Temperature on the Mechanical, Thermal and Barrier Property of Polyurethane

P I Yeap1, N Y Yuhana2, S Fariz3, and M Z Otoh3
1Department of Chemical and Process Engineering, Universiti Kebangsaan Malaysia, Bangi, Selangor, Malaysia
2Research Centre for Sustainable Process Technology (CESPRO), Universiti Kebangsaan Malaysia, 43000 Bangi, Selangor, Malaysia
3Eureka Efektif Sdn Bhd, No. 30, Jalan Perindustrian Suntrack Hub Perindustrian Suntrack Off Jalan P/1A, Seksyen 13, Bandar Baru Bangi, 43650 Bangi, Selangor, Malaysia

Email: yuliana@ukm.edu.my

Abstract. Polyurethane is a type of segmented polymer which is synthesized from polyisocyanate, polyol and chain extender. The reaction between isocyanate and hydroxyl bond is known as polymerization. Two-step synthesis is used in synthesizing polyurethane, where polyisocyanate reacts with polyol to form pre-polymer, follows by the reaction between pre-polymer and diol. In this research, different weight percentages of triethylenediamine catalyst (0.0%, 0.2%, 0.4%, 0.6% and 0.8%) are used. Moreover, curing time and temperature that examined in this research is at a temperature of 70ºC for 24 hours (Set A), which is practised in the industry. Curing at shorter time and higher temperature is proposed, which is 70ºC for 2 hours followed by 100ºC for 3 hours (Set B). Mechanical property and absorption property of polyurethane is studied by Shore A hardness test and water absorption test respectively. Morphology of polyurethane is studied by Scanning Electron Microscopy (SEM). Moreover, density test, Thermogravimetric Analysis (TGA) and Fourier Transform Infrared Spectroscopy (FTIR) analysis are carried out.

1. Introduction

Polyurethane is a type of segmented polymer, where it consists of soft and hard segment alternately [7]. The soft segment consists of polyol that gives chemical resistance whereas hard segment consists of isocyanate that gives hardness and tensile strength to polyurethane [8]. Polyurethane is produced by the chemical reaction between polyol and polyisocyanate in the presence of catalyst, chain extender, filler, colorant and additive. Additional polymerization occurs between the hydroxyl (-OH) and isocyanate group (-NCO) to produce urethane group (-NHC=O), which is the functional group of polyurethane.

Polyurethane has high tensile strength and high melting point. These make polyurethane even more durable. Polyurethane is a good replacement for plastic as it has degradation resistance towards water, oil and solvent [3]. However, polyurethane is weak in terms of thermal stability and barrier property. Polyurethane is difficult to be melted or recycled as most polyurethane is thermoset polymer [10].

Triethylenediamine, is a tertiary amine that widely used in polyurethane industry. According to Sharmin & Zafar, the catalytic activity of polyurethane is determined by the structure and basicity of amine, in which the reaction increases with increasing of basicity and decreasing of
steric hindrance [9]. Triethylenediamine based catalyst is often used to avoid fogging and odour problems [6].

Curing of polyurethane involves the formation of a three-dimensional network through reactions among polyisocyanates and polyols. The curing process starts with linear growth of chain, follows by branching and lastly cross linking [4]. High curing temperature will increase the mobility of molecules and thus promotes the cross linking to occur at higher rate [5].

Density is an important parameter in influencing the properties and performances of polyurethane. Density affects the water absorption property, mechanical property and morphology as well as the thermal stability of polyurethane. Research shows that increasing in density will cause the increase in hardness and decrease in the water absorption property [12]. As reported by Dahlia Z. et al., polyurethane synthesized by using waste paper as filler has higher hardness in the presence of triethylenediamine catalyst. This shows that catalyst will produce a more compact structure. Thus increases the hardness of polyurethane [2]. High curing temperature also increases the hardness of polyurethane [1]. Network of cross links will prevent the diffusion of water molecules and thus prevent the water molecules from residing in available volume [11]. Therefore, high curing temperature will decrease the water absorption property of polyurethane. As reported by Anna Andersson, high curing temperature with short curing time is insufficient for isocyanate to react completely. The high percentage of absorption peaks at 2260 cm\(^{-1}\) indicating that there are lots of isocyanate present in polyurethane [1].

Therefore, the objective of this study is to investigate the mechanical property, absorption property and morphology of polyurethane by varying the weight percentage of triethylenediamine catalyst. Moreover, the properties of polyurethane are also investigated at different curing time and temperature.

### 2. Methodology

#### 2.1 Materials

In this study, we use methylene diphenyl diisocyanate (MDI), polyester polyol (Polyol), 1,4-butandiol (BDO), triethylenediamine (TEDA) and polydimethylsiloxane-polyol (AAA). All of the materials were supplied by Covestro, France.

#### 2.2 Sample Preparation

The raw materials were prepared according to the mass as shown in Table 1 below by using weighing device PB4002-S. MDI was prepared and heated to 40°C by heating plate MS-H280-Pro. Then polyol, AAA and TEDA were added accordingly into the container. Mixture was stirred at 195rpm for 15minutes (off heating). Lastly, BDO was added and stirred at 195rpm for 3minutes. Polyurethane is then cured at 70°C for 24hours in oven. Different weight percentages of catalyst are repeated. The samples prepared are denoted as set A. Another set of polyurethane is prepared by using different weight percentage of catalyst and being cured at 70°C for 2hours followed by 100°C for 3hours. These samples are denoted as set B. The sample codes used in this study are shown in Table 2.

| Table 1. Composition of Raw Materials |
|---------------------------------------|
| Raw Material                          | Weight Percentage (%) per 100g |
| Methylene Diphenyl Dusocyanate (MDI)  | 38.34                           |
| Polyester Polyol (Polyol)             | 57.52                           |
| 1,4-butandiol (BDO)                   | 4.14                            |
| Polydimethylsiloxane-Polyol (AAA)     | 0.30                            |
| Triethylenediamine (TEDA)             | 0.00                            |
### Table 2. Sample Coding and Catalyst Amount in Polyurethane

| Sample   | Curing Condition | Weight Percentage (%) |
|----------|------------------|------------------------|
| PU0.0A   | A                | 0.0                    |
| PU0.2A   | A                | 0.2                    |
| PU0.4A   | A                | 0.4                    |
| PU0.6A   | A                | 0.6                    |
| PU0.8A   | A                | 0.8                    |
| PU0.0B   | B                | 0.0                    |
| PU0.2B   | B                | 0.2                    |
| PU0.4B   | B                | 0.4                    |
| PU0.6B   | B                | 0.6                    |
| PU0.8B   | B                | 0.8                    |

Curing Condition of A = 70°C (24 hours), B = 70°C (2 hours) 100°C (3 hours)

2.3 Characterization

All the samples were prepared then sent to the following characterization:

- **Hardness**
  
  Testing was done by using Durometer with accordance to standard ASTM D2240, where the sample size is 50mm x 75mm x 6mm. The sample was placed on a flat hard surface. The indenter was pressed into the sample and Shore A hardness value was recorded within one second.

- **Water Absorption**
  
  Testing was done with accordance to standard ASTM D570, where the sample size is 20mm x 20mm x 6mm. Firstly, sample was dried in oven at 50°C for 24 hours. The sample was weighted by using weighing scale HR-250AZ to obtain original weight before immersed in water. Then, the sample was immersed in distilled water at 24°C for 24 hours. The sample was removed and dried by using cloth. Finally, the sample was weighted. Placed back the sample and repeated the process of weight measurement for one week. Percentage of water absorption was calculated according to equation (1).

\[
\text{Percentage of Water Absorption} \ (%) = \frac{W_t - W_0}{W_0} \times 100\%
\]  

where \( W_t \) and \( W_0 \) are the weight at time \( t \) and original weight respectively.

- **Scanning Electron Microscope (SEM)**
  
  Leo 1450VP SEM was used in SEM analysis. Samples were prepared at low temperature by immersing in liquefied nitrogen. All samples were coated with a layer of gold before characterization.

- **Density Meter**
  
  Density of sample is tested by using density meter MH-300A, where the sample size is 50mm x 25mm x 6mm. Make sure the sample and density meter were free from dust. Distilled water was filled into the container of density meter. The sample density was calculated by using the equation (2).

\[
\text{Density} \left( \frac{\text{kg}}{\text{m}^3} \right) = \text{Specific Gravity} \times \text{Distilled Water Density} \left( \frac{\text{kg}}{\text{m}^3} \right)
\]  

- **Fourier Transform Infrared Spectroscopy (FTIR)**
  
  Measurements were performed at room temperature. Single beam spectra of the samples were obtained after averaging 40 scans between 4000 cm\(^{-1}\) and 500 cm\(^{-1}\).

- **Thermogravimetric Analysis (TGA)**
  
  Thermogravimetric analysis was carried out at temperature range of 25°C to 600°C, with the heating
rate of 10°C/min.

3. Results and Discussion

3.1 Hardness

Polyurethanes with the presence of catalyst have hardness greater than that of polyurethanes without catalyst. Polymerization reaction catalyzed by triethylenediamine catalyst has greater reaction rate, which is then further increased the cross linking level. Higher cross linking creates closer packed structure and increases the hardness. Polyurethanes with 0.4% of catalyst have the highest hardness, where hardness of PU0.4A and PU0.4B are 41.60 Shore A and 45.20 Shore A respectively. Hardness of polyurethane for set A and set B decrease in the order of: PU0.4, PU0.2, PU0.6, PU0.8 and PU0.0. When the catalyst weight percentage achieves optimum value, 0.4%; hardness of polyurethane decreases. High amount of catalyst triggers fast gelling reaction between polyisocyanate and polyol. Therefore, diffusional restriction of curing agent, 1,4-butanediol reduces the extent of conversion. Decrement of cross linking level reduces the polyurethane hardness. Hardness of polyurethane set B is observed to be greater than that of set A. At higher curing temperature, mobility of reactants is increased. This allows densification of urethane segment and follows by increasing in hardness.

3.2 Density

Increasing of density leads to the increasing of cross linking and thus increases the hardness of polyurethane. Polyurethanes PU0.2, PU0.4, PU0.6 and PU0.8 for set A and set B have high density and hardness. However, polyurethane PU0.0A and PU0.0B have the highest density with lowest hardness. This is due to the porous structure that retains water molecules on the surface during density test. High curing temperature increases mobility of reactants and thus increases the cross link and density. Therefore, polyurethane set B has higher density than set A.
3.3 Water Absorption Property

The decline in polyurethane density shows the decline in cross linking, where the diffusion of water molecules into polyurethane network will be increased. This is because the cross link will prevent water molecules to penetrate and reside in the polyurethane structure. Therefore, water absorption properties increase with decreasing density. However, polyurethane PU0.0A and PU0.0B have high density with high water absorption property. The high density of PU0.0A and PU0.0B is due to water molecules that remain on porous structure during density test. Polyurethane for set B gives lower water absorption percentage. High curing temperature increases mobility of reactants and thus increases the cross link and density. High cross link level can resist the diffusion of water molecules. Therefore, water absorption property decreases with increasing of density.

3.4 Fourier Transform Infrared Spectroscopy (FTIR) Studies
No isocyanate peak at 2270 cm\(^{-1}\) was observed in IR spectra for polyurethane set A and set B. This indicates that the isocyanate is converted completely into polyurethane and no residues of isocyanate. Peak at 3300 cm\(^{-1}\) indicates that all N-H group polyurethanes involve in hydrogen bond formation. Peaks at around 1220 cm\(^{-1}\) and 1079 cm\(^{-1}\) represent O-C=O bond at soft segment and C-O-C bond at urethane respectively. The strong and sharp absorption peaks at 1220 cm\(^{-1}\) and 1079 cm\(^{-1}\) are shown at IR spectra of polyurethane without catalyst (PU0.0A and PU0.0B). This indicates that the urethane bond formed is lesser than that of polyurethane with catalyst.
3.5 Thermal Analysis

Figure 6. TG Curve for Polyurethane PU0.4A and PU0.4B

Figure 7. DTG Curve for Polyurethane PU0.4A and PU0.4B

TG curve shows that there are two stages of degradation, at which the weight of polyurethane is decreased. For both polyurethanes, decrement of weight at first stage happened at the range of 210ºC and 310ºC. This indicates that the degradation of polyurethane starts at urethane bond where C-O bond is broken. At second stage, degradation of urethane bonds lead to the formation of primary amine and olefin or formation of secondary amine and carbon dioxide. C-H and C-N bonds are broken at second stage of degradation [13]. Moreover, TG curve of polyurethane PU0.4A is almost similar with polyurethane PU0.4B. This shows that curing time and temperature does not have significant effect on thermal stability. Polyurethane PU0.4B has greater maximum degradation temperature and degradation onset temperature shows that it has better thermal stability compared to polyurethane PU0.4A. However, only slight differences. DTG curve with only one peak indicates that mixture of pre-polymer reacted completely.
Table 3 TGA Data for Polyurethane PU0.4A and PU0.4B

| Sample | Maximum Degradation Temperature (ºC) | Degradation Onset Temperature (ºC) | Weight at 600ºC (%) |
|--------|--------------------------------------|-----------------------------------|---------------------|
| PU0.4A | 404.16                               | 226.64                            | 8.5826              |
| PU0.4B | 404.66                               | 228.95                            | 8.0523              |

3.6 Morphology

Polyurethane PU0.4A has porous structure which consists of cell. The surface of polyurethane is rough and filled with spherical cell. In comparison, structure of polyurethane PU0.4B is packed structure with little cell. High curing temperature of polyurethane PU0.4B has higher cross linking level due to high mobility of reactants. Therefore, structure of polyurethane is much closer and packed.

Figure 8. SEM Cross Sectional View of Polyurethane PU0.4A

Figure 9. SEM Cross Sectional View of Polyurethane PU0.4B
Figure 10 and Figure 11 shows that polyurethane PU0.4A and PU0.4B have a uniform matrix with small whitish speckled. Moreover, there are also spherulitic-like structures protruded on the surface of both polyurethanes. These represent the content of hard segment. However, there are no significant differences between polyurethane PU0.4A and PU0.4B.

4. Conclusion
Polyurethane with 0.4% of triethylenediamine catalyst gives the best mechanical property; highest Shore A hardness. It has also the weakest water absorption property. Polyurethanes that are being cured at 70ºC for 2 hours followed by 100ºC for 3 hours have higher hardness, higher density and poorer water absorption property compared to polyurethanes that are being cured at 70ºC for 24 hours. The thermal stability of polyurethane PU0.4B is observed to be slightly better than that of polyurethane PU0.4A. Polyurethane PU0.4B has more closed and packed structure compared to polyurethane PU0.4A. All of the polyurethanes reacted completely to form urethane bond with no residues of isocyanate as shown in IR spectra.

References
[1] Andersson A. 2011. Characterisation of the influence of curing temperature on the properties of 2K waterborne topcoat waterborne topcoat. Sweden.
[2] Dahlia Z., Salmah H. & Azlin O. 2009. The Effect of Triethylene Diamine on the Properties
of Waste Paper Foam Composites. *Journal of Physical Science*, 20(1), 49–57. Retrieved from http://www.usm.my/jps/20-1-09/JPS 20(1) ART 5 (49-57) NEW.pdf

[3] Howard G. T. 2011. 7. Microbial biodegradation of polyurethane. University Hammond Louisiana.

[4] Li S., Vatanparast R. & Lemmetyinen H. 2000. Cross-linking kinetics and swelling behaviour of aliphatic polyurethane. *Polymer, 41*(June 1999), 5571–5576.

[5] Lucio B., Luis J. & Fuente D. 2014. Thermochimica Acta Rheological cure characterization of an advanced functional polyurethane. *Thermochimica Acta, 596*, 6–13. doi:10.1016/j.tca.2014.09.012

[6] Parasar B., Jing G. W., Yuan D., Kun W., Wang P. & Dasgupta A. (n.d.). Copper Replaces Tin: A Copper based Gelling Catalyst for from Discarded Motherboard 1–24.

[7] Rehman F.-. 2010. Synthesis and Characterization of Speciality Polyurethane Elastomers.

[8] S. Gopalakrishnan and T. Linda Fernando. 2011. Studies of Aging Performance of Some Novel Polyurehances. *Journal of Chemical and Pharmaceutical Research*, 2, 848–862.

[9] Sharmin E. & Zafar F. 2012. Polyurethane: An Introduction. *Polyurethane*, 3–16. doi:10.5772/51663

[10] Sivertsen K. 2007. Polymer foams 1–17.

[11] Tan S. G. & Chow W. S. 2011. Thermal properties, curing characteristics and water absorption of soybean oil-based thermoset. *eXPRESS Polymer Letters*, 5(6), 480–492. doi:10.3144/expresspolymlett.2011.47

[12] Thirumal M., Khastgir D., Singha N. K., Manjunath B. S. & Naik Y. P. 2008. Effect of foam density on the properties of water blown rigid polyurethane foam. Retrieved from http://onlinelibrary.wiley.com/doi/10.1002/app.27712/abstract

[13] Zamzam, M. M. 2005. A Study on the Thermal Degradation Resistance of Thermoplastic Polyurethane Coatings.