Appendix A:

Appendix_Chapter 2_2.2.1

1) PET Flakes

Post-consumer soft drink clear PET bottles were cleaned and washed with detergent, dried in room temperature before shredded into PET flakes by rapid granulator.

Figure A2-1 PET flakes from post-consumer PET bottles

Appendix_Chapter 2_2.2.2

2) Experimental setup of glycolysis process

Glycolysis reaction was carried out in a laboratory-scale round bottom flask as a reactor, which equipped with a thermometer, propeller stirrer, and reflux condenser as well as heating mantle.

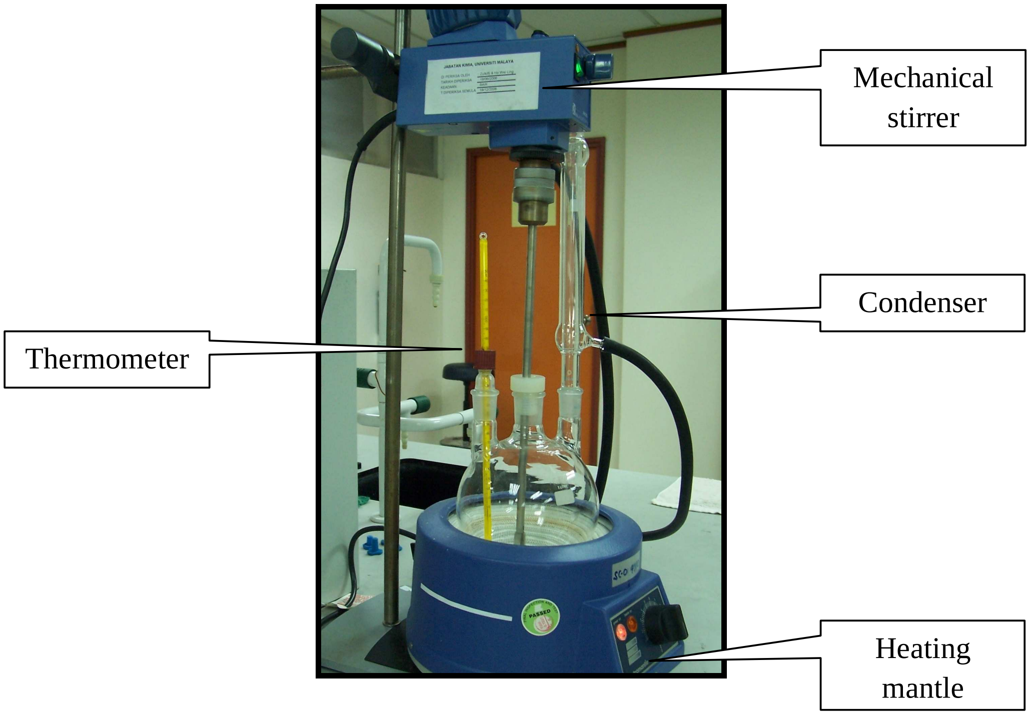


Figure A2-2 Experimental setup of glycolysis process

Appendix_Chapter 2_2.2.3

3) Example calculation for preparation of glycolysed PET.

As described in Chapter 2 part 2.2.3, Table 2.3 shows the example calculation in the preparation of glycolysed PET. When 96.1169 g of the PET reacted with 92.4570 g of glycerol, this will introduce 2.9825 equivalent weight of hydroxyl group into 188.5739 g of the product and considered as the hydroxyl excess.

Table Ap2-1 Example calculation in the preparation of glycolysed PET

Materials	Wt. (g)	EW	eB
PET	96.1169	-	-
Glycerol	92.4570	31	2.9825
Total	188.5739	-	-

*Formula weight of PET repeating unit = 192 g/mol

Equivalent weight of glycerol = 92/3 g/equivalent

Therefore, expected hydroxyl value can be calculated as follows:

Expected hydroxyl value = (56100 x hydroxyl excess) / ΣW

= (56100 x 2.9825)/188.5739

= 887.28 mg KOH/g sample

Expected OHv is used as a guide in the determination of hydroxyl value by titration method.

Appendix_Chapter 2_2.2.4

4) Determination of Hydroxyl value, OHv.

The procedure are as follows:

(i) Standardisation of sodium hydroxide

Potassium hydrogen phthalate ($KHC_8H_4O_4$) was dried in the oven at 100 °C for two hours and was allowed to cool in desiccator before used. 4.0±1.0 g of potassium hydrogen phthalate was weighed directly into a conical flask. 200 ml of water that was free of carbon dioxide and a few drops of phenolphthalein indicator solution (10 g/L, 1 g of phenolphthalein in 100 ml of pyridine) were added into the flask. The mixture was swirled until the salt was dissolved and titrated to a pink end point with the 1.0 N NaOH solution using a 50 ml burette.

(ii) Preparation of phthalic anhydride solution

111 to 116 g of phthalic anhydride was weighed into 1 L brown bottle. 700 ml of distilled pyridine was added to phthalic anhydride and was shaken vigorously until dissolved. Reagent was left overnight before used.

(iii) Procedure of hydroxyl value determination

The amount of sample, as calculated below, was weighed into the flask.

$$\text{Sample size, g} = 561 / \text{estimated OH number}$$

25 ml of phthalic anhydride solution was transferred to the flask and swirled to result in a solution of the sample. The flask was equipped with air condenser and heated in an oil bath at 115±2 °C for one hour. After the heating period, the mixture was left to cool to

room temperature before washing down the condenser with 50 ml of pyridine. It was then titrated with 1.0 N NaOH solution to the pink end point that persisted for at least 15 seconds. A blank solution was run in a same manner where sample was omitted. The hydroxyl value was calculated using the following formula:

$$\text{Hydroxyl number (mg KOH/g)} = \frac{[(A - B)\ N \times 56.1]}{W}$$

Where A is the volume (ml) of sodium hydroxide required for the titration, B is the volume (ml) of sodium hydroxide required for the blank, N is the normality of the standardised sodium hydroxide solution and W (g) is the weight of sample used.

Table Ap2-2 OHv calculation of glycolysed PET (GP-1B)

Materials	Wt.(g)	EW	eA	eB
PET	135.0723	-	-	-
Gly	86.0457	31	-	2.7757
Total	221.1180		-	-

Excess OH = 2.7757 equivalent

1) Expected OHv = 704.2247 mg KOH/g sample

2) Sample size = 0.7966 g

3) NaOH (1.0 M) Standardization

$KHC_8H_4O_4$	Burette readings	NaOH

		(ml)		(ml)		
	Wt. (g)	Initial	Final		Normality	N_{Ave}
A	2.0287	15.70	25.50	9.80	1.0138	
B	2.2191	25.50	36.30	10.80	1.0062	1.0100

4) OHv Determination

		Burette readings (ml)		NaOH (ml)		
Blank	Wt. (g)	Initial	Final		OHv	$Blank_{Ave}$
B1	-	0.60	45.35	44.75	-	
B2	-	0.80	45.55	44.75	-	44.75

		Burette readings (ml)		NaOH (ml)		
Sample	Wt. (g)	Initial	Final.		OHv	OHv_{Ave}
S1	0.7987	0.80	36.50	35.70	642.02	
S2	0.7978	2.50	38.10	35.60	649.84	
S3	0.8010	11.60	47.20	35.60	647.25	646.37

5) Deviation % = -8.21

∴ Actual OHv is 646.37 mg KOH/g

This value is 8% lower than the expected hydroxyl value

5) Determination of moisture content

Water content of the glycolysed PET was determined by Karl Fisher titrator, DL 31, with electrode DM 143-SC from Mettler Toledo as shown in Appendix A-3. Weight of sample used was in range of 0.4 to 1.4 grams and was ensured to be homogenized before the test.

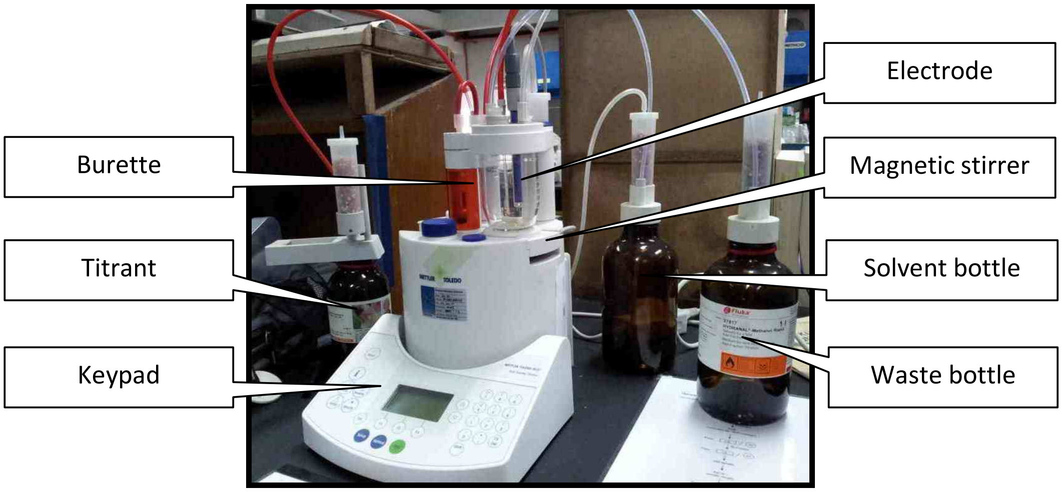


Figure A2-3: The Karl Fischer titrator

6) Determination of acid value

Standardisation of potassium hydroxide solution was carried out prior to the determination of acid value. Potassium hydrogen phthalate ($KHC_8H_4O_4$) was dried in the oven at 100°C for two hours and was allowed to cool in desiccator before use. 0.8 ± 0.1 g of potassium hydrogen phthalate was weighed directly into a conical flask. 100 ml of water that is free of carbon dioxide and a few drops of phenolphthalein indicator solution (5 g/L, 0.5 g phenolphthalein in 100 ml of a mixture of equal volumes of water and ethyl alcohol) were added into the flask. The mixture was swirled until all the salt has completely dissolved before titrated with 0.08 N of potassium hydroxide to the first appearance of permanent pink color.

In order to determine the acid number of the glycolysed PET, about 1 g of the glycolysed product was weighed accurately into a conical flask. The sample was then dissolved in 50 ml of titration solvent which is a mixture of toluene and ethanol 1/1 (v/v). The resulting single-phase solution is titrated at room temperature with 0.08 N alcoholic potassium hydroxide solutions to the end point as indicated by the color change of the added phenolphthalein. Each polyol was titrated twice and the average value was reported. A blank titration was also carried out. Theoretical calculation of the acid number, in milligrams of KOH/gram of sample is shown below and an example of acid value calculation is shown in Table 2.7.

Theoretical calculation of acid number

i) Standardisation of potassium hydroxide solution

Normality, N of the potassium hydroxide solution was calculated as follows:

$$N = \frac{W}{(V \times 0.2042)}$$

Where, W = Weight of potassium hydrogen phthalate in g

V = Volume of the potassium hydroxide solution used for the sample titration in ml

ii) Determination of acid value

The acid number, Av is calculated by using the following formula:

$$Av = \frac{[(A-B)\ N \times 56.1]}{W}$$

Where, A = Volume of KOH solution required for titration of the sample in ml

B = Volume of KOH solution required for titration of the blank in ml

N = Normality

W = Weight of sample used in gram

Table Ap2-3 Example of acid value calculation of the glycolysed product

Potassium Hydroxide (0.1N) Standardization						
	Wt. (g)	Burette readings (ml)				
	$KHC_8H_4O_4$	Initial R.	Final R.	KOH (ml)	Normality	N_{Ave}
A	0.8081	0.10	46.30	46.20	0.0857	0.0857
B	0.8087	0.50	46.69	46.19	0.0857	
Av Determination		Burette readings (ml)				
Blank	Wt. (g)	Initial R.	Final R.	KOH (ml)	Av	$Blank_{Ave}$
B1	-	2.80	2.90	0.10	-	0.10
B2	-	2.90	3.00	0.10		
		Burette readings (ml)				
Sample	Wt. (g)	Initial R.	Final R.	KOH (ml)	Av	Av_{Ave}
S1	1.2135	5.30	6.40	1.10	3.96	
S2	1.3022	3.30	4.45	1.15	3.88	

S3	1.2210	5.20	6.30	1.10	3.94	3.9254

∴ Acid value = 3.9254 mg KOH/g

7) Thermogravimetric analysis (TGA)

Thermogravimetric measurement was carried out on a Perkin Elmer 4000, as shown below.

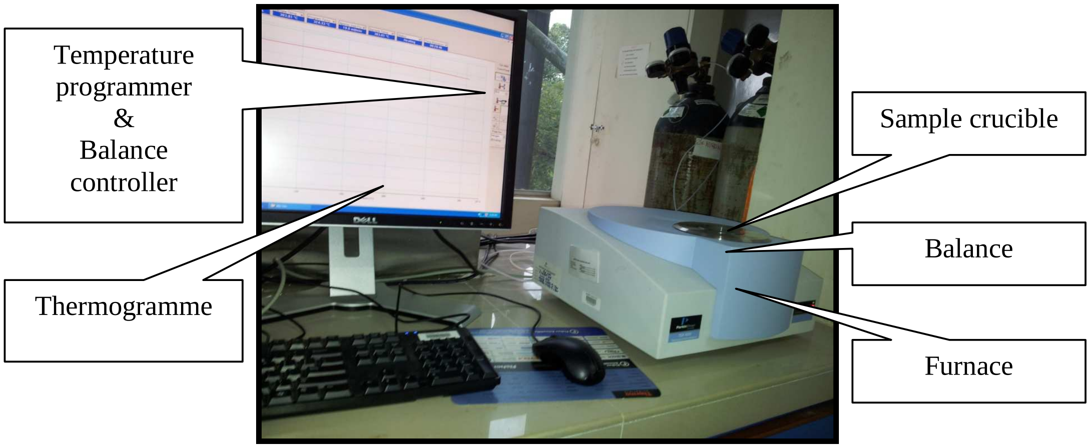
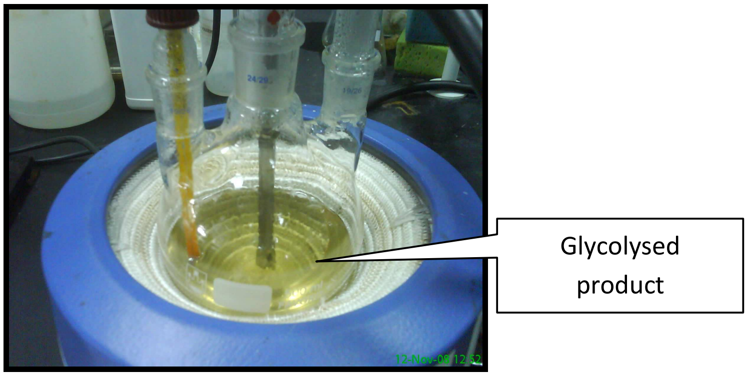


Figure A2-4 The Rheomatic TGA

Appendix_Chapter 2_2.3.1

8) Glycolysis of PET flakes

Glycolysed PET obtained from the glycolysis of PET flakes with glycerol is a brownish liquid which becomes viscous at room temperature.



Figur82e A2-5 Brownish liquid of glycolysed product

Appendix_Chapter 2_2.3.1.2

9) Activation energy, Ea

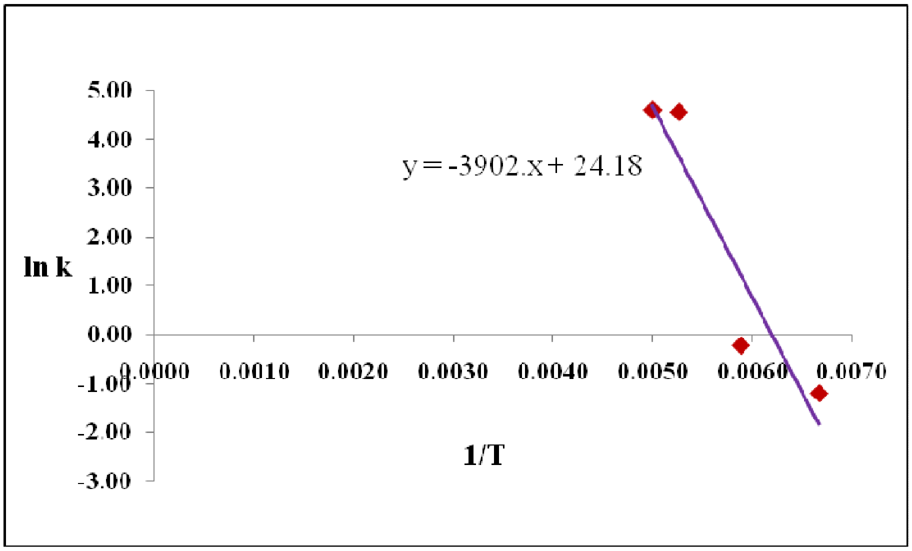


Figure A2-6 ln k vs. 1/T

Graph equation, y = -3902x + 20.14
m = -3902
-Ea/R = -3902
-Ea = -3902 (8.314 x 10-13 kJ/mol/K)
∴-Ea = 32.44 kJ/mol

Appendix B:

Appendix_Chapter 3_3.2.3.2

1) Example calculation of foam blending

Table below gives an example of the calculation of the weight of materials used for the formulation of the foam samples with isocyanate index of 100.

Table Ap3-1 An example of foam blending theoretical calculation for the formulation of PU foam at isocyanate index 100

M/F/100/1	OHv	Equivalent weight	Weight used (g)	Weight of MDI required (g)
Polyol GP-1B	646[a]	86.84	3.00	4.63
Polyol FA703	33[b]	1700.00	15.00	1.18
Surfactant			0.44	
Catalyst A33			0.13	
Blowing agent, H_2O		9.0	0.65	9.65
MDI		134[b]		

a = titration

b = manufacturer

Comp. A = 19.22

Comp. B = 15.46

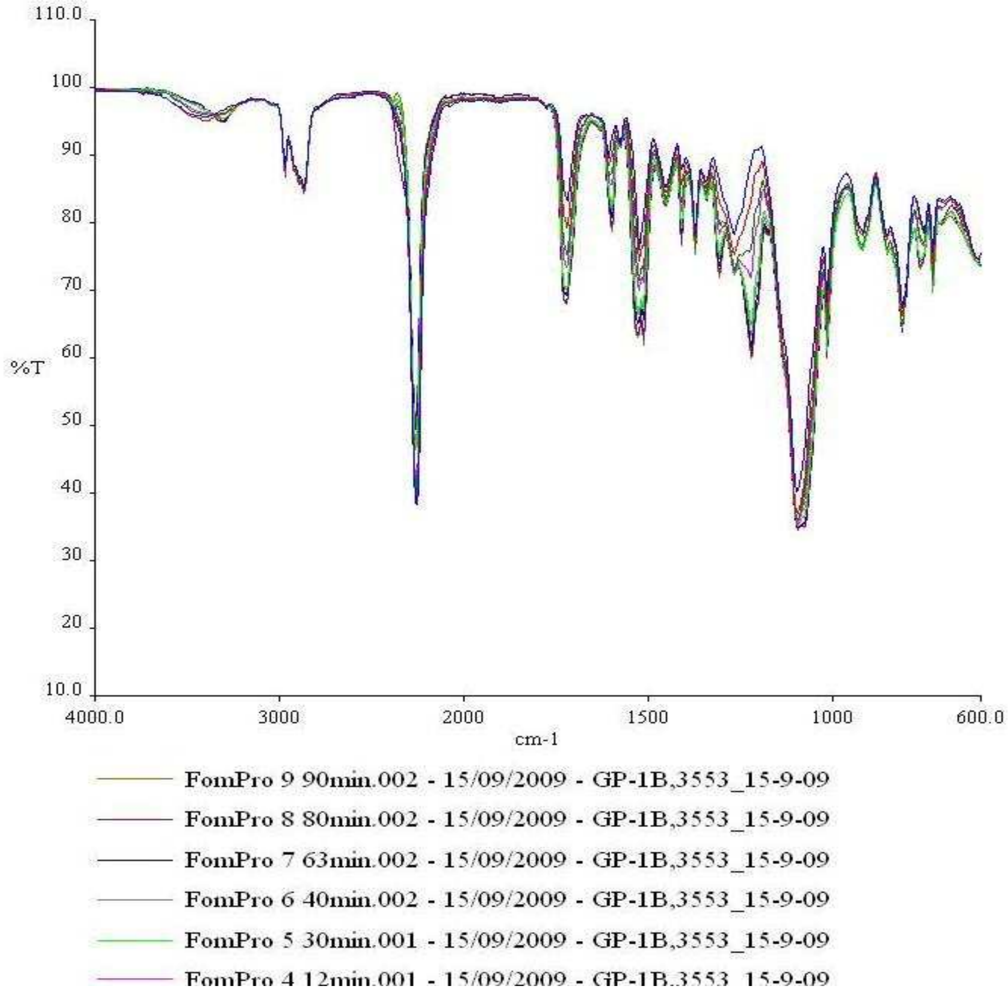
Table Ap3-1, continued

No.	Property	Formula
1	Equivalent weight	= (56100/OHv) or (Relative molecular mass/functionality)
2	Weight of surfactant	$= \frac{\text{(typical amount of surfactant)(weight of polyol used)}}{\text{typical amount of polyol}}$ = (2 x weight of polyol) / 100
3	Weight of catalyst	$= \frac{\text{(typical amount of catalyst)(weight of polyol used)}}{\text{typical amount of polyol}}$ = (0.5 x weight of polyol) / 100
4	Weight of blowing agent	$= \frac{\text{(typical amount of water)(weight of polyol used)}}{\text{typical amount of polyol}}$ = (4 x weight of polyol) / 100
5	Weight of MDI used	$= \frac{\text{(MDI equivalent weight)(weight of polyol)}}{\text{polyol equivalent weight}}$ = (134 x weight of polyol) / polyol equivalent weight

Appendix_Chapter 3_3.3.2.2

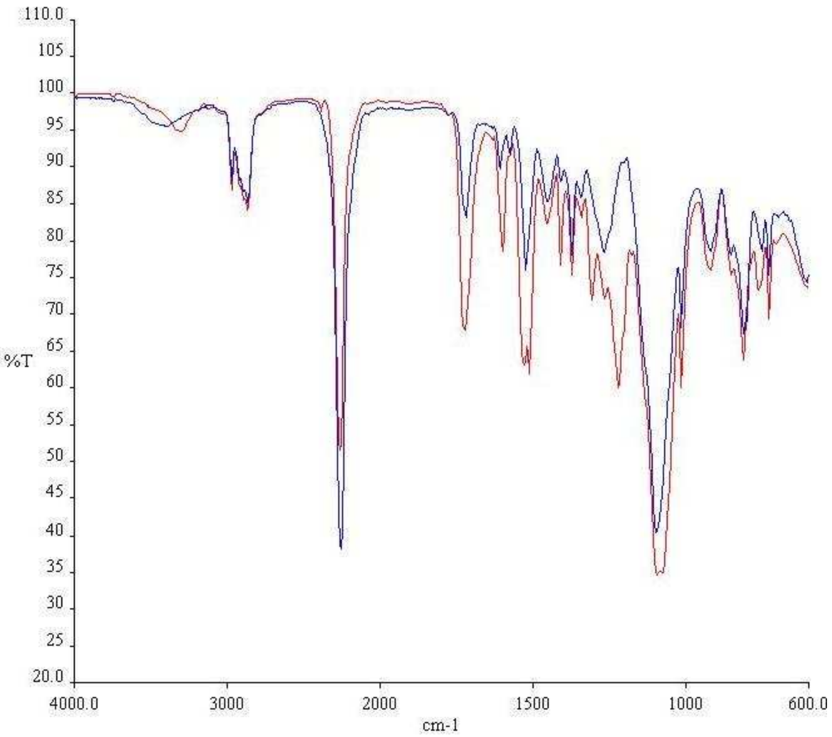
2) FTIR during foaming process

FTIR spectra during foaming process are shown in Figure A-7 (a) recorded at 1, 3, 7, 12, 30, 40, 63, 80 and 90 min from the initial part of PU blending and (b)



(a)

Figure A3-1 FTIR spectra during foaming process (a) and (b)



(b)

Figure A3-1, continued

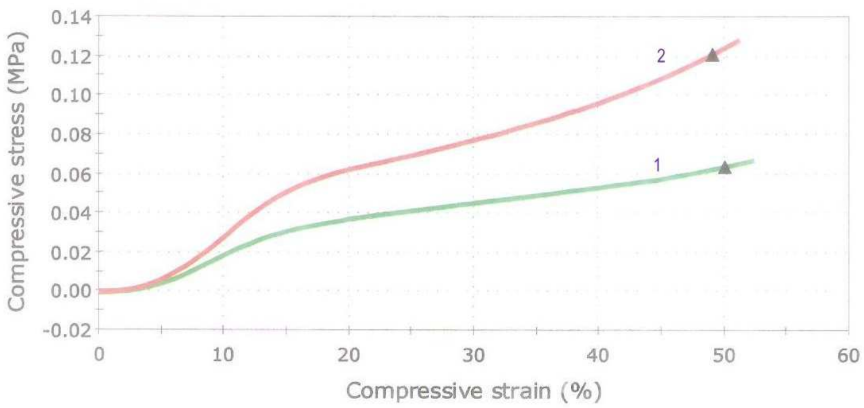
Appendix_Chapter 3_3.3.2.4

Table Ap3-2 Effect of top and bottom core of foams on their density and compression strength

Samples code		Density (kg m^{-3})	Compression strength (kPa)
M/F/100/1	i)	80	152
	ii)	67	94
M/F/100/4a	i)	72	123
	ii)	51	64
M/F/100/4b	i)	77	127
	ii)	54	66
M/F/100/5a	i)	79	202
	ii)	67	124

Note: i) top core, ii) bottom core

Figure shows the compressive stress (MPa) versus compressive strain (%) of top core and bottom core samples from the sample code M/F/100/4a.



Specimen #1 = bottom core sample

Specimen #2 = top core sample

Figure 3.10 Stress-strain curves of top core and bottom core of PU foams.