

# Development of Rigid Biocomposite Polyurethane Foam for Load Bearing Application

Mohd Haziq Dzulkipli<sup>a\*</sup>, Mohd Yazid Yahya<sup>a</sup>, Farhana Shakira Md Akhir<sup>b</sup>, Rohah Abd Majid<sup>b</sup>

<sup>a</sup>Centre for Composites (CfC), Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia

<sup>b</sup>Faculty of Chemical Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia

\*Corresponding author: mohadz90@yahoo.com

## Article history

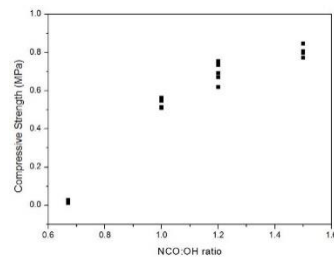
Received :1 January 2014

Received in revised form :

15 February 2014

Accepted :18 March 2014

## Graphical abstract



## Abstract

Polyurethane (PU) foams are widely used today in automotive and as insulation system. Due to environmental issues, efforts have been made to replace petrochemical polyol with natural-based polyol in PU foam production, without sacrificing any properties. This study aims as to produce palm oil-based polyurethane composite foam for load bearing purposes. Palm oil-based polyol (POP) was reacted with polymeric 4,4-diphenylmethane diisocyanate (*p*-MDI) with water as blowing agent and silicone surfactant to produce rigid PU foams. The foams obtained were varied by NCO:OH ratios and water content and characterized for their morphology and compressive strength. Scanning electron micrographs (SEM) indicated the cells within the obtained foams are closed cells. Compressive strength of obtained foams shows considerable improvement but only up to NCO:OH ratio of 1:1.35.

**Keywords:** Rigid polyurethane foams; palm oil polyol; mechanical properties; thermal properties

© 2014 Penerbit UTM Press. All rights reserved.

## 1.0 INTRODUCTION

Usage of polymeric foams in industries is nothing new. Polymers like polyurethanes (PU), polyvinyl chlorides (PVC), and polyimide are widely utilized as insulation, acoustic damper, bedding, coating, furniture, and even to the extent of aircraft and automotive parts [1-4]. Among other polymeric foams, PU foams account for the largest global market of 53%, with 23% of total production are rigid PU foams [5]. Like any other polymeric foams, PU rely on petrochemical feedstock. Due to environmental and sustainability issues, as well as depleting petroleum supply all over the world, efforts have been made in recent years to develop a bio-based PU foam by using vegetable oils such as castor oil, soybean oil, canola oil, rapeseed oil, and palm oils [1-10]. Except for castor oil, these vegetables can be transformed into polyols via transesterification; and among all these natural oils, palm oil polyol have attracted interest for study, due to its economic price range and abundance in Malaysia.

To date, quite a number of researches were reported utilizing palm oil-based polyol in the production of PU foam. [1, 2, 4, 6, 7, 9]. Prociak *et al.* for instance modified the formulation of flexible PU foams by partly replacing petroleum-based polyol with that of palm-oil; and comparing the obtained result with PU foam of rapeseed oil-based polyol [2]. It is found out that both modified PU

foams exhibit better compressive strength, impact absorbance ability, and thermal stability; with palm oil-based PU foam illustrating better characteristics than rapeseed oil-based PU foam. Chian and Gan developed rigid PU foam from chemically derivatized refined-bleached-deodorized (RBD) palm oil polyol [4]. Their findings indicated that palm oil-based polyol is a suitable alternative in synthesizing polyurethane as obtained foam characteristics such as compressive strength exhibit high values especially at high density of foams. Badri *et al.* synthesized refined, bleached, and deodorized palm kernel oil (RBD PKO) for insulation purposes; and compared the result with addition of empty fruit bunch (EFB) fiber [9]. Findings indicate that foam produced from said polyol shows good mechanical properties as compared to its conventional counterpart.

Many studies have been conducted on the application of polymeric foam cores; yet very few work noticed to be done specifically to study the application of bio-based polymeric foams [11-14]. Rejab for example proposed the use of polyurethane foam as sandwich core for side-door impact beam of a car [11]. In the study, it is found out that integrating polymeric foam core into the hollow tube of the side-door impact beam increases the impact and energy absorption properties of the beam itself as compared to that of without the foam. Shen *et al.* investigated the effect of polyurethane foam density and thickness on the sandwich panel

behavior, which is intended to be utilized as building structure or cladding for use in high wind areas [12]. Results indicate that the proposed structure can be used as lightweight cladding system used in high wind areas. However, these applied polymeric foams are of petroleum-based; and as illustrated in earlier parts, many efforts are given to replace these petrochemical-based foams with a bio-renewable polymeric foams. With these illustrated applications and many more, it is rather essential to investigate whether bio-based polymeric foams can be incorporated into these systems as alternative for the conventional foams; with no mechanical property deterioration.

This paper presents the preliminary work on the development of green composite PU foam for load bearing applications like in automotive and aeronautical industry. Foams of different NCO:OH ratios and water content are fabricated in closed mold, and characterized for their morphology and compression strength. The nature-based PU foams obtained are compared to that of petroleum-based PU foams to observe whether exchanging the components in PU production deteriorates any properties of the foam.

## 2.0 EXPERIMENTAL

### 2.1 Materials

The raw materials used in this study include palm oil-based polyols, polymeric diphenylmethane-4,4'-diisocyanate (*p*-MDI), silicone surfactant Tegostab B-8404, and distilled water.

### 2.2 Preparation of foam

The formation of PU foam in this study resulted from the exothermic reaction between Solutions A (mixture of palm oil-based polyol, silicone surfactant, and distilled water) and B (*p*-MDI). The polyol was first weighed according to desired formulation as illustrated in Table 1 together with silicone surfactant and distilled water prior to being stirred for 2 minutes with magnetic stirrer at 1500 rpm for homogeneity; forming Solution A. After being weighed also, *p*-MDI was reacted with Solution A and stirred at 1500 rpm for 45 seconds before transferred into mold (100 x 200 x 30 mm) for self-rising. The foam is conditioned at room temperature for at least 24 hours before demolded, and undergoes another 24 hours of room conditioning before cut into specimens and testing is carried out.

### 2.3 Foam Density

Foam sample density was determined using the standard ASTM D1622. Samples were cut into cubes of size 30 mm<sup>3</sup> using bench saw prior to being weighed using digital balance. Dimensions of the samples were measured using digital vernier caliper. Average of at least five samples was taken into consideration.

### 2.4 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopic measurements of the PU foams were carried out using a Fourier-transform infrared (FTIR) spectroscopy analyzer Perkin-Elmer Frontier. Sample foams were scrapped into powder form and pressed against ATR crystal for total contact with force gauge maintained at value of 80. Infrared spectroscopy was carried out within the range of 4000-650 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup> with a total of 16 scans were taken.

### 2.5 Scanning Electron Micrography (SEM)

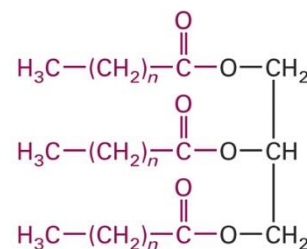
Morphology of the cell structure was observed using Scanning Electron Microscope (SEM) Phillips ZL 40. Specimens were prepared by sputter coating with thin film of platinum and opening voltage of 10 kV. Computerized image analyzer Zeiss KS300 Imaging System software is used to analyze the obtained result.

### 2.6 Compression Test

Compression test was conducted in accordance to standard ASTM D1261. The foams were cut into sample size of 50 x 50 x 30 mm and tested using the Universal Testing Machine Instron D100X with crosshead speed of 5mm/min. Data of compressive load and displacement were sampled via test machine's computer control software at a rate of 10 points per second. Compressive strength was determined following procedure A (absence of yield point, stress taken at 10% deformation). An average of five samples was taken and reported.

**Table 1** formulation of PU foams in this study

Sample	NCO:OH ratio	<i>p</i> -MDI (g)	POP (g)	Water (pbw)	Surfactant (pbw)
S1	1:1	50	50	0	2
S2	1:1	50	50	1	2
S3	1:1	50	50	2	2
S4	1:1	50	50	1	3
S5	1:1.5	40	60	1	2
S6	1:0.82	55	45	1	2
S7	1:0.67	60	40	1	2



**Figure 1** Structure of triacylglycerol

## 3.0 RESULTS AND DISCUSSION

### 3.1 Foam Density

Density of foam with water as blowing agent is determined by the residual water content in the polyol; and it is rather uncommon to obtain variation of densities in different positions of the foam [4]. In this study, no significant difference was found in between different position of the foam. Though not included in this study, it is however predicted that the skin density of the foam varies slightly as compared to the mid-section of the rise direction of the foam. This is because while the mid-part of the produced rigid foam exhibits evenly distributed porosity, the skin layer in contact with the mold is harder and less porous. This finding is also reported in [4]. The obtained foam densities vary within the range of 103.80 to 182.32 kg/m<sup>3</sup>, depending on the foam formulation. Formulation of foam with higher polyol content tends to produce higher density foams, due to the unreacted hydroxyl groups. The obtained results are rather comparable with previous studies [3, 4].

### 3.2 Fourier-Transform Infrared (FTIR) Spectroscopy

FTIR is used to determine the completion of reaction and formation of the polyurethane. Foam spectra of various NCO:OH ratios are as illustrated in Figure 2. Spectra for all the foam formulation shows almost similar pattern, indicating formation of urethane linkages. With reference to the obtained spectra, it can be observed the stretching of hydrogen bonded urethane N-H at  $3310\text{ cm}^{-1}$ . This wide band can also be attributed to the remaining OH groups in the system. As can be seen, the band width tends to increase as the amount of the polyol in the formulation increases, indicating unreacted hydroxyl groups left in the system. These findings might also suggest the less reactivity between the palm oil-based polyol and the isocyanates. Even for a system with OH ratio lower than that of NCO, there are still unreacted groups of OH left, as proven by the spectra for the NCO:OH ratios of 1:0.82 and 1:0.67. The reason behind this phenomenon is perhaps due to the fact that palm oil is a triacylglycerol, which structure is as illustrated in Figure 1, with lower-reactivity secondary hydroxyl groups exist in the polyol. A study by [1] also reported the same unreactivity phenomenon. The bands at  $1510$ ,  $1216$ , and  $1203\text{ cm}^{-1}$  indicate the urethane linkages of N-H, C-N, and C=O, thus confirming the formation of PU foam, while at  $1708\text{ cm}^{-1}$  shows the formation of interurethane hydrogen bonding as the stretching of hydrogen-bonded carbonyl group between N-H and C=O is represented by this band [3]. Free, unreacted isocyanate NCO is represented by the band  $2276\text{ cm}^{-1}$ . As can be observed from the spectra, no free isocyanate is present when the NCO:OH ratio is 1:1 and higher; indicating all the NCO is used up or reacted.

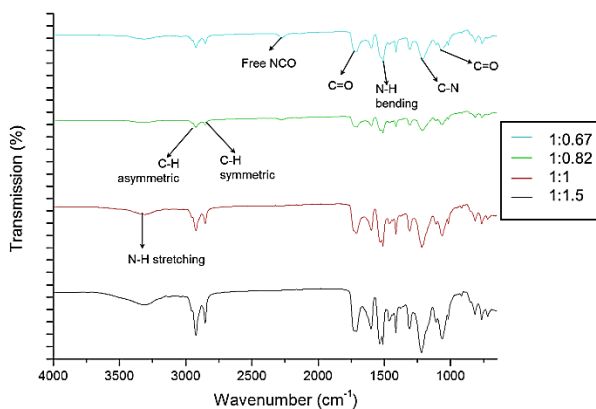


Figure 2 Spectra of PU foams of various NCO:OH ratios

### 3.3 Scanning Electron Micrograph (SEM)

Scanning electron micrographs of the foam surface in the rise direction indicate that the obtained foams are of closed cells. Results also indicate that at different NCO:OH ratios, no apparent differences can be concluded on the cell sizes and arrangements. However, at the addition of more polyol to the system, the cell becomes more regular in shape and uniform in arrangement. PU foam formulations with higher polyol premix content contributes to regular cell structure, producing a well-defined and uniform size. This is due to the existence of excess polyols which act as additional surfactant; thus producing higher amount of closed cell.

However, at constant ratios of NCO:OH, cell size increases as content of distilled water in the system increases. The hydroxyl group reacts with isocyanates to generate  $\text{CO}_2$ . Increase of water

contents produces more  $\text{CO}_2$  and favors coalescence, increasing the cell sizes. The finding is agreeable with past study [3].

### 3.4 Compression Properties

The compressive properties of the obtained PU foams are tested varying the NCO:OH ratios and the water content in each formulation of the foam. The compressive strength of palm oil-based PU foams at 10% strain for both mentioned attributes are as shown in Figure 3 and Figure 4, respectively. In general, the compressive strength of the foam increases with increasing NCO content in each formulation. This is because NCO contributed to the formation of 'hard segments' in urethane linkages. As excess of NCO produces more hard segments and in turn gives the brittle structure to the foam, it is believed that the foam had actually become brittle at NCO:OH ratios beyond 1:1.2. As can be observed from the graph, the compressive strengths attained at ratio 1:1.5 have already actually starting to deteriorate with the maximum strength is believed to be achieved somewhere at the ratio of 1:1.35. These findings also suggests that compressive strengths of palm oil-based PU foams increases even with decreasing foam density as the results obtained clearly indicate that foams with higher isocyanates content are of relatively lower density, even though it is made known that the mechanical properties of rigid PU foams depends on the density of the foam [1]. However, study by [2] also agrees that the increase of compressive strength is due to the higher content of hard segment in the foams. It is believed that due to the lower reactivity of bio-based polyol discussed earlier contributed to this phenomenon as the less reactive hydroxyl groups act as adding weight to the foam, rather than forming urethane linkages; and thus increasing the foams density without actually improving the foams compressive properties.

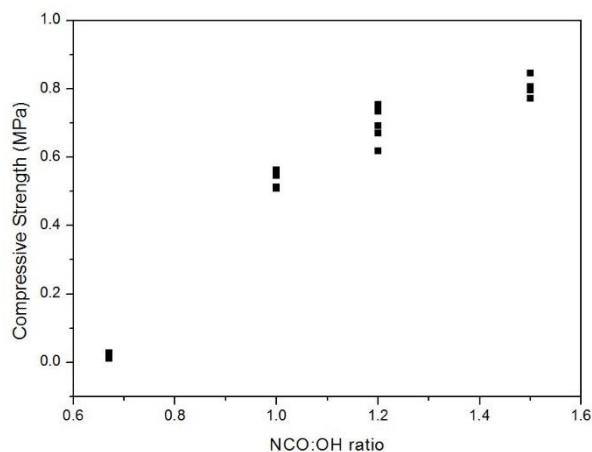
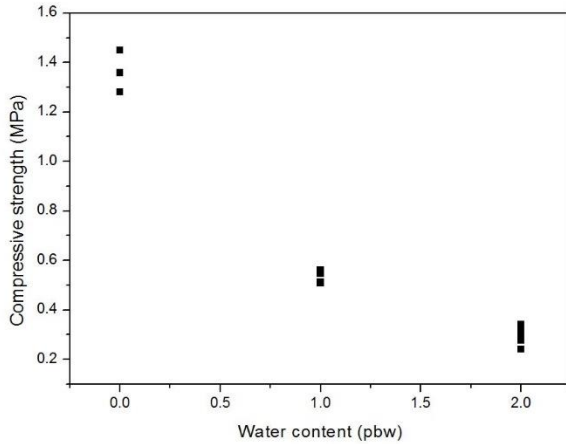


Figure 3 Compressive strength of PU foams at various NCO:OH ratios



**Figure 4** compressive strength of PU foams at various water content

Intensity of blowing agent is also a factor influencing the mechanical characteristics of PU foams. As blowing agents controls the cell structure of the foams, it is vital to find the optimum amount of blowing agents to be added to the foam formulation. In this study, it is found out that increase in among of water as blowing agent at constant ratios of NCO:OH decreases the compressive strength of the foam at a very significant range. At no addition of distilled water to the formulation, the rigid PU foam can have compressive strength as high as 1.45 MPa, but addition of 1 pbw of distilled water caused deterioration of of compressive strength of approximately 185 percent; and further subsequent addition of 1 pbw further decreases 133 percent. This is because blowing agents reacts with diisocyanates to liberate carbon dioxide CO<sub>2</sub> gas; and addition of more blowing agent into the formulation induces formation of bubbles with larger cell sizes, which then in turns deteriorates the foam density and compressive strength [3].

#### 4.0 CONCLUSION

Development of load-bearing capable rigid palm oil-based polyurethane foam was achieved by substituting the petrochemical-based polyol with the bio-renewable counterpart. Results show that the bio-based polyol is suitable for reaction with polymeric diisocyanates to form polyurethane foams, with addition of blowing agents and surfactants in the foam production to further improve the foam structure. The isocyanates to hydroxyl ratio, NCO:OH ratio and water content is varied in the foam formulation; and its effect on the foam morphology and compressive strength are investigated in this study.

This preliminary results shows promising future for palm oil-based PU foams for load bearing applications as obtained foams

exhibit high compression strength and foam density. More work is currently underway to optimize the reactivity of the palm oil-based polyol, as well as to further enhance the mechanical properties of the bio-renewable PU foams.

#### Acknowledgement

The authors are grateful to UTM for the Zamalah scholarship.

#### References

- [1] Chuayjuljit, S., Maungchareon, A., and Saravari, O. 2010. Preparation and Properties of Palm Oil-Based Rigid Polyurethane Foams. *Journal of Reinforced Plastics and Composites*. 29(2): 218–225.
- [2] Prociak, A., Rojek, P., and Pawlik, H. 2012. Flexible Polyurethane Foams Modified with Natural Oil Based Polyols. *Journal of Cellular Plastics*. 48(6): 489–499.
- [3] Rashmi, B. J., Rusu, D., Prashantha, K., Lacrampe, M. F., and Krawczak, P. 2012. Development of Water-Blown Bio-Based Thermoplastic Polyurethane Foams Using Bio-derived Chain Extender. *Journal of Applied Polymer Science*. 128: 292–303.
- [4] Chian, K. S., and Gan, L. H. 1998. Development of a Rigid Polyurethane Foam from Palm Oil. *Journal of Applied Polymer Science*. 68: 509–515.
- [5] Tan, S., Abraham, T., Ference, D., and Macosko, C.W. 2011. Rigid polyurethane foams from a soybean-based Polyol. *Polymer*. 52(13): 2840–2846.
- [6] Ali, E.S., and Ahmad, A. 2012. Bionanocomposite Hybrid Polyurethane Foam Reinforced with Empty Fruit Bunch and Nanoclay. *Composites: Part B*. 43(7): 2813–2816.
- [7] Tanaka, R., Hirose, S., and Hatakeyama, H. 2008. Preparation and Characterization of Polyurethane Foams Using a Palm Oil-based Polyol. *Bioresource Technology*. 99(9): 3810–3816.
- [8] Ji, D., Fang, Z., Wan, Z., Chen, H., He, W., Li, X., and Guo, K. 2013. Rigid Polyurethane Foam Based on Modified Soybean Oil. *Advanced Materials Research*. 724–725: 1681–1684.
- [9] Badri, K. H., Othman, Z., Ahmad, S. H. 2004. Rigid Polyurethane Foams from Oil Palm Resources. *Journal of Materials Science*. 39: 5541–5542.
- [10] Veronese, V. B., Menger, R. K., Forte, M. M. de C., and Petzhold, C. L. 2011. Rigid Polyurethane Foam Based on Modified Vegetable Oil. *Journal of Applied Polymer Science*. 120: 530–537.
- [11] Mat Rejab, M. R. 2004. *Polymeric Foam as Core of Side Door Impact Beam*. Master Thesis. Universiti Teknologi Malaysia.
- [12] Shen, S. Y., Masters, F. J., Upjohn II, H. L., and Ferraro, C. C. 2013. Mechanical Resistance properties of FRP/polyol-isocyanate foam sandwich panel. *Composite Structures*. 99: 419–432.
- [13] Siriruk, A., Weitsman, Y. J., and Penumadu, D. 2009. Polymeric Foams and Sandwich Composites: Material Properties, Environmental Effect, and Shear-lag Modeling. *Composites Science and Technology*. 69: 814–820.
- [14] Langdon, G. S., von Klamperer, C. J., Rowland, B. K., and Nurick, G. N. 2012. The Response of Sandwich Structures with Composite Face Sheets and Polymer Cores to Air-blast Loading: Preliminary Experiment. *Engineering Structures*. 36: 104–112.