

Identification of Urethane Linkage, Soft Segment Polyol and Hard Segment Polyurea in Polyuretan from Palm Oil Based Polyol

¹La Ifa, ¹Nurdjannah, ¹Andi Aladin, ¹Zakir Sabara and ²Kamaruzaman Jusoff

¹Department of Chemical Engineering, Faculty of Industrial Technology,
Jalan Urip Sumoharjo Km 05 Makassar, Universitas Muslim Indonesia, South Sulawesi, Indonesia

²Department of Forest Production, Faculty of Forestry, Universiti Putra Malaysia,
43400 UPM Serdang, Selangor Darul Ehsan, Malaysia

Submitted: Sep 24, 2013; **Accepted:** Nov 26, 2013; **Published:** Dec 20, 2013

Abstract: The objective of this paper is to identify the existence of urethane linkage, soft segment polyol and hard segment polyurea in polyurethane from palm oil-based polyol. The method used to produce this polyurethane is the one-shoot method. In this method, palm oil-based polyol and additives such as water, surfactant, catalyst and methylene chloride was mixed in a reactor, then toluene diisocyanate (TDI) was poured into the reactor and stirred. Polyurethane produced was then poured into a cast and cured. The structure of polyuretan yielded was analysed by using Differential Scanning Calorimeter to investigate soft segment and hard segment polyurea. Fourier Transform Infra Red (FTIR) Spectroscopy was used to identify the existence of urethane linkage. Results indicated that the type of polyurethane yielded is flexible polyurethane foam with glass transition temperature of 23.9°C for soft segment and 65°C for hard segment polyurea, respectively. Therefore, it is possible to develop polyurethane from palm oil based polyol. Future research should focus on its commercial applications for industrial use and benefits.

Key words: Palm oil • Polyol • Flexible polyurethane foam • Soft segment polyol • Hard segment • Polyurea

INTRODUCTION

Flexible polyurethane (PU) foam is one of the major products from urethane. It is basically produced by polyol, isocyanate, water, catalyst and surfactant. Among all, polyol and isocyanate are mixed to form PU linkage. Other component such as water is added as a blowing agent to form the foam. Catalyst and surfactant act as its development stage. PU is polymer which consists of repetitions of urethane linkage [1]. PU can be produced from a reaction between isocyanate and hydroxyl group molecule such as polyol [2]. Flexible PU foams are widely used in many industrial applications, such as upholstered furniture and mattresses, automotive applications, etc. The chemical nature of the PU, the high air permeability and the high inner surface area of the foam structure cause this material to be highly flammable [3]. Polyol has been commercially used in the production of PU is derived from fuel oil namely ethylene oxide and propylene oxide.

Due to a limited source of fuel oil, it is important to look for a renewable source such as palm oil. Indonesia is one of the biggest producers of palm oil in the world. Palm oil contains molecules with double bonds, e.g. oleic acid, linoleic acid, which can be transformed to epoxy group through epoxidation and then the epoxy undergoes hydroxylation to form hydroxyl [4-7]. The majority of feedstock for PU is still based on crude oil, but in recent years alternatives based from renewable resources have been developed, like polyols based on vegetable oils [8]. Vegetable oils, such as soybean oil, palm oil, contain a mixture of fatty acids [9].

PU is a very important polymer and has a surprising array of commercial applications. In recent years, PU foams remain the largest demand sector, accounting for two-thirds of the total PU demand. In addition, this demand for PU foams especially in construction and transportation continues to strengthen across the globe.

The main raw materials of PU foams are polyol and isocyanate, both are derived from petroleum. However, in recent years, high energy and feedstock costs have undercut margins, forcing producers to raise price significantly for polyol and isocyanate. Also, the polyol supply is tight as demand increases greatly globally, especially in emerging regions such as China, the Middle East and Africa. Increasing costs of petrochemical feedstock and public desire for environmentally friendly green products motivate many researchers to explore sustainable and renewable biobased polyols to replace petrochemical polyols [10].

Basically, PU foams can be classified into two distinct groups, rigid and flexible, depending on their mechanical properties and cross-linking densities. Flexible PU foams are widely used in many diverse applications such as bedding, furniture and in the automotive industry. This is caused by their unparallel performance characteristics, *i.e.*, vibration damping, sound insulation, energy and shock absorption, shape conformance, consumer comfort and protection from impact. These characteristics result from a specific open cell structure of flexible foams, which is built of struts and plateau borders. Properties of PU networks are the result of cross-linking densities related to the number of hydroxyl groups in polyols, their distribution in oils and the position in fatty acids chains. The usage of vegetable oil-based polyols with different functionalities determines the PU chemical structure [1].

Natural oils consist mainly of triglycerides of saturated and unsaturated fatty acids. They also contain small amounts of mono- and diglycerols, free fatty acids, sterols and tocopherols. The hydroxyl functional derivatives of vegetable oils can be used as green raw materials for the production of PU for various applications. The polyols on the basis of natural oils can be obtained by introduction of hydroxyl groups at the position of double bonds by different ways: hydroformylation or ozonolysis and subsequent hydrogenation, epoxidation followed by oxirane opening, halogen addition and nucleophilic substitution, as well as microbial conversion. Vegetable oil-based polyols derived from oil seeds, such as sunflower, castor oil, soybean, palm oil, canola and rapeseed, were applied in PU flexible foams synthesis. These modifications had limited success, instead partial incorporation of vegetable oil-based polyols is much more successful [9, 11].

Polyols based on natural oils can be used in formulations of various PU materials including foams with the cell structure and properties required for their typical applications. Vegetable oils such as rapeseed and palm

oils were used as raw materials for preparing flexible PU foams. The reference PU systems were elaborated on the basis of petrochemical polyols. These formulations were modified with rapeseed and palm oil based polyols. The application of both vegetable oil based polyols allowed to obtain the foams with higher ability for energy absorbing and better thermal stability [12]. The properties of these foams can be modulated by industrial producer, by the individuation of the most efficient chain extenders, thus introducing flexible chains in the macromolecular structure that can reduce the glass transition temperature of the materials and generate foams with higher flexibility. The quality of the foams are compatible with several applications especially in packaging of furniture and for the interior part of car seats [13].

PU foam is a block co-polymer with the formation of $(HS_m)_n$. H is a hard segment polyurea and S_m is soft segment polyol with the degree of polymerisation of m, while n is the degree of polymerisation of block copolymer. Both segments are connected through urethane group [14]. The objective of this paper is therefore to identify the existence of urethane linkage in PU from palm oil based polyol so that the optimum conditions to produce PU can be well understood.

MATERIALS AND METHODS

The main raw materials used in this research were toluene diisocyanate and palm oil based polyol. Toluene diisocyanate (TDI) was purchased from Baye. Other materials used were polypropylene glycol (PPG), ethylene diamine, triethylene diamine, stannous octoate, silicone glycol, methylene chloride, sulphuric acid, sulphuric acid glacial, methanol, isopropanol, hydrogen peroxide, sodium sulfate and distilled water.

PU foams were prepared using a palm oil-based. In the first stage, the polyol was made by adding a peroxyacetic acid formed in situ from H_2O_2 and CH_3COOH with H_2SO_4 as catalyst to palm oil to form epoxidized palm oil. The epoxidized palm oil was added to a mixture of methanol, isopropanol and catalytic amount of H_2SO_4 within two hours at $60^\circ C$ to form palm oil-based polyol [15]. In the second stage, PU foams were prepared from mixtures of the polyol and PPG and an isocyanate compound. This study may lead to a development of a new type of PU foams using palm oil as a raw material. The reaction was performed in a 500 mL pyrex-three neck flask-batch reactor equipped with a stirrer, thermometer, reflux condenser and water bath. The production of PU was studied by varying the volume ratio of palm oil based polyol to PPG with 50: 50:75: 25: 80:20 and 100: 0 [15] using the one-shoot method [13].

The reaction was started by mixing 100 ml of polyol, 1 ml of water, 1 ml of silicone glycol as surfactant, 0.3 ml stannous octoate as metal catalyst, 0.2 ml tri ethylene diamin as the base catalyst and 4.5 ml mehtilene cloryde as the blowing agent. Water was used as blowing agent in order to increase the green nature of the reinforced foams [16]. The mixture was stirred and TDI was finally added and stirred continuously until when there was a sign of rising in the mixture which was immediately poured in the mould. The foam was allowed to solidify for about 1 minute in the mould before being removed. The foam was allowed to stay for 20-24 hours for its total curing after it had been removed from the mould before testing [17]. The PU formed was a broken white color flexible foam.

RESULTS AND DISCUSSION

It was found that PU produced from the polyol to PPG was shrunk, brittle and fragile with a ratio of 80: 20 and 100: 0. By adding 25 ml and 30 ml TDI to the mixture, the PU collapsed, brittle and shrunk due to weak bond linkages. By adding 33 ml TDI to the mixture, it was found that flexible PU produced was with a ratio of 50: 50 and 75: 25 polyol to PPG. The best PU in this study was produced at the ratio of 50:50 and 33 ml TDI polyol to PPG. This PU was analysed using Fourier Transform Infrared Spectroscopy (FTIR) to identify the molecular and hydrogen bonds on flexible PU foams. Quantitative knowledge of the polymer structure and dynamics by these methods provides a significant insight on understanding the microphase separation and the domain structure of urethane and urea hard segments and

polyether soft segments in foam. Glass transition (T_g) temperature of the PU was analysed using Differential Scanning Calorimeter (DSC). Characterization of the foams was carried out by thermal and mechanical analyses [15].

Both the polyol-isocyanate and water-isocyanate reactions were exothermic. During the foaming process, CO_2 was generated from the reaction of water and isocyanate. Due to the release of heat from the exothermic reactions, the carbon dioxide bubbles grew and expanded the polymerizing polymer to form a foam volume. In the control foam, rapid mixing of the polyol mixture and isocyanate brought many microbubbles of air into the liquid system, which served as the medium for bubble growth [10].

Fourier Transform Infra Red (FTIR) Spectra: An FTIR analysis was used to identify urethane, carbonyl group and hydrogen bond from FTIR spectra [18]. FTIR can also be used to quantitatively analyse soft segment and hard segment in PU foam. Figure 1 shows FTIR spectra of PU 50:50 at 33 ml TDI. It can be seen that the isocyanate group (NCO) was identified at a wave length of 2253.66 cm^{-1} . Figure 1.b₁ and 1.b₂ showed FTIR microscopic spectrum compilation of flexible PU. Interatomic bonds were identified in several wave lengths. Figure 1.b₂ shows that the interatomic bonds can be seen at 3454.53 cm^{-1} (N-H stretch), this indicates soft segment polyol in the structure of polyuretan; 2921.88 cm^{-1} (C-H stretch) in $-\text{CH}_3-$; 2853.29 cm^{-1} ; 2361.31 cm^{-1} ; 1641 cm^{-1} (C=O stretch), 1408.84 cm^{-1} and 1098.30 cm^{-1} (C-O stretch) indicate that urethane linkage is existed. The reaction between TDI and polyol will be ended if NCO (2270 cm^{-1}) could not be found, while N-H and C=O appear in FTIR spectra [15].

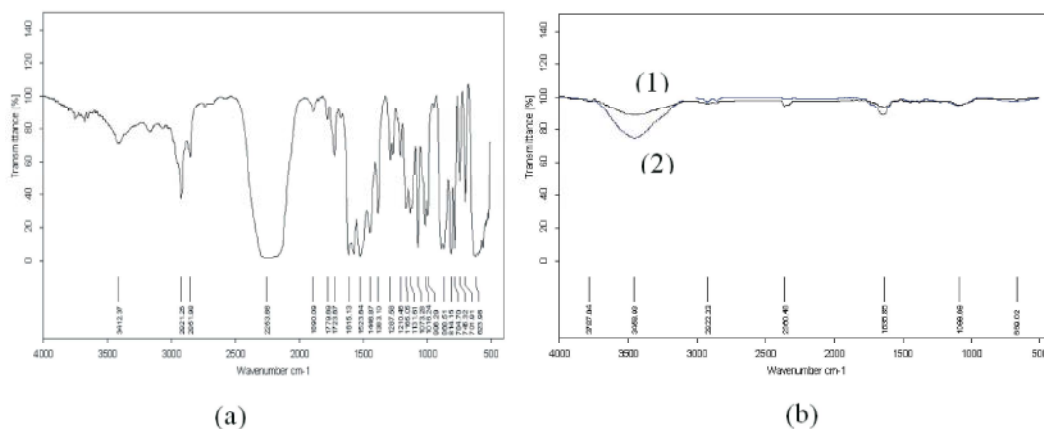


Fig. 1: (a) Spectrum FTIR PU (b) Combination of FTIR (1) polyuretan FTIR spectra from polyol and PPG [19]. (b2) PU FTIR spectra from palm oil based polyol.

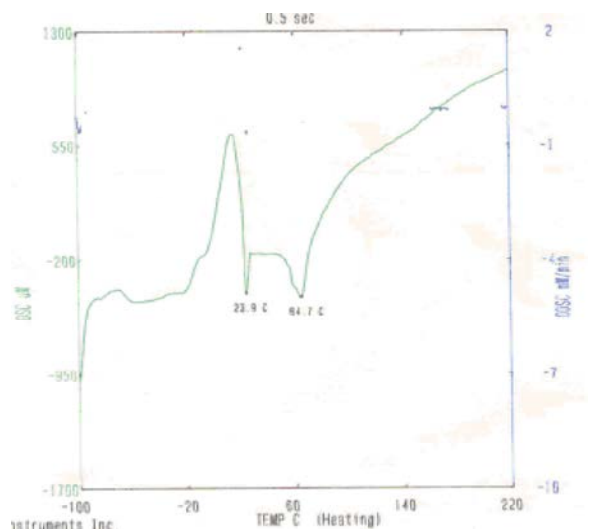


Fig. 2: DSC of PU Foam

From Figure 1 it can be seen that there is urethane linkage and soft segment polyol in the PU derived from palm oil based polyol and PPG. It is also found that the PU was already formed. This is indicated by the inexistence of isocyanate NCO (2270 cm^{-1}) in the spectra.

Glass Transition Temperature (T_g) Analysis: T_g was analysed using DSC on the PU yielded from palm oil based polyol and PPG at the weight ratio of 50:50. The result of the analysis is shown in Figure 2.

It can be seen from Figure 2 that there are two (2) glass transition temperatures. The first T_g is $23.9\text{ }^{\circ}\text{C}$ for soft segment and $65\text{ }^{\circ}\text{C}$ for hard segment. The presence of the PU structures glass transition is noticed on the DSC curves around 65°C , which reveals the predominant crystalline nature of the polymer [20]. The results are in accordance with the theory which says that block copolymer in flexible PU foam is a cross-link microstructure consisted of a non polar soft segment with low glass transition temperature and a polar hard segment with high glass transition temperature. The hard segment has a crystal melting point higher than a room temperature.

CONCLUSION

The wave length of 3454.53 cm^{-1} (N-H stretch) obtained from the FTIR spectra of polyurethane from palm oil based polyol – PPG indicated that there was a soft segment polyol in the PU structure. The wave lengths of 2921.88 cm^{-1} (C-H stretch) in $-\text{CH}_3-$; 2853.29 cm^{-1} ;

2361.31 cm^{-1} ; 1641 cm^{-1} (C=O stretch), 1408.84 cm^{-1} and 1098.30 cm^{-1} (C-O stretch) indicated that there was an urethane bond linkage. The end of the reaction between toluene diisocyanat and polyol was marked by the disappearance of NCO (2270 cm^{-1}) and the appearance of N-H and C=O in the FTIR spectra. There were two glass temperatures, i.e. $23.9\text{ }^{\circ}\text{C}$ for soft segment and $65\text{ }^{\circ}\text{C}$ for hard segment.

REFERENCES

1. Shan, C.W., M.I. Idris and M.I. Ghazali, 2012. Study of Flexible Polyurethane Foams Reinforced with Coir Fibres and Tyre Particles. *International Journal of Applied Physics and Mathematics*. 2: 123-130.
2. Salmiah, 2002. Palm-Based Polyols and Polyurethanes, Artikel: MPOB Technology, 24: 1-29.
3. Konig, A., U. Fehrenbacher, T. Hirth and A. Kroke, 2008. Flexible Polyurethane Foam with the Flame-retardant Melamine. *Journal of Cellular Plastics* 44: 469-480.
4. Chasar, Dwight W. and J. Hughes, Michael, 2003. Method of Making Oleo Chemical Oil-Based Polyols. US Patent No: 20030088054.
5. Petrovic, Zoran, Guo andrew and Javni, Ivan, 2003. Process for the preparation of vegetable oil-based polyols and electro insulating casting compounds created from vegetable oil-based polyols. US Patent No 6.573.354.
6. Ramirez-de-Arellano-Aburto, Cohen-Barki, Cruz-Gomez. 2003. Process for the Production of Oleo Chemical Polyols. US Patent No: 6,548,609.
7. Tran, P., D. Graiver and R. Narayan, 2005. Ozone Mediated Polyol Synthesis from Soybean Oil. *JAACS*. 82: 653-659.
8. Avar, G., U. Meier-Westhues, H. Casselmann and D. Achten, 2012. Polyurethanes. *Polymer Science: A Comprehensive Reference*, 10: 411-441.
9. Zhang, L., Hyun K. Jeon, Jeff Malsam, Ron Herrington and Christopher W. Macosko, 2007. Substituting soybean oil-based polyol into polyurethane flexible foams. *Journal Polymer*, 48: 6656–6667.
10. Fan, H., A. Tekeci, J. Galen, Suppes and F. Hsieh, 2012. Properties of Biobased Rigid Polyurethane Foams Reinforced with Fillers: Microspheres and Nanoclay. *International Journal of Polymer Science*, Article ID 474803, doi:10.1155/2012/474803

11. Uldis, S., B. Lazdiņa, D. Vilsone, M.J. Lopez, M.G. Garcia, F.S. Francisca and J. Moreno, 2012. Structure and properties of the polyurethane and polyurethane foam synthesized from castor oil polyols. *Journal of Cellular Plastics*, 48: 476-488.
12. Aleksander, P., P. Rojek and H. Pawlik, 2012. Flexible polyurethane foams modified with natural oil based polyol. *Journal of Cellular Plastics*, 48: 489-499.
13. Patrizia, C., I. Anguillesi and A. Lazzeri, 2013. Green synthesis of flexible polyurethane foams from liquefied lignin. *European Polymer Journal* (In Press, Corrected Proof). Accessed online 13th April 2013.
14. Maznee, T.N., Z.K.S. Norin, T.L. Ooi, A. Salmiah and L.H. Gan, 2011. Effects of Additives on Palm-Base Polyurethane Foams. *Journal of Oil Palm Research*, 13: 7-15.
15. La Ifa, Sumarno, Susianto, Mahfud. Pembuatan Flexible Polyurethane Foam dari Polyol Berbasis Minyak Sawit. *Journal Industri*. 7:1-8. (In Indonesian).
16. Silva, V.R., A. Mirna Mosiewicki, Maria Irene Yoshida, Mercês Coelho da Silva, Pablo M. Stefani and E. Norma, 2013. Marcovich. Polyurethane foams based on modified tung oil and reinforced with rice husk ash I: Synthesis and physical chemical characterization. *Polymer Testing*, 32: 438-445.
17. Onuegbu, T.U., E.T. Umoh and I.E. 3 Iwuchukwu, 2012. Flame Retardant Effects on Flexible Polyurethane Foam Treated with Potassium Aluminum Sulphate. *Journal of Science and Technology*, 2: 1097-1101.
18. Oka, H., Y. Tokunaga, T. Masuda and H. Yoshimura, 2006. Characterization of Local Structures in Flexible Polyurethane Foams by Solid-state NMR and FTIR Spectroscopy. *Journal of Cellular Plastics*, 42: 307-323.
19. Sumarno, Hendrawati, N. and E.A. Nenorum, 2007. Aplikasi Teknik Prasaturasi pada Pembuatan Flexible Polyurethane Foam, *Jurnal Polymer Indonesian*, 10: 47-53. (In Indonesian).
20. Alina, H., C.M. Soica, S. Ardelean, R. Ambrus, D. Muntean, A. Galuscan, Dragos, D. Ionescu and F. Borcan, 2013. Influence of emulsifiers on the characteristics of polyurethane structures used as drug carrier. *Chemistry Central Journal*, 7: 66 doi: 10.1186/1752-153X-7-66.