

Formation of Lightweight Materials of Polyurethane

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Abstract— Lightweight materials, made up from either from natural and/or derived from the industrial process can be used to solve problems in construction for civil or even road as it is lower in density contrasting to the volume, but possess high strength in mechanical properties. The highlight in this study is the impact strength of rigid polyurethanes (RPU) using different composition of water content in formulation and the relations to the pore size and density properties of the RPU. The diphenylmethane 4,4-Diisocyanate (p-MDI) was reacted with formulated polyol with water as blowing agent in presence of catalyst and surfactant. The sample of the Polyurethane foam was made of formulated polyol of 1%, 2% and 3% of water content produced difference in viscosity of mixture affecting their cell morphology and mechanical strength of impact strength. Results focus on the possibility of the formulation of RPU foam to reach adequate performance, in terms of low density with high excellent outcome allowing lightweight materials of RPU to be used in future application for construction.

Keywords—Blowing Agent, Cell morphology, Compressive Strength, Lightweight Materials, Rigid Polyurethane

I. INTRODUCTION

The settlement of the embankment base is one of the critical problems encountered during construction of the road structure, often causing severe damage on the overlaying layers of pavement structures. Variety of materials included the expanded Polystyrene blocks (EPS-geofoam) grouped with the polymeric foams was involved in the construction and made well known as the source of solution for the problems occurred in the road construction (Marradi, 2012).

The usage of polymeric foams such as RPU in industries and construction is nothing new as they are widely utilized as insulation, acoustic damper, coating, and even to the extent of aircraft and automotive part (Dzulkifli, 2014). These applied polymeric foams are made of petroleum-based and many studies were done in order to incorporate more of the RPU rigid in the industry approachably using bio-based materials but facing difficulties in maintaining good properties of mechanical. The physical properties, as well as the chemical structure, of polyurethane depend on the structure of the original

reactants. The characteristics of the polyols - relative molecular mass, the number of reactive functional groups per molecule, and the molecular structure differs the final product of polymer as it influences the properties of the final polymer. The differences in properties make polyurethanes be able to have wide range of applications as insulator and also lightweight materials as highlighted for the composition and in each formulation was different (Lazonby, 2017).

The distinguishing feature of the materials having lightweight properties is that they all have low densities. Densities range from polymers which have the low density, to titanium and also alloys rather than the basic materials. In addition, unfilled polymers have rather low tensile strengths and some of the lightweight materials can only have certain specifications of characteristics.

The cross-linking density of the formed polymer network was directly modified by polyol mixture ratio, and microstructure and properties also changed in consonance. Ugarte *et al.* (2015) studied previously was discussed further in this paper. Higher amount of water was in fact one of the parameters leads to faster reaction in the RPU thus reducing density of foam. The increase in water content as blowing agent created higher formation of walls which are thicker at the centre but thinner at the end (Ferkl *et al.*, 2018).

The current study was set in the aims of achieving result of PU foams formulation effect to the dynamics results on RPU impact strength in relations to the cell morphology and density. This article thus presents two novel approaches for higher quality of RPU made-formulation.

II. METHODOLOGY

2.1 Materials

The main materials used in the study is the Polyol and Diphenylmethane 4,4-Diisocyanate (p-MDI). Both materials were mixed to form the Polyurethane. The water content tested in this project was using distilled water. Other than that, the materials used are Triethylamine for the catalyst and Polyethylene glycol of 200Da as the surfactant.

2.2 Preparation of foam

The formation of PU foam in this study resulted from the mixing of Diphenylmethane 4,4-Diisocyanate (p-MDI) and solution A (formulated Polyol). The polyol was first weighed according to desired formulation as illustrated in Table 1 together with the distilled water, catalyst and

surfactant then stirred for about 15 seconds to become homogenous. After p-MDI was weighed also, both solution was mixed and stirred until become cream look (cream time) and the solution will begin to form polyurethane. The mixture is poured into an open mold made of aluminium foil (100 x 200 x 30 mm) to produce free-rise foams. This foamed mixture is cured at room temperature for more three to five days to remove unreacted solution and to release the reaction heat. The cure time was made in order for the Polyurethane to become fully rigid before ready to be cut.

2.3 Foam Density

The density of sample was determined using ISO 845 used for Cellular Plastics and Rubbers Determination of Apparent (Bulk) using electronic weighing balance of precision of 0.01 g. Dimensions of the sample were cut into cubes of size 75 cm³. At least five sample was taken into consideration.

2.4 Fourier Transform Infrared (FTIR) Spectroscopy

Infrared spectroscopy measurements of PU foams were carried out using a Fourier-transform Infrared (FTIR) spectroscopy analyzer. The sample foam was sliced into thin layer and pressed against ATR crystal for total contact with force gauge maintained at value ranging 80-100. Infrared spectroscopy was carried out within range 4000-650 cm⁻¹.

2.5 Pore Size Analysis

The region of interest of the sample was taken at area of 2cm x 2cm for the analysis. The analysis was done in the laboratory using microscope of Olympus DP72 and the software provided for the measurement of the pore size by length of open pore.

2.6 Impact Test

Impact strength of the rigid PU tested using Izod Testing Machine Tinius Olsen 503 of Standard ASTM D256 of ISO 180. The specimen was prepared in order to be able to fit the size of the machine and standard using the notcher Machine Tinius Olsen before proceeded using the Izod impact Test.

Table 1: Formulation of PU used in this study

ID	p-MDI (g)	Polyol (g)	Water (%)	Surfactant (%)	Catalyst (%)
S1	20	20	0	0	1
S2	20	20	0	1	1
S3	20	20	1	1	1
S4	20	20	2	1	1
S5	20	20	3	1	1

*Solution A : polyol with different composition of water, surfactant and catalyst

*Ratio of isocyanate : polyol always 1:1.

*The addition of water content reduce the viscosity of Solution A

III. RESULTS AND DISCUSSION

3.1 Pore Size Analysis

Apparent pore size increases due to addition of water in the formulation of PU foams. The formulation with higher percentage of water recorded made the cell morphology becoming more unrigid around the cell wall and no defined walls can be detected. Reasonably, the cell morphology built within the cell as open pore was proved as the opening of the pore increase with the increased percentage of water.

According to previous studies, normally compressive strength decreases gradually when the water content is over 1.5%, which is probably related to the cell morphology as stated in (Huang & Wang, 2017). The pore size of the rigid PU give the sample less properties in terms of strength as the occurrence of wall on the cell reduced with increase in water content.

The higher percentage of water in the formulation tend to make the premix of the foam formulation have less viscosity yet tend to trap more air in the open space on the cell side and resulting in the formation of larger pore. The lower viscosity of PU foams during viscosity cause more homogenous distribution of particles during stirring process (El-Shekeil *et al*, 2012). Consequently, the irregular cell structure attribute to poor load transfer.

3.2 Foam Density

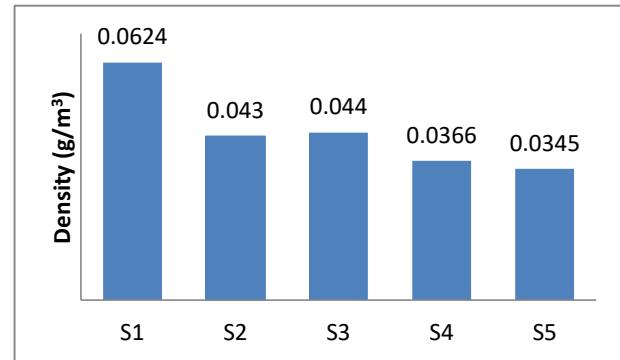


Figure 1: Density of RPUs with different formulation

The density of the RPU for increasing water content is decreasing relatively. However with basis of surfactant presence such as in the formulation of sample 1(S1) and Sample 2 (S2) as experimented, it can be seen that both sample without water content in the formulation have shown different values from each other as in Figure 1. Sample1 without surfactant in the absent of water have higher density than the sample with surfactant. This result highly likely happened in conjunction of the role of surfactant in formation of PU foam.

As stated in the Stevens (1993), the surfactant roles provide less surface tension during the formation of polyurethane foam which help increased the number of air bubbles trapped during mixing with present of blowing agent. Hence, this proves that the surfactant present in the formulation supported the roles of water as blowing agent when water was in the indication of formulation.

The density of foam with water as blowing agent is determined by the residual water content in the polyol (Dzulkifli, 2014). The result can be monitored relatively close to the result on Figure 1 off density decreasing in increment of water content for S3, S4 and S5. Formulation of foam with higher content-polyol tends to produce higher density foams, due to unreacted hydroxyl groups in the composition consist less water. The result of density will be marked closely as the effect of having lower density affecting the mechanical properties of RPUs.

3.2 Characterization of Rigid Polyurethane

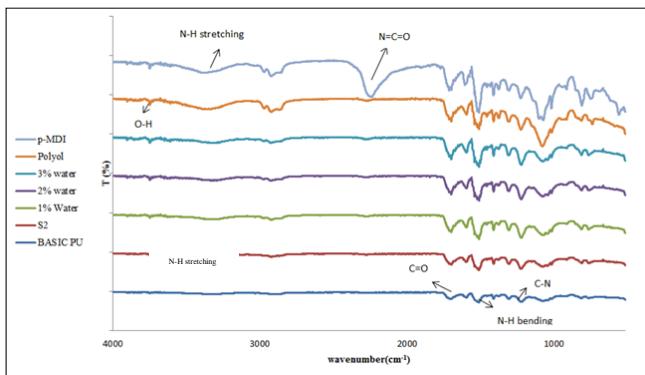


Figure 2: Spectra of PU foams of various formulation

The function of Fourier Transform Infra-Red Spectroscopy (FTIR) analysis is to determine the presence of certain functional groups in a molecule. FTIR is used to determine the completion of reaction and formation of the rigid Polyurethane. Foam spectra of various NCO:OH ratio are illustrated in Figure 2. Spectra for all the foam formulation shows almost similar patterns, indicating similar formation of urethane linkage. With the references to the spectra, it can be observed that all the sample success in making the urethane linkage at 1510 cm^{-1} and 1216 cm^{-1} indicates the formation of the Polyurethane was confirmed to be happened in the sample.

As can be seen, the band width tends to increases depending on the amount of polyols in the formulation. No free isocyanate can be detected when the NCO:OH ratio is 1:1 indicating all the NCO is used up or reacted. The relation can be concluded successful in producing urethane linkage.

The FTIR spectrum of the RPUs have numerous peaks which will determine their origin of the group. The RPUs composition have different ratio nevertheless they share some similar traits as they share the similar peaks. The peaks at 2916 cm^{-1} , 2848 cm^{-1} and 1466 cm^{-1} indicate the presence of polyurethane. Subsequently, the Figure 2 demonstrated that the peak at bond C=O decreases as the percentage of polyurethane increases. This is due formation of the composite that has developed at the bond.

Free, unreacted isocyanate NCO is represented by the band 2276 cm^{-1} . As can be observed from the spectra, no free isocyanate is present when the polyurethane formulation to 1:1 ratio indicating all the NCO is used up or reacted.

3.3 Impact Strength

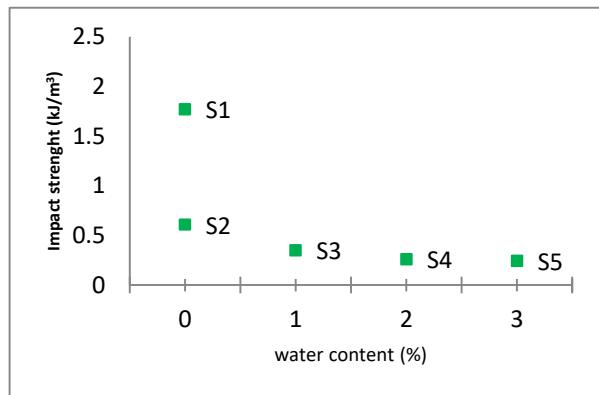


Figure 3: Water Content vs Impact Strength

The impact test was done in order to determine the capability of a material on withstanding applied load and expressed in terms of energy. From the data it can be seen that the loading impacts increases with presence of higher water content in the formulation of PU foams. The highest impact strength was achieved by the both sample made without water as one of the content, the ratio of polyol to isocyanate of 1:1 resulted in highest achievement of absorbing sudden shock from outer sources. Based on the study by Bakare *et al.* (2010), the impact strength varies depending on the viscosity and the present of fibre loading in the samples. It can be speculated that the absent of water in the formulation helps increasing the viscosity of the mixture yet trapping little air than the other Pus compound with the presence of water. Hence, the samples with higher water content made the way as lower viscosity resulting in low impact strength.

IV. CONCLUSION

Development of polymer making made the Polyurethane as one of the substitution for usage of EPS and other lightweight materials. Results show that the formulation Polyurethane proposed in the research was suitable for reaction of controlled water content.

With the addition of water as blowing agent, surfactant and catalyst presence help to further improve the foam structure of low density with comparable mechanical strength to the EPS characteristics. ratio varied by the water content used in the formulation, and its effect on the foam morphology and compressive strength was successfully investigated and studied in this study.

The preliminary result shows promising future for usage of RPUs as lightweight materials taking place in construction replacing EPS. More work currently on the way to optimize and making the rigid Polyurethane more bio-based using bio-renewable sources with much better properties and achievements.

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References

- 1) Bakare, I. O., Okieimen, F. E., Pavithran, C., Abdul Khalil, H. P. S., & Brahmakumar, M. (2010). Mechanical and thermal properties of sisal fiber-reinforced rubber seed oil-based polyurethane composites. *Materials & Design*, 31(9), 4274-4280. doi:<https://doi.org/10.1016/j.matdes.2010.04.013>
- 2) Dzulkifli, M. H. Y., M.Y. ; Md Akhirb, F.S. ;Abd Majid, R. (2014). Development of Rigid Biocomposite Polyurethane Foam for Load Bearing Application. *Jurnal Teknologi (Sciences & Engineering)* ,68:3, 53-56.
- 3) Ferkl, P., Kršková, I., & Kosek, J. (2018). Evolution of mass distribution in walls of rigid polyurethane foams. *Chemical Engineering Science*, 176, 50-58. doi:<https://doi.org/10.1016/j.ces.2017.10.024>
- 4) Huang, G., & Wang, P. (2017). Effects of preparation conditions on properties of rigid polyurethane foam composites based on liquefied bagasse and jute fibre. *Polymer Testing*, 60(Supplement C), 266-273. doi:<https://doi.org/10.1016/j.polymertesting.2017.04.006>
- 5) Lazonby, J. (2017). Polyurethanes. Retrieved from The Essential Chemical Industry-online website: <http://www.essentialchemicalindustry.org/polymers/polyurethane.html>
- 6) Marradi, A. P., U.; Betti, G. (2012). The Use of lightweight materials in road embankment construction. *Social and Behavioral Sciences*, 53, 1001-1010.
- 7) Stevens, M. P. (1993). Polymer additives: III. Surface property and processing modifiers. *Journal of Chemical Education*, 70(9), 713. doi:10.1021/ed070p713
- 8) Ugarte, L., Gómez-Fernández, S., Peña-Rodríguez, C., Prociak, A., Corcuera, M. A., & Eceiza, A. (2015). Tailoring Mechanical Properties of Rigid Polyurethane Foams by Sorbitol and Corn Derived Biopolyol Mixtures. *ACS Sustainable Chemistry & Engineering*, 3(12), 3382-3387. doi:10.1021/acssuschemeng.5b01094
- 9) Pinto, M. L. (1981). Formulation, Preparation, and Characterization of Polyurethane Foams. *Journal of Chemical Education*, 87(2), 212-215. doi:10.1021/ed8000599
- 10) Sapuan, S. M., Pua, F.-l., El-Shekeil, Y. A., & Al-Oqla, F. M. (2013). Mechanical properties of soil buried kenaf fibre reinforced thermoplastic polyurethane composites. *Materials & Design*, 50 (Supplement C), 467-470. doi:<https://doi.org/10.1016/j.matdes.2013.03.013>