The disappearance of this peak shows the complete consumption of C=C crosslink with other monomers. In addition, the CF stretching can be observed at 1024cm^{-1} that shows the successful of HDFDMA addition [16]. The weaker N-H peak at 3542cm^{-1} was observed as compared to Method 2 due to the lower reaction of AEPO with IPDI due to complex structure of AEPO. Instead, IPDI tends to react with HEA to form prepolymer rather than direct reaction with AEPO [22]. The complex structure of AEPO hindered the OH reactivity making it difficult to bond with isocyanates and form urethane structure.

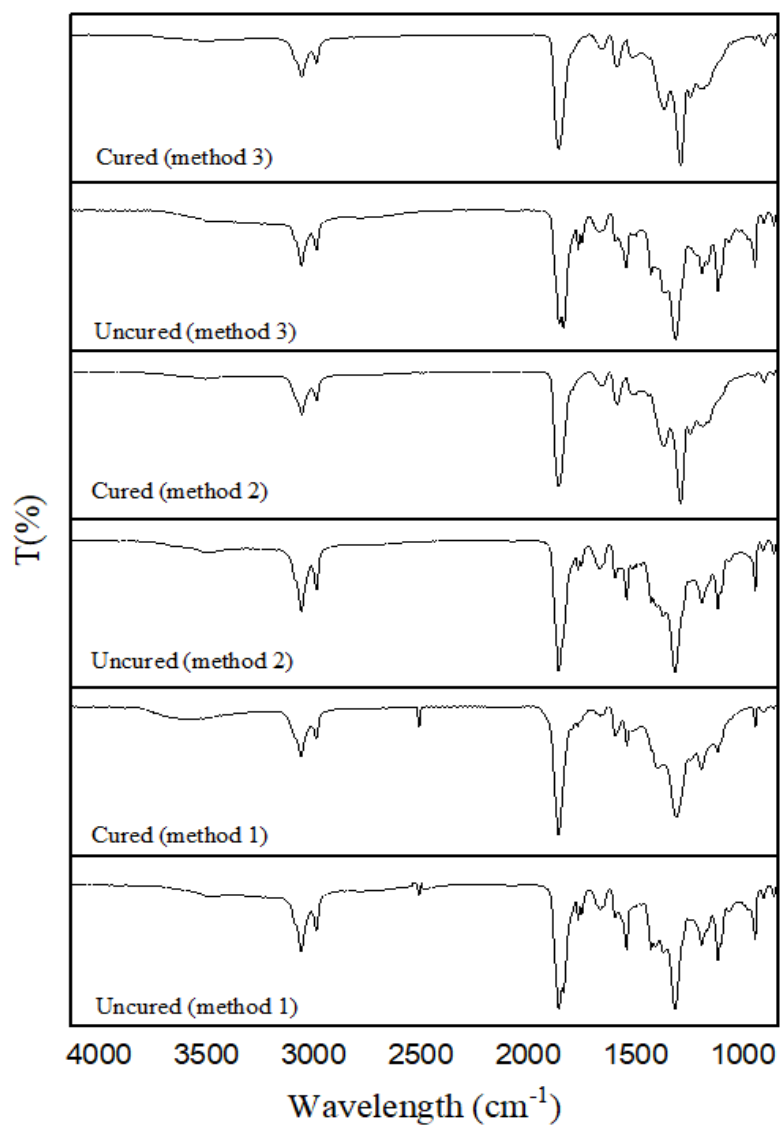


Fig.1. FTIR spectrum for method 1,2, and 3 before and after curing.

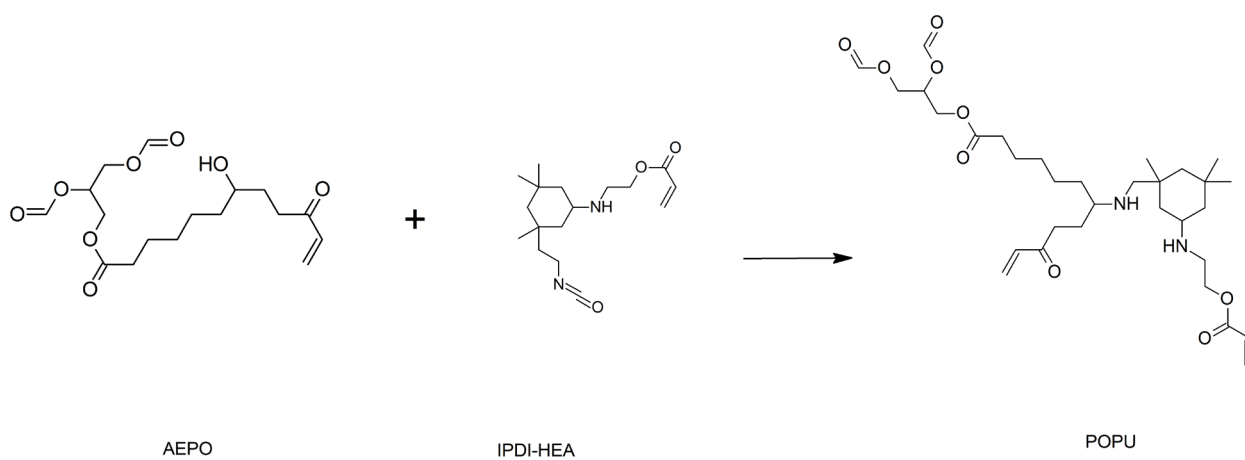


Fig. 2. Complete urethane linkage formation

Conclusion

In conclusion, POPU was successfully modified by addition of HDFDMA as monomer. C-F stretching can be seen throughout all 3 methods. POPU was successfully prepared by using 3 different methods. From observation, method 2 which are reaction of IPDI with HEA first followed by addition of AEPO at 60°C temperature reaction is the suitable method of laboratory synthesis as FTIR spectrum for method 2 shows all functional group needed for urethane linkage to form. Further study on structure elucidation is needed for further analysis.

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