CHAPTER 3

MODIFICATION OF POLYESTER POLYOL FROM PET FLAKES TO PRODUCE POLYURETHANE FOAM

Contents

3.1 INTRODUCTION

Post-consumer waste PET bottles were successfully converted into a polyester polyol as described in previous chapter. This tri-functional group of glycolysed PET can be a potential polyol to be used as a raw material in making polyurethane (PU) foam. This chapter describes the modification of the glycolysed PET and explains on why and how the modification was done. Using polyol mixture as a raw material in PU synthesis is already known to have desired properties of foam. One of the previous studies which use mixture of polyols in the preparation of PU foam is the invention by Dirckx V.M.R., E.J. Gerard, and H.F. Vermeire. The polyol component comprises a polyol blend of a polyolefin polyol and a polyether polyol [1].

3.2 EXPERIMENTAL

3.2.1 Materials and reagents

In the production of PU foam, polyol component comes from the glycolysed PET which has been synthesized as reported in Chapter 2 and commercial polyether polyol which is marketed under the trade name FA-703 and was a kind gift from local company. Polyol FA-703 is a highly reactive polyether which has hydroxyl number in the range of 30.0-35.0 mg KOH/g, whereas isocyanate component was obtained from modified MDI (diphenylmethane-4,4’-diisocynate) having an isocyanate equivalent weight of 134.0 and functionality of 2.7 isocyanate groups per molecule. The highly efficient silicone stabilizer and excellent in foam openness, L3002, was used as a surfactant. Besides low shrinkage properties, this surfactant also helps in yielding low force-to-crush foam as described in the material description. Other additive used was PU catalyst which contains 33% triethylenediamine liquid catalyst and known as

Catalyst A-33 in the market. Theoretically, this tertiary amine catalyst is for highly active isocyanate and polyol reaction, so that cross-linked foam is formed. Another important material is distilled water which was used as the blowing agent by generating *in situ* carbon dioxide.

3.2.2 Preparation of polyol mixture

A series of polyol mixtures were prepared by blending 0 wt% to 60 wt% of the glycolysed PET with the polyol FA-703 as shown in Table 3.1. It was then heated slowly using a hotplate stirrer at 60-70 °C for 1 hour. At the same time, the mixture was stirred thoroughly and continuously with magnetic stirrer bar to ensure proper mixing. Magnetic bar was unable to spin at the beginning due to the highly viscous nature of glycolysed PET. However when the temperature was increased up to 50 °C, it became less viscous and started to blend with the polyol FA-703. At this stage, the clear color of polyether polyol was changed to cloudy and milky white. There was no precipitate of glycolysed PET observed in the mixture when cooled to room temperature and even after one night of storage. This condition shows that the mixture of glycolysed PET and polyether polyol was well blended. The polyol mixture was then tested for viscosity. The same method was used in the preparation of polyol component in the synthesis of PU foam.

Table 3.1 Composition of polyol mixture containing glycolysed PET polyol FA-703

Polyol mixture code	Glycolysed PET (wt. %)	Polyol FA-703 (wt. %)	Glycolysed PET (wt. g)	Polyol FA-703 (wt. g)
M0	0	100	0	18
M10	10	90	1.8	16.2
M15	15	85	2.7	15.3
M20	20	80	3.6	14.4
M40	40	60	7.2	10.8
M60	60	40	10.8	7.2
GP-1B	100	0	18	0

3.2.3 Formation of PU foams from polyol mixture

The polyol mixture was prepared by blending the glycolysed PET with the polyol FA-703 and ready to be mixed with catalyst and other additives as described further in section 3.2.3.1.

3.2.3.1 Free rise foaming

A polyol mixture was prepared for use in the preparation of semi-rigid PU foam in a plastic cup. The polyol mixture contained 20 parts by weight (pbw) of glycolysed PET (GP-1B) having a hydroxyl value of 646 mg KOH/g, and 100 pbw of the polyol FA-703 having a hydroxyl value of 33 mg KOH/g. The preparation method of the polyol mixture was followed as mentioned in previous section.

Formulation of PU was adapted from the successfully tested formulation of flexible foam which is normally based on 100 g of polyol as shown in Table 3.2. To the polyol mixture was added 2.44 pbw per 100 parts of the polyol mixture of a commercial surfactant, (Surfactant L3002) and 0.70 pbw of commercial catalyst, (Catalyst A33). In addition, 3.60 pbw of water per 100 parts of the total polyol mixture was added as the (chemical) blowing agent. All these ingredients were weighed into 400 ml plastic cup and by using a mechanical stirrer equipped with a 2-inch diameter mixing blade, the mixture was stirred for about 60 seconds to ensure homogeneity. This mixture was labeled as Component-A.

Table 3.2 Typical amount of component-A for flexible foam

Materials	Parts by weight (pbw) of materials (based on 100 g of polyol)	
	Typical amount[1]	this work
Polyol	100.00	100.00
Surfactant	3.00	2.44
Amine catalyst	0.20	-
Tin catalyst	0.5	-
Catalyst A33	-	0.7
Blowing agent	3.60	3.60

1-Handbook of PU

Subsequently, at the end of the mixing period, pre-measured Component-B comprising of 100 pbw per 100 parts of polyol mixture of polymeric MDI was added to the cup and the mixing continued for another 90 seconds. The foam was allowed to rise at room temperature until it stopped rising and then transferred into a pre-heated curing oven under a controlled temperature of 60 ± 1 °C for 10 minutes. The foam was hand crushed after half an hour to open the cell windows and prevent foam shrinkage. After the foaming process was completed, the foam was allowed to cool at room temperature (28-31) °C in a relative humidity of about 50% for a minimum of 12 hours before carrying out any measurements. During the foaming process, mixing time, cream time, gel time and rise time were recorded by stopwatch.

3.2.3.2 Determination and variation of isocyanate index

The amount of isocyanate used relative to the theoretical equivalent amount is known as the isocyanate index which is calculated as follows:

$$\text{Isocyanate index} = \frac{\text{Actual amount of isocyanate used}}{\text{Theoretical amount of isocyanate required}} \times 100$$

The experiment as described in section 3.2.3.1 was repeated a number of times, each time using a different amounts of polymeric MDI based on different isocyanate indices. This will help in the study of the effect of isocyanate index variation on the foam properties. Depending on theoretical calculation shown in appendix, Table Ap3-1, the weight percentage of glycolysed PET in the polyol mixture was fixed to 17 wt% of the total weight and a group of PU foams with different isocyanate indices in the range of 95 to 120 was generated. Table 3.3 below shows the variation of isocyanate index

Table 3.3 Variation of isocyanate index

Sample code	Isocyanate Index
M/F/95	95
M/F/100	100
M/F/110	110
M/F/115	115
M/F/120	120

3.2.3.3 Variation of percentage of glycolysed PET in polyol mixture

The isocyanate index was set to 100 while glycolysed PET content was varied from 0 to 100 wt percent of the amount of total polyol mixture. The preparation method as well as the formulation of PU foam was similar to that described in section 3.2.3.1.

Table 3.4 Variation of percentage of glycolysed PET in polyol mixture

Sample code	Glycolysed PET (%)
F/100/3	0
M/F/100/2	10
M/F/100/1	17
M/F/100/4	20
M/F/100/5	40
M/F/100/6	100

3.2.4 Characterisation

3.2.4.1 Polyol mixture viscosity

Viscosity measures the resistance of a fluid to uniformly continuous flow without turbulences or other forces. Polyol mixtures which consist of glycolysed PET and polyol FA-703 were set as described in section 3.2.2. The test was carried out immediately after the blending process and once the mixture has reached the room temperature. Viscosities of glycolysed PET and mixtures of the glycolysed PET with polyol FA-703 were examined using Rheometer R/S plus Brookfield at room temperature.

In the determination of viscosity of polyol mixture, 10 wt% to 60 wt% of glycolysed PET namely GP-1B, was used.

3.2.4.2 Cell structure of the PU foam

Rigid and flexible PU foams differ not only in molecular structure but also in the type of foam cell structure which is either closed cell or open cell. In this study, cell structure was successfully captured by the optical microscope.

3.2.4.3 FTIR of PU foam

Infrared spectrum analysis of PU foam was measured using Spotlight 400 Perkin Elmer Spectrometer at resolution 4 cm^{-1} and 15 scanning numbers using attenuated total reflectance (ATR) method. Wavelength used was from 4000 - 400 cm^{-1}.

3.2.4.4 Determination of foam density

Density is a key for most type of PU foam specifications. It is an important indicator of foam performance with regard to comfort, support and durability. It is also an indicator of the relative economics of the foam. Foam density is a measurement of mass per unit volume of the foam.

PU foams produced were cut out from its core portion into a cube size with the dimension of (50 x 50 x 25) mm. The length, width and height as well as the weight of the foam sample were recorded and used to calculate the density of the foam by dividing the weight of the test piece by its volume.

3.2.4.5 Compression strength of foam

Compression strength of foam determines the degree of deformation, which will occur when a pressure is applied to the foam. In this study, compression strength was measured on cubic foam samples of a size of (50 x 50 x 25) mm placed between two parallel plates with a larger area than the specimen. A force of 50 kN was required to compress the foam at a constant rate of 5 mm/min at room temperature and five number of samples were tested. The samples were compressed to 50% of the sample's original thickness. Tests were done to study the difference between top core of foam and its bottom core. The samples were randomly taken from the foam series in which the isocyanate index was 100 while the polyol component had different percentages of the glycolysed PET in the polyol mixture. PU foam obtained was cut out from the upper core and lower core as illustrated in Figure 3.1.

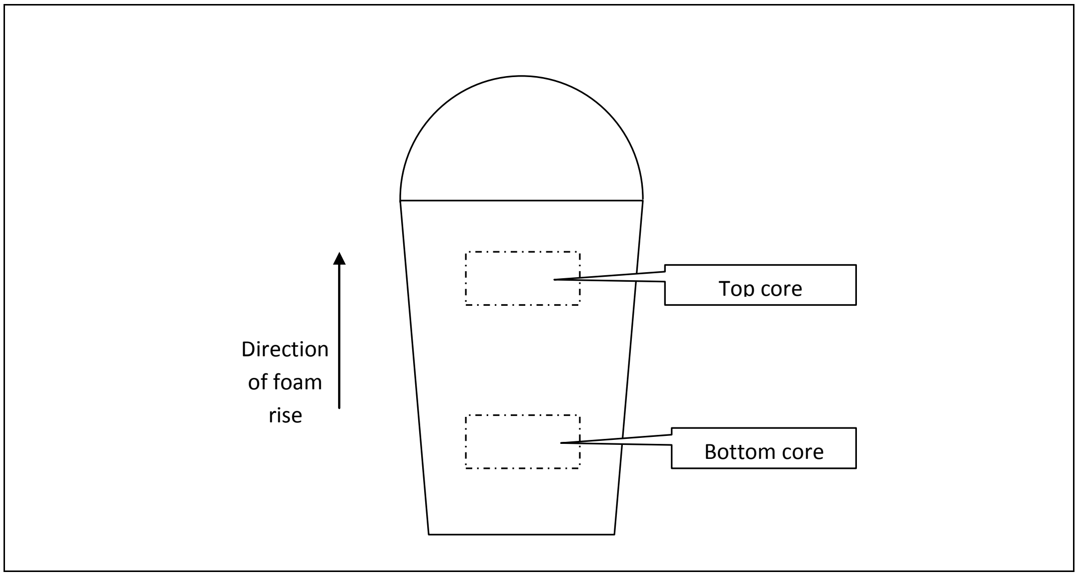


Figure 3.1 Position of samples taken from cup-rise foam and direction of foam rise

Investigation on effect of the cell orientation on the compression stress was also carried out with more than five samples of foams being tested. Direction of foam rise is as shown in Figure 3.2. In this study, test specimen was oriented parallel to the direction of foam rise on the compression plate as shown in Figure 3.2 (a).

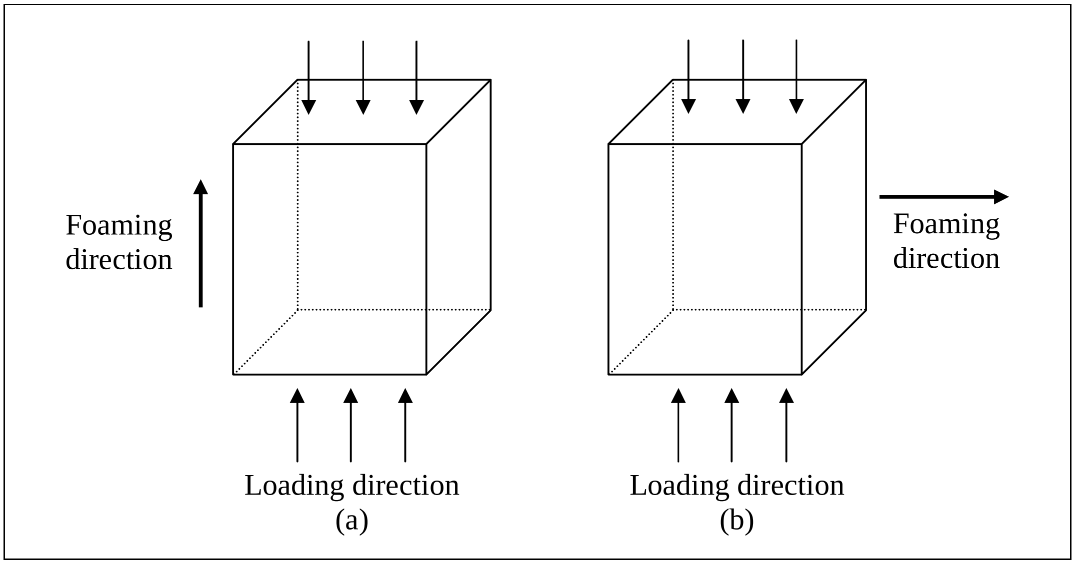


Figure 3.2 Schematic of the compression loading:
(a) parallel to foaming direction and (b) perpendicular to foaming direction

After the compression test, the specimen was left for more than 2 hrs before the compression test was repeated with the foam cells oriented in the direction perpendicular to foam rise as shown in Figure 3.2 (b).

3.3 RESULTS AND DISCUSSION

3.3.1 Polyol mixture of glycolysed PET

3.3.1.1 Viscosity

Glycolysed PET which was obtained in Chapter 2 is a highly viscous liquid especially at room condition where the temperature is 25 °C. Even though it became thin liquid above 50 °C, it is quite difficult to maintain the high temperature or handle the viscous component in the blending system of PU. Therefore, viscous liquid of glycolysed PET has been mixed with a commercial polyether polyol to help reducing the viscosity and ease the handling process of the blending.

Viscosity is an important parameter in defining the ease with which the polyol and isocyanate component can be mixed and adhere with the formulation. Graph of viscosity values versus glycolysed PET/polyol FA-703 mixture is shown in Figure 3.3 where glycolysed PET can be mixed with 30-60% of polyether polyol. Up to 60-80% of the glycolysed PET are miscible with 40-20% of polyol FA-703.

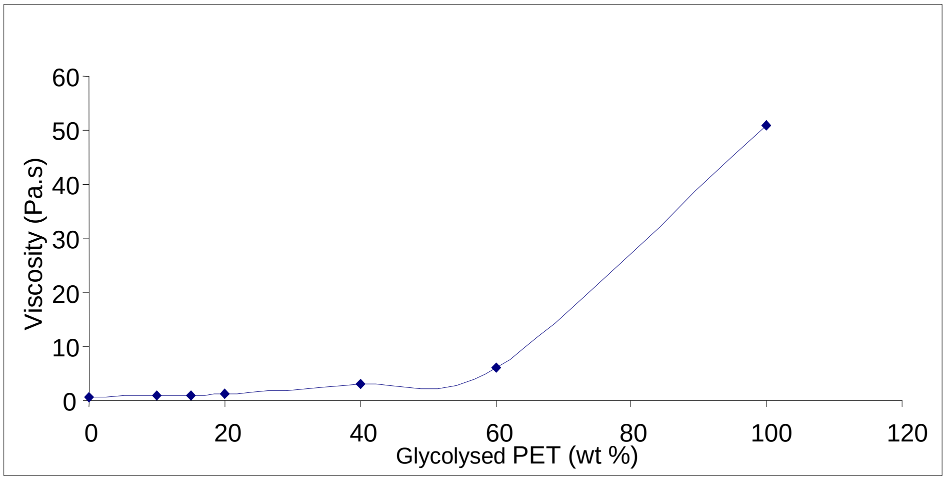
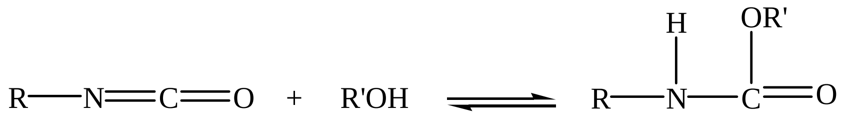


Figure 3.3 Effect of variation of glycolysed PET in the polyol mixture on viscosity

Since the glycolysed PET obtained was more viscous (about 50 Pa s) and was quite difficult to flow, blending it with polyether polyol which has low viscosity (0.6 Pa s) helps to reduce the viscosity of glycolysed PET and ease the handling process. Besides, the isocyanate was also chosen so as to have low viscosity in the range of 0.15-0.22 Pa s at 25 °C to facilitate the preparation of PU foam. Polyol and isocyanate are not instantaneously miscible when initially mixed, but rapidly become fully miscible when some urethane reactions have occurred (Figure 3.4). Moreover the mixing technique is essential and in this work, stirring has been done in all directions of the mixture and not only pointed at the centre or base of the mixture. In addition, the high stirring by the speed stirrer helps to provide sufficient energy to the chemical stream to ensure good homogeneity.



$$R-N=C=O \;+\; R'OH \;\rightleftharpoons\; R-\overset{H}{\overset{|}{N}}-\overset{OR'}{\overset{|}{C}}=O$$

Isocyanate **Alcohol** **Carbamate (Urethane)**

H = hydrogen
C = carbon
N = nitrogen
O = oxygen
R = an attached
hydrocarbon group

Figure 3.4 Urethane reaction

3.3.1.2 Effect of hydroxyl value

Theoretically in the preparation of rigid foams, the preferred hydroxyl value of the polyol ranges from 250 to 1000 mg KOH/g, as determined by ASTM D2849A and this value is higher than hydroxyl value required for semi-rigid foams. If semi-rigid foam is to be prepared, hydroxyl value of polyol preferably ranges from 100 to 400 mg

KOH/g [1]. In this research, polyol FA-703 has hydroxyl number 33 mg KOH/g while glycolysed PET obtained has hydroxyl number 646 mg KOH/g. Even though the hydroxyl values for both of these polyols lie outside the above ranges, the average hydroxyl value of the polyol mixture which consists of the both polyols was kept in the range of the semi-rigid foam given above. Therefore, semi-rigid foam was successfully obtained.

That is also the reason why GP-1B has been used for polyol mixture instead of other batches of glycolysed PET. With reference to Table 2.6 in Chapter 2 and Table 3.5 below, hydroxyl value for other batches of glycolysed PET is higher than GP-1B. When they are mixed with the commercial polyol, the average hydroxyl value will be out of the range for semi-rigid foam except for GP-2A and GP-7 with hydroxyl values of 710 and 726 mg KOH/g respectively. All these polyol mixtures produced rigid foams where hydroxyl value of polyol mixture can be up to 424 mg KOH/g.

Table 3.5 Hydroxyl value of polyol mixture

Sample code	OHv (mg KOH/g)	
	Glycolysed PET	Polyol mixture*
GP-1B	646	340
GP-2A	710	372
GP-3B	805	419
GP-4	815	424
GP-5	796	415
GP-6B	774	404
GP-7	726	380

*Average of OHv calculated from glycolysed PET and FA-703 (33 mg KOH/g)

3.3.2 Formation of PU foam

The foam formulations designed in this work have successfully produced the semi-rigid foams. This was based on physical examination of its condition which was considerably harder than flexible foams. Figure 3.5 shows an example of PU foam produced through the cup rise foaming. The colors of foams are from white creamy to slightly yellowish when it wasstored for a few months.

Figure 3.5 Semi-rigid PU foams

3.3.2.1 Effect of materials used

Polyol mixture was formulated with suitable amount of catalysts and other additives before reacting with MDI to form foams as shown in Table 3.6. The amount of catalyst used is normally in the range from 0.01 to 5.0 pbw, preferably in the range from 0.2 to 2.0 pbw per 100 parts of polyol mixture [1]. The catalyst A33 used in this study was 0.7 pbw, which is within the range, and this amount is shown to be compatible with the system. Catalyst A33 is also important in the blending since the reaction of water and isocyanate is generally slow in the absence of the catalyst.

Table 3.6 Polyol formulation

Materials	Pbw per 100 parts of polyol		
	This work	Reference $_1$	Reference $_2$
Total polyol	100	100	100
Catalyst	0.7	0.2-2.0	0.1-12
Surfactant	2.4	0.5-2.0	1.4-3.2
Blowing agent	3.6	0.1-5.0	14-24

Reference $_1$ = *Dirckx et al.*, 1999
Reference $_2$ = *Coppola et al.*,1978

Surfactants or surface-active additive is used in the manufacturing of most PU foams. The silicon-based surfactant is preferably employed in a proportion from 1.4 to 3.2 parts per every 100 parts of total polyol [2]. This is to prevent the foam from collapsing when too little surfactant is used and to avoid foam shrinkage when too much of surfactant is utilised. In this study the desirable amount of surfactant was 2.4 pbw per 100 parts of polyol mixture. The surfactant helps in mixing the incompatible components and stabilizing the early stages of the reacting foam structure until sufficient polymerization has occurred to form a self-supporting polymer network. The most important function of the surfactant in this foam is bubble stabilization. To obtain the most efficient bubble stability and prevent coalescence the correct balance of foam reactivity and surfactant activity must be obtained. In most PU systems, the surfactant must act within a few minutes since if this balance is not optimized the surfactant will not be able to be effective and surface film rupture and defoaming can occur [3].

As for blowing agent, a variety of blowing agents are obtainable in the market. There are two fundamentally different types of blowing agent available, which are chemical and physical blowing agents. Physical blowing agents are low-boiling compounds which are evaporated by the heat of reaction like hydrochlorofluorocarbons (HCFCs). They are either mixed in with the polyol component or added separately.

However in this research, water was chosen as a chemical blowing agent. The use of water for gas formation is already well known. Water was added in an amount of 3.6 parts by weight (pbw) per 100 parts of polyol mixture. In particular, distilled water was utilised, as impurities may affect the foam reaction. The chemical blowing agent is formed during the course of the polyaddition reaction. Water which was added to the polyol reacts with isocyanate group, thus releasing carbon dioxide (CO_2) and causes the blow to happen. The initial reaction product is a carbamic acid, which breaks down into carbon dioxide and a primary amine. The amine will then react immediately with another isocyanate to form a symmetric urea [3]. Equation in Figure 3.6 shows the reaction of chemical blowing agents, water with the isocyanate.

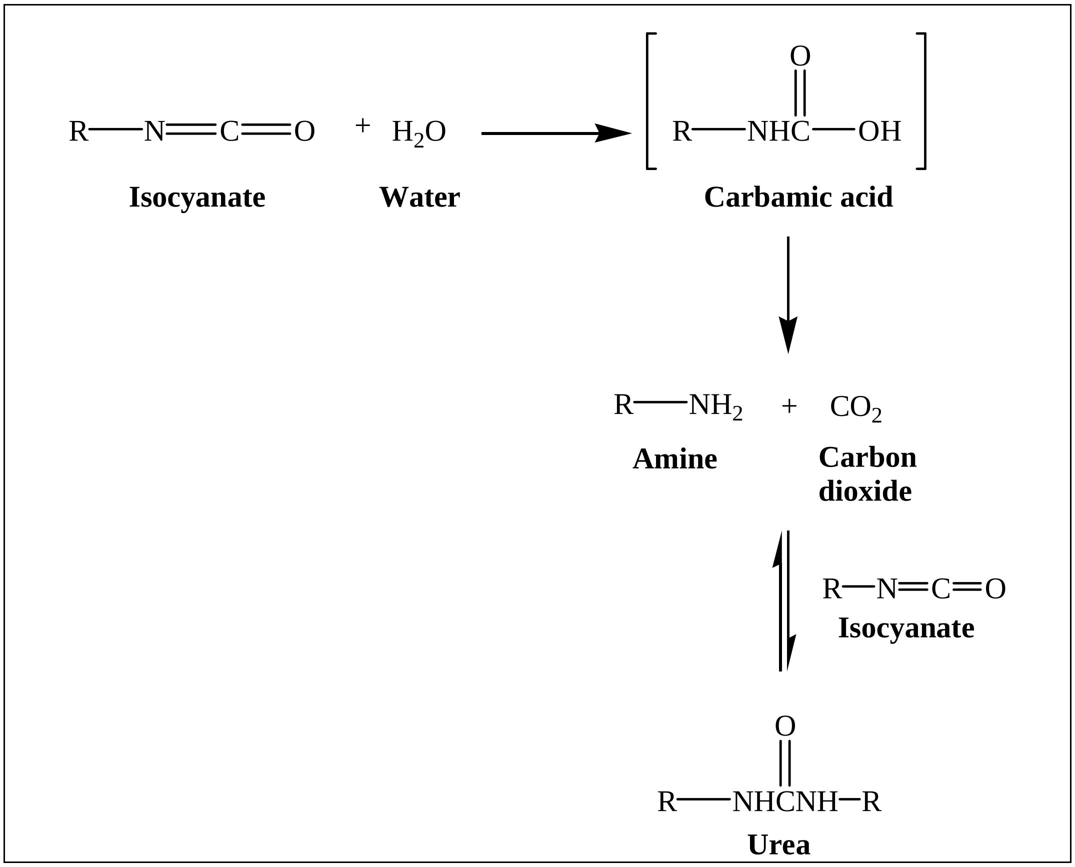


Figure 3.6 Water reactions with isocyanate

Due to the formation of carbon dioxide, the water reaction is frequently used as a blowing agent as the level of blow can be tailored, simply by adjusting the amount of water in the formulation. However in this research, the amount of water has been fixed to 3.6 parts per 100 pbw polyol as a constant variable while the other variables like isocyanate index were manipulated as shown earlier.

3.3.2.2 FTIR of PU foam

As described earlier, polyol mixture, isocyanate, amine catalyst and silicone surfactant are used as starting materials in the preparation of PU foam. Even though the foam is a complex mixture of these components, the isocyanate and polyol plays an important role in the reactivity and the functionality of the foam. The FTIR analysis is used to examine the common functional groups present in the PU foam. Figure 3.7 shows the overlaid spectra of the isocyanate, the polyol and the PU foam.

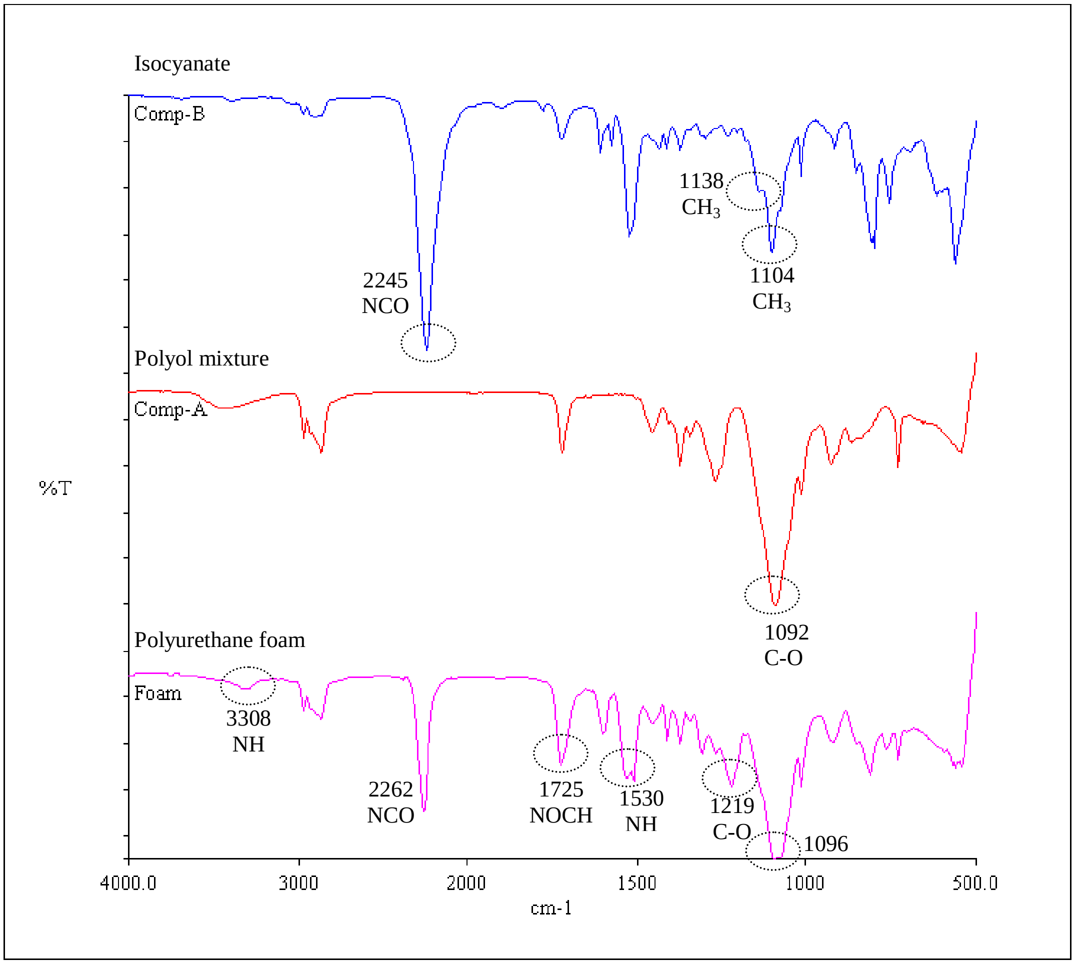


Figure 3.7 FTIR spectra of PU foam, polyol mixture and isocyanate

The characteristic band observed at 3308 cm^{-1} is weak and is assigned to NH stretching. Another band observed at 1725 cm^{-1} shows the existence of another functional group, the amide group, which is associated to the urethane linkage. This peak has medium intensity compared to small peaks observed in the spectra of isocyanate and polyol components. Appearance of 1725 cm^{-1} peak is also an indicator that formation of urethane (NOCH) has occurred. The peak at 1530 cm^{-1} shows the existence of N-H bending while peak attributed to C-O stretching can be seen at 1219 cm^{-1}. The isocyanate spectrum shows a strong peak at 2245 cm^{-1} which is assigned to NCO and it shows that the reaction with polyol mixture has occurred. However the intensity of the peak is reduced as seen in PU foam spectrum. At the same time the peak position is shifted to higher wavenumber at 2262 cm^{-1} peak as recorded in PU foam spectrum which is believed to be due to the un-reacted MDI.

Peng S. and Jackson P. (2000) had reported that absorptions of the carbonyl stretching for urethane was shown at 1730 cm^{-1}, aromatic reference at 1600 cm^{-1} and NCO peak at 2273 cm^{-1} [4]. This is comparable to the PU foam spectrum in Figure 3.7 which shows urethane peak at 1725 cm^{-1}, aromatic reference at 1599 cm^{-1} and NCO peak at 2262 cm^{-1}. FTIR spectra during foaming process are shown in appendix Figure A3-1 and recorded at 1, 3, 7, 12, 30, 40, 63, 80 and 90 min from the initial part of PU blending. Spectra obtained show decrease in intensity of NCO peak at 2262 cm^{-1} and increase in urethane peak at 1725 cm^{-1} due to cross-linking reaction. The changes are obviously seen when spectrum at the first and 90th min are overlaid as shown in Figure 3.8.

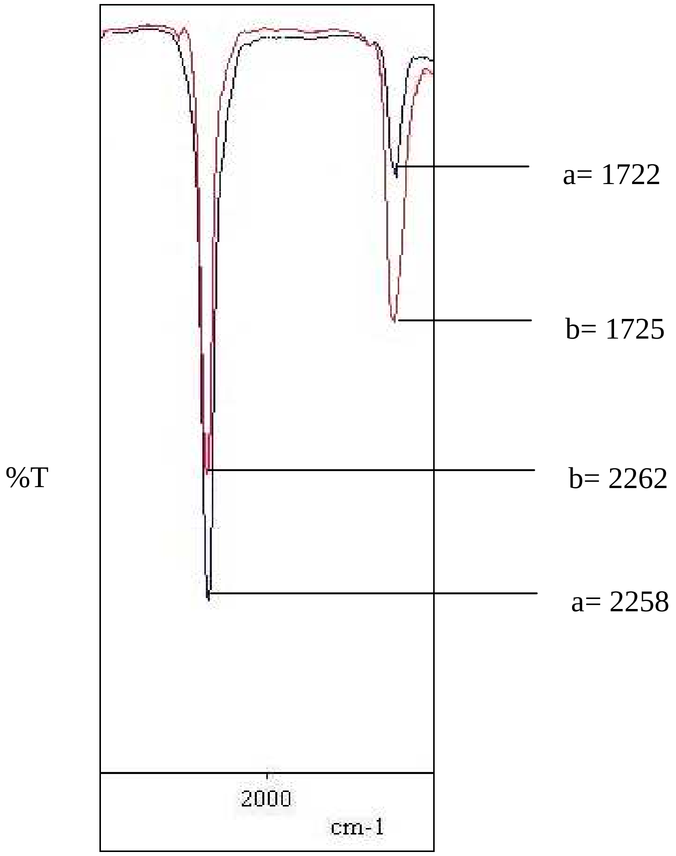


Figure 3.8 FTIR spectrum of foaming process at a) 1 minute b) 90 min

3.3.2.3 Cell structure of the PU foam

A thin slice of foam was cut out from the core and was observed under optical microscope and the photos obtained are shown in Figure 3.9. Various sizes of pentagon and hexagon shaped cells could be seen. Generally, semi-rigid foam produced does not form appreciable skin during the foaming process and they tend to have open-celled, like flexible foams. According to Leppkes (2003), throughout the last stage of the foaming operation in flexible PU foams, the cell walls rupture and the polymer material retracts to form a web of elastic strands. The elastic web structure is responsible for the cushioning effect of the foam produced. The cushioning effect is observed in the foams produced from this work. Infact, the foam slowly returns to its original position after impact.

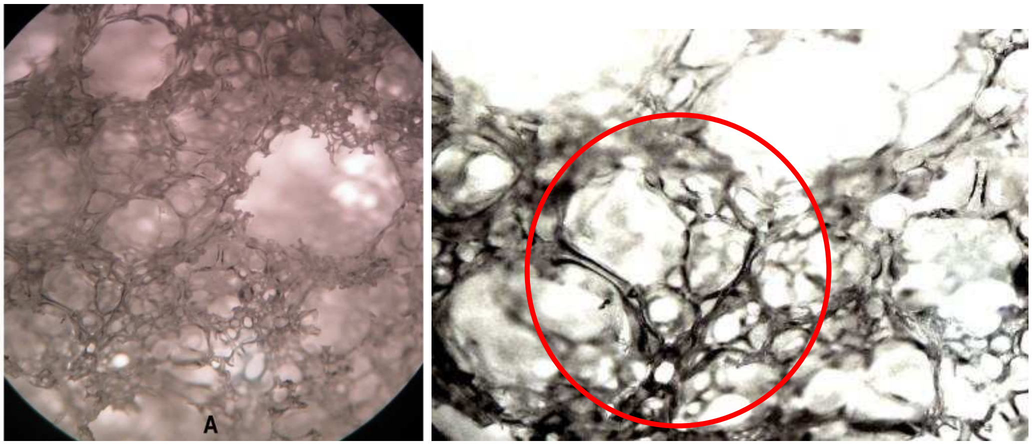


Figure 3.9 Optical microscope images of the semi-rigid foam

3.3.2.4 Density and compression strength

Semi-rigid foam has some flexibility compared to rigid foam. Thus the foam does not chip or crack easily, yet it still has some load bearing property that resists compression forces. Compression stress of the semi-rigid foam obtained was calculated by dividing the compressive force with the initial surface area of the test specimen.

Top core of foam and its bottom core were compared in term of their density and compressive strength as shown in Figure 3.10 (a) and (b) respectively. Densities of test specimens were measured before the compressive test.

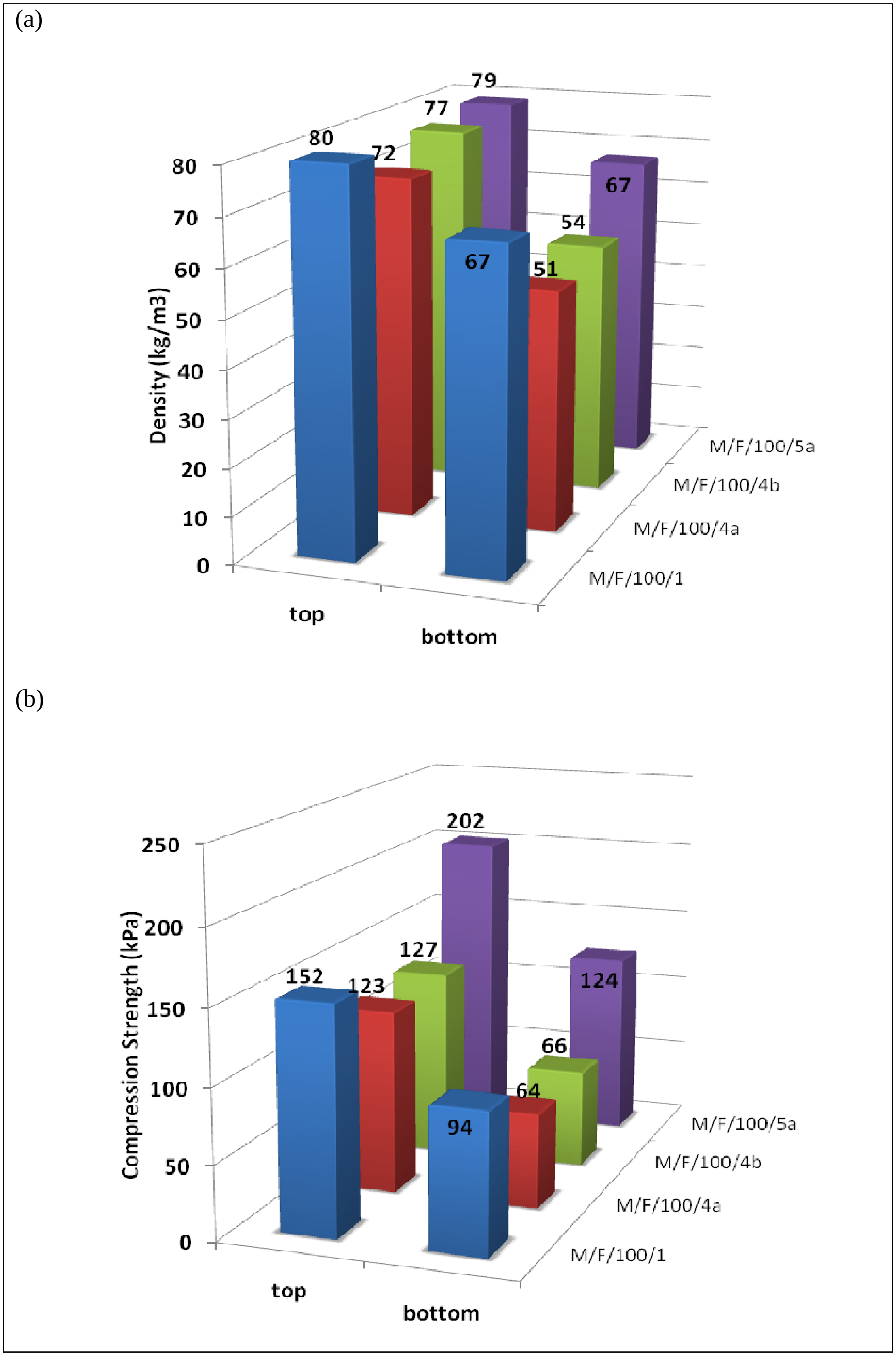
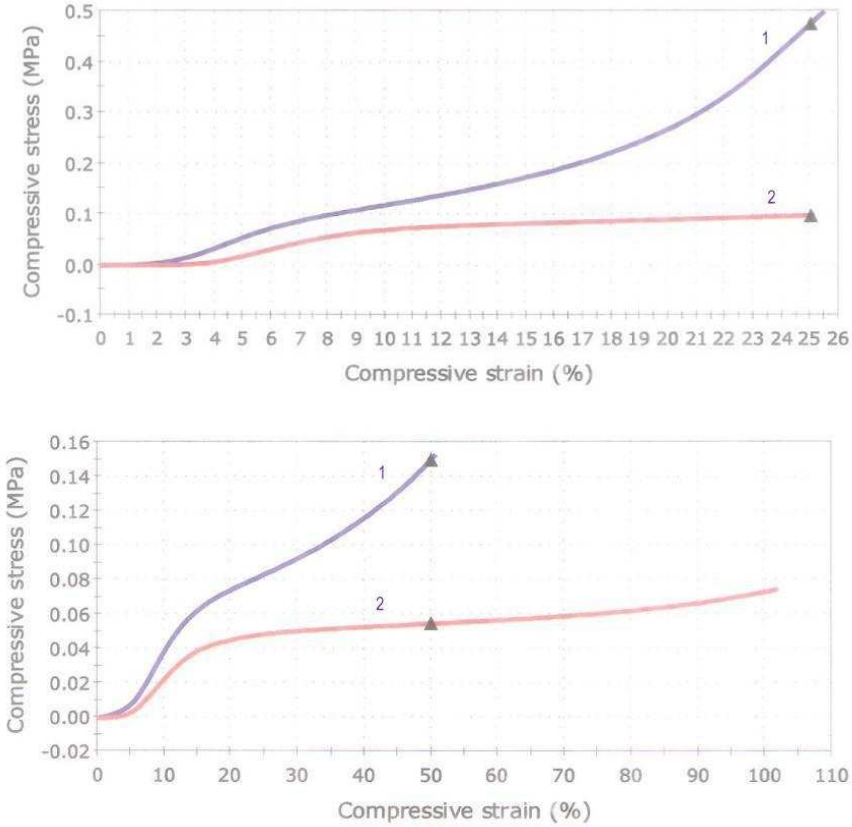


Figure 3.10 Effect of top and bottom core of PU foam on density (a) and compression strength (b)

The graph shows that five batches of PU foams have been tested and all of them show a similar trend where top core area has higher compression stress value and density compared to bottom core area (Appendix, Table Ap3-2). The graph also shows that density and compression strength for each of samples code differ from each other because of each samples code has different percentages of glycolysed PET in the polyol component for foam formation.

In the investigation on effect of cells orientation on compression stress, Figure 3.11 (a) shows the compressive stress-strain curve of one of the samples.



(a)

(b)

Specimen #1 = foam cells oriented in the direction of parallel to foam rise
Specimen #2 = foam cells oriented in the direction of perpendicular to foam rise

Figure 3.11 Stress-strain curves of foam cells position at (a) 25% and (b) 50% compressive strain

At 25% of compressive strain, compressive stress of the foam cells oriented in the direction parallel to foam rise is 0.47 MPa, higher than the compression of foam cell oriented perpendicular to foam rise (0.1 MPa). The situation remains unchanged even when the compressive strain has increased up to 50% as shown in Figure 3.11 (b). All of the graphs obtained in this work agrees well with the correlation that when the foam cells were oriented in the direction of foam rise, the compression stress parallel to rise was much higher than the one perpendicular to foam rise [3]. The semi-rigid foams tend to be anisotropic. During the initial foaming, the small nucleation bubbles are spherical, but as they expand under the increasing pressure as a result of the generation of carbon dioxide, they tend to elongate in the direction of foam rise. The fewer and larger the size of the bubbles, the greater is their elongation.

In Xu and friends (2011) study on mechanics of solid and liquid foams, they had discussed the cell model as shown in Figure 3.12, (a) shows a model in foam rise direction and (b) in perpendicular to foam rise direction.

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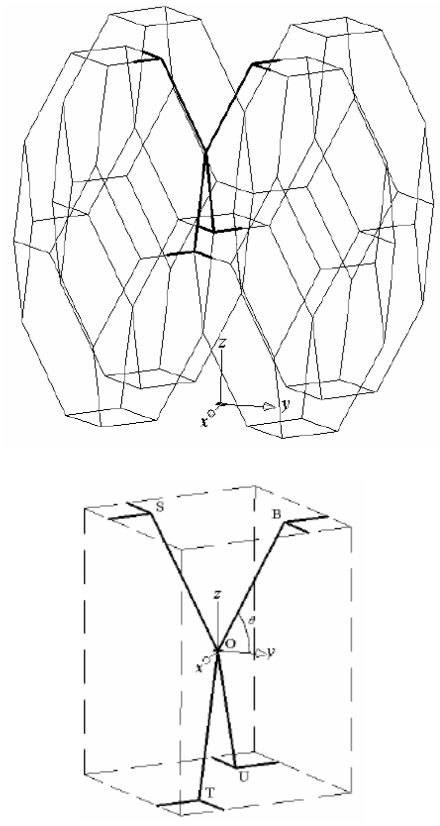
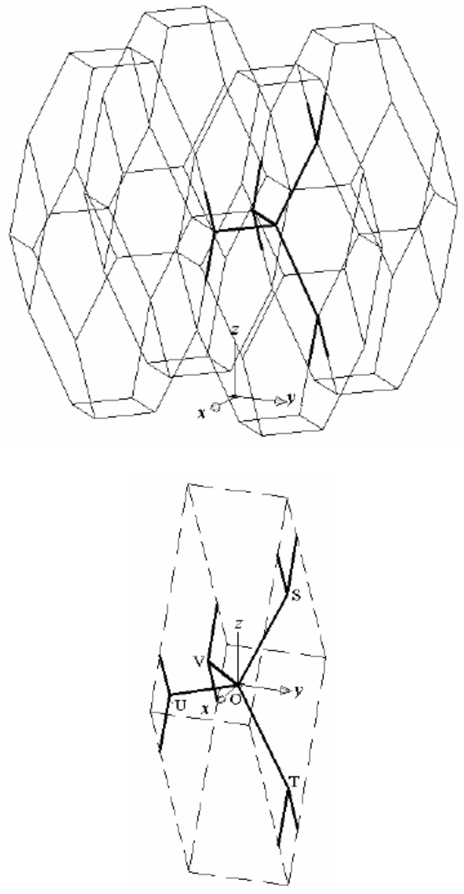
<td>

(a) Foam direction</td>
<td>

(b) Transverse direction</td>
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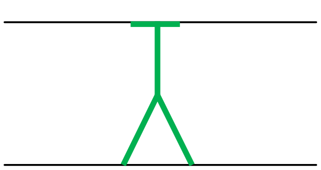
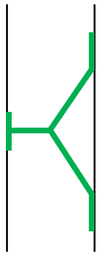
<td>
1/8 cell loaded in foam rise direction</td>
<td>
1/8 cell loaded in transverse direction</td>
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Figure 3.12 Cell models of foams. Xu (2011)

According to this model study, differences in compression stress are the result of deformation modes associated with loading directions. In the direction of foam rise, localized gross buckling of cell layers dominates followed by propagation to the rest of the foam sample, while perpendicular to foam rise direction, more uniformly-distributed deformation prevails.

3.3.2.5 Effect of isocyanate index

The effect of isocyanate index is important in PU foams and can be used to tailor the specific physical properties. As such how the knowledge on index affects the foam is important to be sure that slight errors in the index will not have major negative effects on the physical properties. To study the effect of isocyanate index on compression strength and density of the semi rigid foam obtained, variation of the isocyanate index was done in a range of 95 to 120. An isocyanate index of 120, sometimes written as 1.20, indicates that there is a 20 per cent excess of isocyanate. The correlation between compression strength and density of the foams when the isocyanate is varied from 95 to 120 is shown in Figure 3.13. Amount of isocyanate used was increased with the increase of their isocyanate index. For each index, the amount of glycolysed PET utilised in the mixture of polyol has been fixed to 17% per total polyol. Based on Table 3.3 as shown earlier, the formulation of PU foam at isocyanate index 100, 15.46 g of MDI is used in the foam blending. At isocyanate index of 110, isocyanate used is increased 10% from 15.46 g and become 17.01 g. As well as at isocyanate index of 120 where the blending system has 20% excess of isocyanate.

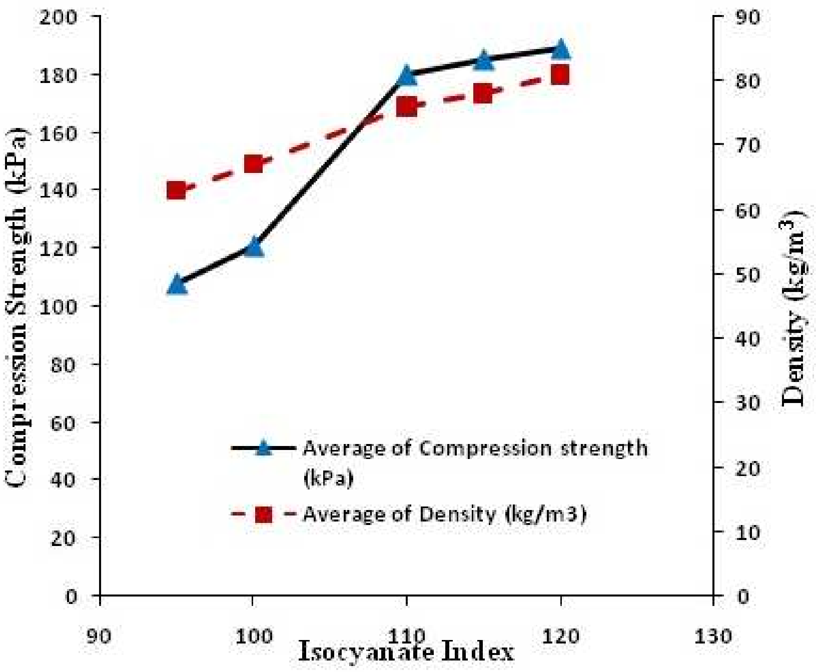

Figure 3.13 Effect of isocyanate index on the compression strength and density of the foam

Compression strength of the foam slightly increases when the isocyanate index increases from 95 to 100 but obviously higher when the isocyanate index is further increased to 110, 115 and 120. The increase in compression strength with the increasing of isocyanate index is due to the polymer matrix becoming more highly crosslinked and thus more resistant to compression. It is worth mentioning that in this study, although foam produced with isocyanate index of 120 shows higher compression strength, the foam found to be slightly brittle. This is reasonable as using a larger excess of –NCO usually tends to give higher strength but also a more brittle foam [5].

With regards to density of the foam, the increase is linear with increase in isocyanate index from 95 to 120. Apparently the more isocyanate used, the denser will be the foam. Higher addition of isocyanate in the foam results in more volumetric fractions, thus increase in foam density. Besides, the foam also becomes harder with the increasing of isocyanate index. There is however, a point beyond which hardness does not increase further and other physical properties begin to suffer [6]. Increasing in isocyanate index also affect the reactivity of foam formation. As shown in Table 3.7, even though the differences are small, cream time is reduced as well as gel time decreases while rise time increases with increasing index value.

Table 3.7 Reactivity during foam formation

Foam reactivity	Isocyanate Index			
	95	100	110	120
Cream time (s)	115	112	108	105
Gel time (s)	420	415	413	382
Rise time (s)	495	498	501	539

The decreasing tendency of gel time is probably due to the increased mixture mobility and allophonate reactions (Figure 3.14), which are favored with more of the free isocyanate [7]. The presence of more un-reacted isocyanate also slows the rate of foam cure.

Figure 3.13 also shows that the compression strength is related to density of the foam where compression strength of foam increases with increasing density [3].

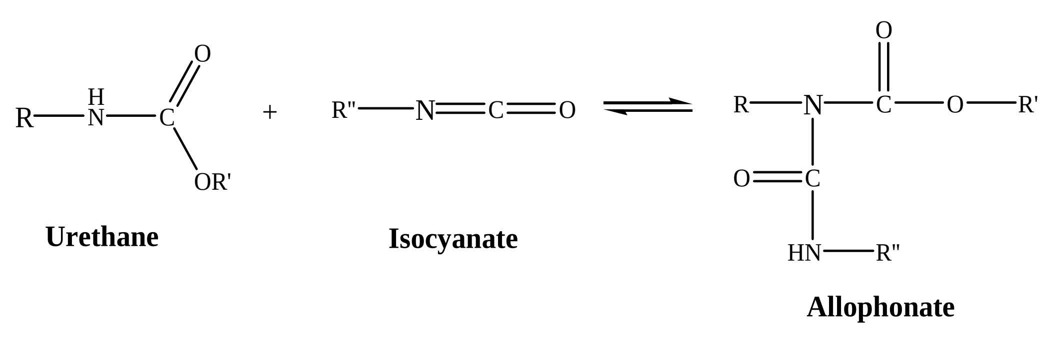

Figure 3.14 Allophanate reactions [3]

3.3.2.6 Variation in percentages of glycolysed PET

Percentage of glycolysed PET in polyol mixture for PU foam was varied from 0% to 100% of the total polyol and for each batch, isocyanate index was fixed to 100. The results of compression strength and density of the foams are shown in Figure 3.15. The polyol mixture consisting only of polyol FA-703 with no glycolysed PET shows the lowest compression strength of 7 kPa and the foam produced is totally flexible. When glycolysed PET has been introduced to the polyol component, the compression strength is obviously increased. With only 10% of glycolysed PET used in the polyol component, the compression strength has jumped up to 99 kPa and continues to increase with the increase in the percentage of glycolysed PET. When the percentage of glycolysed PET is more than 40%, the process of handling PU blending is found to be more difficult because of its high viscosity at room temperature and when 100% of the glycolysed PET has been used as the polyol component, mixing with isocyanate did not lead to proper blending. The viscosity can be reduced easily by heating the glycolysed PET to 60°C followed by blending with isocyanate. When the temperature of polyol component increases, gelling and blowing rate during foaming are not balanced. Gelling rate became faster and at the same time cell opening was delayed until the end of the rise time. As a result, a pneumatic foam or foam with too little cell opening was obtained. This situation is obviously unacceptable. In addition, cell opening is related to the process parameters such as temperature and liquid flow. And to produce the stable foams, cell opening should take place when most of the blowing gas has been produced [3].

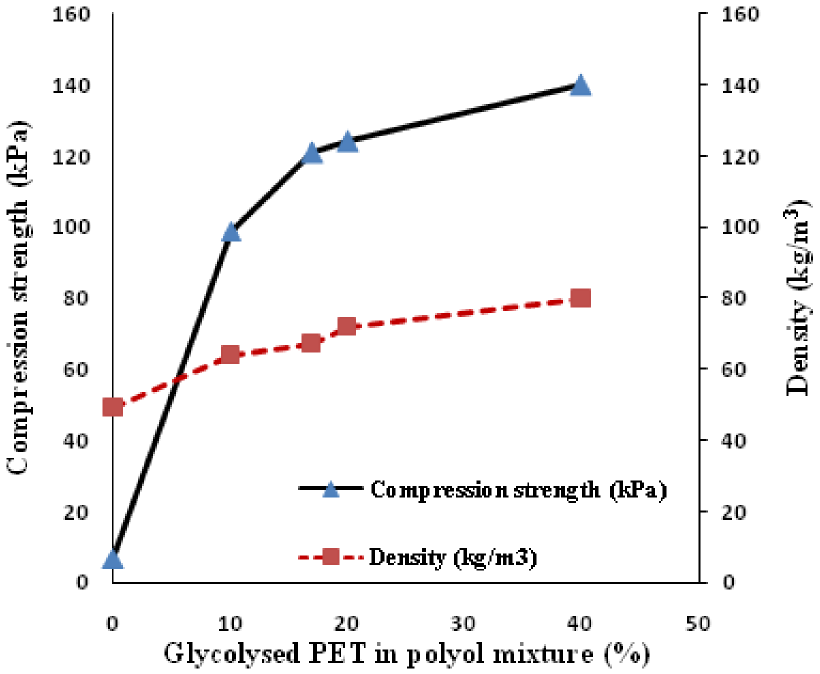

Figure 3.15 Effect of percentage of glycolysed PET on the compression strength and density of the foam

As described earlier, besides the additives used for foam synthesis, the component of polyol has big influence on the properties of the foams. As such the polyol component was blended using glycolysed PET and commercial polyol FA-703. All of the PU foams produced using this polyol mixture has densities ranging from 64 to 80 kg/m^3 (Figure 3.15). This is higher than the density of foam in which the polyol component does not contain the glycolysed PET where the density of the batch is 49 kg/m^3. Figure 3.15 shows that the density is continuously increased with the increasing of percentage of glycolysed PET in the polyol mixture.

3.4 CONCLUSION

Mixture of polyols for use in the preparation of PU foam comprising of 10-40% by weight of glycolysed PET and 60-90% by weight of commercial polyol FA-703 has successfully been made miscible and has reduced the viscosity of glycolysed PET to ease the handling process.

The process for preparing PU foams undertaken comprises of steps of combining certain parts of glycolysed PET and FA-703 polyol with a catalyst, surfactant and water as the blowing agent. The use of glycolysed PET as part of the polyol mixture with polyol FA-703 has increased the hydroxyl value of the polyol FA-703 indirectly. Thus PU foam produced from this polyol mixture is semi-rigid instead of flexible foam if no glycolysed PET is used. The density and compression strength of PU foam are obviously increased with the present of glycolysed PET.

Density of semi-rigid PU foams using the polyol mixture found to be in the range of 50-90 kg/m^3 while compression strength is in the range of 90-210 kPa. The foam density is comparable with the previous study done by Dirckx (1999) whereas compression strength of foams from this work is close to the range value produced by Eisen (2001).

Table 3.8 Comparison of foam density and compression strength with previous study

	Density (kg/m^3)	Compression strength (kPa)
This work	49-90	90-210
Reference [1]	*20-120*	*212 (at 10%)*
Reference [2]	*25-100*	-
Reference [3]	*400-600*	*80-300*

1= Dirckx (1999) [1]
2= Sakai (2001) [8]
3= Eisen (2001) [9]

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