

# Synthesis and Characterization of Flexible and Rigid Polyurethane Foam

Shoaib Suleman<sup>1,2\*</sup>, Shahzad Maqsood Khan<sup>2</sup>, Tahir Jamil<sup>2</sup>, Waqas Aleem<sup>1</sup>, Muhammad Shafiq<sup>2</sup>,  
Nafisa Gull<sup>2</sup>

<sup>1</sup>Department of Chemical Engineering, Universiti Teknologi PETRONAS, Tronoh Perak, Malaysia

<sup>2</sup>Department of Polymer Engineering & Technology, University of the Punjab, Lahore, Pakistan

\*Email: shoaibmalik1 {at} live.com

**ABSTRACT---** Polyurethanes are versatile materials used widely in many applications. Annual production of polyurethanes is increasing day by day. The most important application of polyurethane covering its major market is polyurethane foam. Flexible and rigid foams are two major types of polyurethane foam used widely. Flexible and rigid foam samples were synthesized on lab scale by cup foaming. All samples were characterized by finding density of each sample. Cream, gel and rise time were also estimated for each sample. The chemical compositions of all polyurethane foam samples were characterized by FTIR analysis.

**Keywords---** Polyurethanes, Flexible and rigid polyurethane foam, Cup Foaming

## 1. INTRODUCTION

Polyurethanes are broad class of materials used widely in many applications. Polyurethanes are also written as PUR. Polyurethanes also called as urethanes are characterized by urethane linkage -NH- C (=O) - O - . This linkage is formed due to the reaction of isocyanate group with hydroxyl group[1]. Polyurethanes are discovered by Otto Von Bayer & co- workers in 1937. The characteristic structure of urethanes is given as:

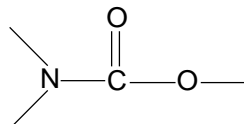


Figure 1: Structure of Polyurethane[1]

And they can be considered as esters or amide esters of carbonic acid. The polyurethanes are also sometimes called as urethanes only and they are also called as isocyanate polymers. They are synthesized by the reaction of polyfunctional hydroxyl compounds with polyfunctional isocyanates. The structure of polyurethane formed from di hydroxyl compound and di isocyanate is given as [2, 3]:

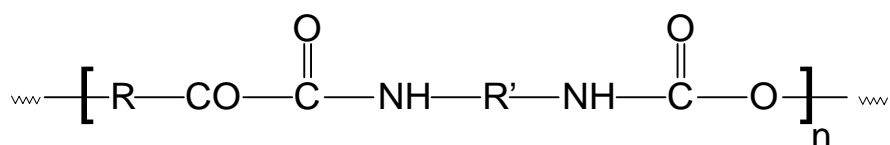


Figure 2: Polyurethane formed from di hydroxyl compound [1]

The total annual production of urethanes is about 8 million tons per year all around the globe and is increasing 4-5 % yearly [4]. Polyurethane is a versatile polymer having unique chemistry with excellent mechanical and optical properties and have good solvent resistance [5]. Polyurethane foam cover almost 29% of the total market of polyurethane [6, 7].

Polyurethane foams can be classified in to the two major groups depending on their physical properties. Flexible and rigid foams are low density foams and semi rigid foams have medium density [8]. Polyurethane foam is the main type of cellular plastics. Due to the versatile chemical characteristics of polyurethane, a wide range of materials like soft flexible foam and tough rigid foam, can be synthesized [9].

The structure and properties of polyurethanes have been studied by many workers. There are various methods for producing polyurethanes according to preparation procedure (solvent-free, in organic solvents). Flexible and rigid foams are prepared mainly by a solvent-free method. The most widely used is the one-shot process, in which direct mixing of co reactants and simultaneous addition of a blowing agent, catalysts and other additives are used [10]. The structure of polyurethane foam is formed due to the foaming system in which all the constituents are mixed and they rise and form an elongated structure having closed or open cells and this orientation of foaming product make it useful in many applications [11]. Moulded polyurethane foams have many advantages over slab stock foams [12]. Wide variety of products are produced from polyurethanes due to which they are useful in many consumer and industrial applications [13]. Polymeric foams are used in many applications due to their low weight, and sound- and shock-absorbing properties. [14] Polyurethane foam is widely used for packing and cushioning and mainly lightweight foams with high porosity and good energy absorption capacity are produced [15]. Polyurethane foam is a complex engineering material. Material Properties also depend on temperature and humidity and one of the important behaviour of foaming products is visco-elastic behaviour [16]. Polyurethane (PU) foam has tremendous potential in environmental applications in pollution control and pollution prevention [17]. The elastomeric microcellular polyurethane foam exhibits a broad range of thermal, physical and mechanical properties [18]. Some properties of polyurethane foam are suitable for thermal insulations and that is why it is also used as insulated material in refrigerated vehicles[19].

## 2. EXPERIMENTAL

### 2.1 Materials

Crude MDI (Di-phenyl Methane di-isocyanate), TDI (Toluene di-isocyanate), blend of TDI & MDI, Blended polyol, Polyether polyol, are taken from local commercial market and are used without any further treatment. Latest advancement in use of polyol is to use different new types of polyols with TDI or MDI which are soyabean oil based polyol, Palm oil polyol, and sugar cane bagasse polyol.[20-23]

### 2.2 Method

Foam was prepared using a standard hand mix procedure or cup foaming. This method is also used to evaluate the foaming systems to compare raw materials and resulting foam properties [1]. Equipment used was Electric Mixer, Paper/ Plastic cups, Stirrer, Stop watch and Weight Balance. Foaming system was kept at constant temperature. Measured quantity of polyol was weighed in a plastic cup by using electronic weight balance model. Catalyst, water, blowing agent and surfactant were added in it with gentle stirring with spatula. Polyisocyanate component was weighed in a separate cup. Polyisocyanate was poured into the cup containing polyol and was thoroughly mixed for 5 seconds. Foaming mixture was allowed to expand and rise in the same cup. Foam block was cured at room temperature overnight. Foam samples were cut for testing from upper parts of the cured foam. Different batches were prepared by changing the amount of raw materials and types. Table 1 show the complete formulation used in different batches and type of foam obtained.

**Table 1:** Experimental data for synthesis of flexible and rigid foam

Batch No.	Crude MDI	Polyether Polyol	Water	Blend of TDI and MDI	Blended Polyol	Lab grade TDI	Results
1.	7 gram	12 gram	Nil	Nil	Nil	Nil	Soft flexible foam
2.	Nil	12 gram	Nil	7 gram	Nil	Nil	Soft flexible foam
3.	5 gram	Nil	Nil	Nil	4.5 gram	Nil	Rigid hard foam
4.	Nil	12 gram	2-3 drops	Nil	Nil	7 gram	Sticky hard & rigid foam
5.	5 gram	9 gram	Nil	Nil	Nil	Nil	Soft flexible foam

## 3. CHARACTERIZATION

### 3.1 Foam Density

Density is a structural property and it is defined as mass per unit volume. For simple shaped samples, density can be calculated by weighing foam sample and then by finding its volume through linear dimensions. In case of complex shaped materials especially polyurethane foams and elastomers the method used for calculating density is described in DIN 53479 [2].

Sample was first weighed in dry conditions. It was again weighed after dipping it into the test liquid. In this case test liquid taken was water. Density of water was taken as 1 g/ cm<sup>3</sup>. Density was calculated by using the formula described in DIN 53479 which is:

$$Q_{PK} = \frac{m_1 Q_v}{m_2 - m_1}$$

Whereas,

Q<sub>PK</sub> = Density of test sample, Q<sub>v</sub> = Density of test liquid, m<sub>1</sub>= weight of dry specimen, m<sub>2</sub>= weight of wet specimen. Calculated densities of the flexible and rigid foam are shown in table 2.

**Table 2:** Densities of flexible and rigid foam

Batch no	m <sub>1</sub> (gram)	m <sub>2</sub> (gram)	Q <sub>v</sub> (g/cm <sup>3</sup> )	Q <sub>PK</sub> (g/cm <sup>3</sup> )
1 flexible	0.306	1.235	1	0.329
2 flexible	0.164	1.308	1	0.14
3 rigid	0.392	1.391	1	0.392

### 3.2 Estimation of cream time

The time interval in which mixture starts to expand is called cream time. It is the bench time of mixing and usually measured in seconds. It is measured by using a stopwatch and it shows time periods in which mixture of all reactants turns creamy [1]. Cream time was measured for all the samples of flexible and rigid foam and values are shown in table 3.

**Table 3:** Cream time values for flexible and rigid foam samples

Batch No.	Cream Time
1.	3 second
2.	3 second
3.	7 second
4.	2 second
5.	3 second

### 3.3 Estimation of gel time

Gel time is the time interval at which mixture turns into the foam of a gel. This is due to the cross linking reactions occurring in the mixture. To test for gel touch the foaming mixture with spatula, a thread will form between spatula and foam. It is also measured in seconds. Gel time is normally more than the cream time [1]. Gel time of all the samples was estimated and values are given in table 4.

**Table 4:** Gel time values for flexible and rigid foam samples

Batch No.	Gel Time
1.	5 second
2.	7 second
3.	15 second
4.	3 second
5.	6 second

### 3.4 Estimation of rise time

Rise Time is the time interval at which mixture starts to rise up. It can be in minutes or seconds depending upon the type of foam synthesized. It is very important in foam synthesis because it shows time at which reaction gets completed and process of formation of foam starts. Rise time is greater than both cream time and gel time [1]. Gel time was determined for all synthesized foam samples and values are given in table 5.

**Table 5:** Rise time values for flexible and rigid foam samples

Batch No.	Rise Time
1.	10 second
2.	12 second
3.	1 minute
4.	7 second
5.	11 second

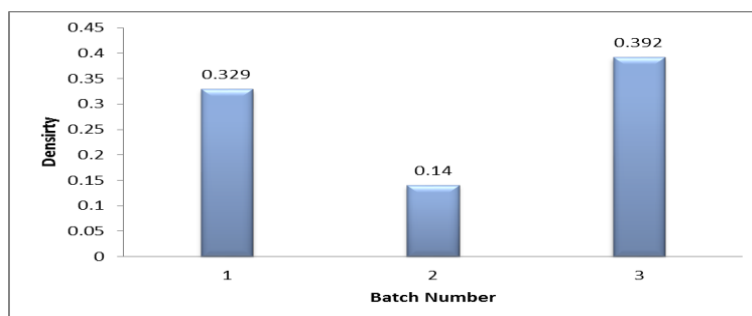
### 3.5 FTIR (Fourier Transform Infrared Spectroscopy)

FTIR analysis of foam samples was done by using Shimadzu IR Prestige-21/DRS-8000 Spectrophotometer at resolution of  $4\text{ cm}^{-1}$  with number of scans 50 and the instrument was run in transmittance mode. The data interval provided by the instrument for a resolution of  $4\text{ cm}^{-1}$  is  $1\text{ cm}^{-1}$ . The software used was IR Solution. All spectra were recorded from  $4000$  to  $800\text{ cm}^{-1}$ .

## 4. RESULTS AND DISCUSSIONS

### 4.1 Density results of flexible and rigid foam samples

Density of rigid foam was found to be  $0.392\text{ g/cm}^3$  and the density of two flexible foam samples is  $0.329\text{ g/cm}^3$  and  $0.14\text{ g/cm}^3$ . Density of one flexible foam sample is almost similar to the density of rigid foam sample. This is because the outer surface of the flexible foam sample was hard and rough like rigid foam. For other sample of flexible foam, the sample is fine and softer than other two. Comparison of different values of densities for different samples of rigid and flexible foam is shown in Figure 3.



**Figure 3:** Variation in density values for flexible and rigid foam

### 4.2 Cream, gel and rise time for flexible and rigid foam samples

Cream time, gel time and rise time for first batch were 3 sec, 5sec and 10 sec respectively. In first batch the foam synthesized was flexible foam. In second batch Cream time, gel time and rise time were 3 sec, 7 sec and 12 sec respectively. Cream time was same as the first batch but there was a slight increase in the gel time and rise time. This is due to the blend of TDI & MDI. In first batch only crude MDI was used so less time was required for completion of reaction. In second batch both TDI & MDI were used. Polyol will react with both of these components. So more time was required which caused the difference in rise time of both batches resulting, rise time of second batch is more than the first batch. But as the reactants rapidly react with each other that's why the time difference was of just 1-2 seconds only.

In third batch rigid foam was synthesized. Cream time, gel time and rise time were 7 s, 15 s and 1 minute respectively. Now in this batch there was a large difference in cream, gel and rise time as compared to previous batches and rise started after long interval this is due to the change of polyol type and it shows that how by changing the single component in the foaming systems the whole product type gets changed with different properties. In this case rise time reaches to 1 minute because blended polyol was used which have gas mixed in it which causes a large time for polyol to react with isocyanate component so the reaction get completed in more time that's why rise started in 1 minute. Fourth batch was also of rigid foam. Cream time, gel time and rise time were 2

s, 3 s and 7 s respectively. As water was used as a blowing agent here so rise time is smaller as compared to the previous batches because water causes the mixture to blow rapidly and as a result reaction gets completed early and mixture starts to rise in the less time.

In fifth batch soft flexible foam was synthesized. Cream time, gel time and rise time were 3 s, 6 s and 11 s respectively. No major difference is observed in rise time as compared to other batches as formulation is same as previous batches resulting in soft and flexible foam. For all these batches the variation in values of cream time, gel time and rise time with batch number is presented in graphical form in figure 4, 5 and 6 respectively.

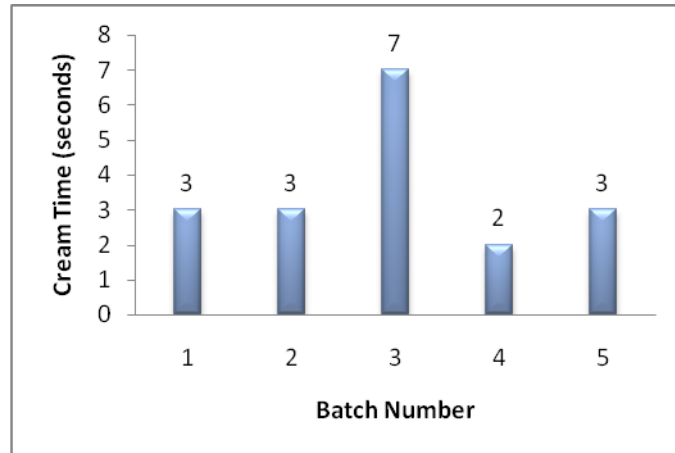


Figure 4: Cream time values variation with batch number for flexible & rigid foam

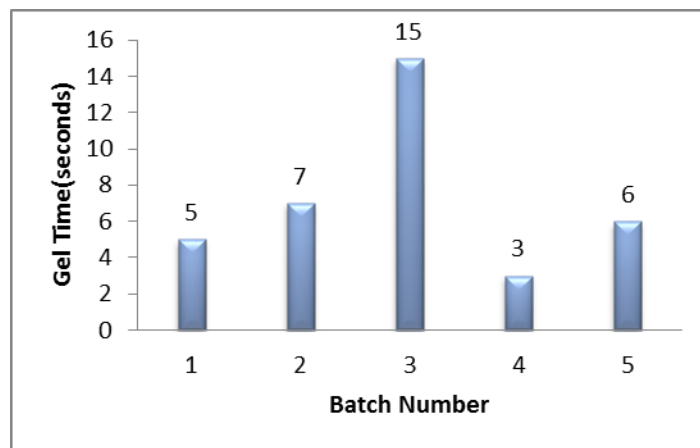


Figure 5: Variation of gel time values w.r.t batch number for flexible and rigid foam.

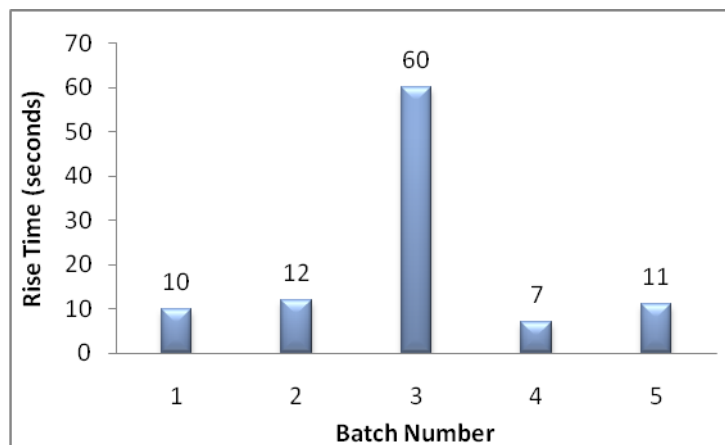


Figure 6: Variation in values of rise time w.r.t batch number in flexible and rigid foam.

### 4.3 Results of FTIR of flexible foam

In figure 7 FTIR spectra for one sample of flexible foam is shown. It shows that the first peak in the spectra at the frequency of  $3342.64\text{ cm}^{-1}$  is due to the presence of alkynes showing specific bond type of C-H stretch. Next peak at  $2976.16\text{ cm}^{-1}$  is due to alkanes C-H but with specific bond  $\text{C}=\text{CH}_2$ . Next peak at  $2872\text{ cm}^{-1}$  is showing the presence of specific methyl bond in C-H and it indicates the presence of MDI due to specific methyl bond. Next peak at  $1703.14\text{ cm}^{-1}$  indicates the presence of carboxylic acid derivatives  $\text{C}=\text{O}$ . This relates to the structure of polyol used as a main ingredient in foam synthesis. Next peak in spectra attributes to the presence of dienes and it is at  $1598.99\text{ cm}^{-1}$ , then the peak at  $1537.27\text{ cm}^{-1}$  indicates the presence of aliphatic nitro compounds N-O which might be due to isocyanates. Peaks at  $1514.12\text{ cm}^{-1}$  and  $1448.54\text{ cm}^{-1}$  indicates the presence of aromatic rings with  $\text{C}=\text{C}$  bonds due to the structure of MDI & TDI. Peak at  $1409.96\text{ cm}^{-1}$  shows C-H bend while peaks at  $1371.39$  and  $1307.74\text{ cm}^{-1}$  show alkanes with specific bond of C-C stretch. Peak in the spectrum at  $1228.66\text{ cm}^{-1}$  attributes to the presence of amines with specific bond of C-N. Peak at  $1097.50\text{ cm}^{-1}$  indicate alkanes with C-C stretch and last three peaks at  $1016.49$ ,  $925.83$  and  $819.75\text{ cm}^{-1}$  shows C-H bond.

Figure 8 shows FTIR spectra of second sample of flexible foam and it shows some different peaks and different frequencies as compared to the spectra of first sample. This indicates the presence of some additional functional groups and bonds not present in the first sample and this was due to the change in chemicals used in the synthesis of this sample. Peak at  $3327.21\text{ cm}^{-1}$  indicates the presence of O-H group which can be alcohols or phenols. Next peak at  $2877.79\text{ cm}^{-1}$  accounts for the presence of alkanes with C-H stretch and it was also present in the first two samples. Peak at  $1712.79\text{ cm}^{-1}$  shows  $\text{C}=\text{O}$  saturated carboxylic acid derivatives same as appeared in the spectra of previous samples. At  $1597.06\text{ cm}^{-1}$  there is a peak showing aromatic ring with specific bond of  $\text{C}=\text{C}$  and it is due to the structure of MDI. The next two peaks at  $1523.76$  and  $1419.61\text{ cm}^{-1}$  shows aromatic nitro compounds with specific bond N-O as in structure of MDI or TDI cyanate group is attached to aromatic ring. Peak at  $1301.95\text{ cm}^{-1}$  and  $1224.80\text{ cm}^{-1}$  indicates C-O ethers due to the presence of polyether polyol. Peak at  $1093.64\text{ cm}^{-1}$  indicates C-C stretch and rest of three peaks show C-H bend till the last peak at  $696.30\text{ cm}^{-1}$  which also shows C-H bend in aromatic rings.

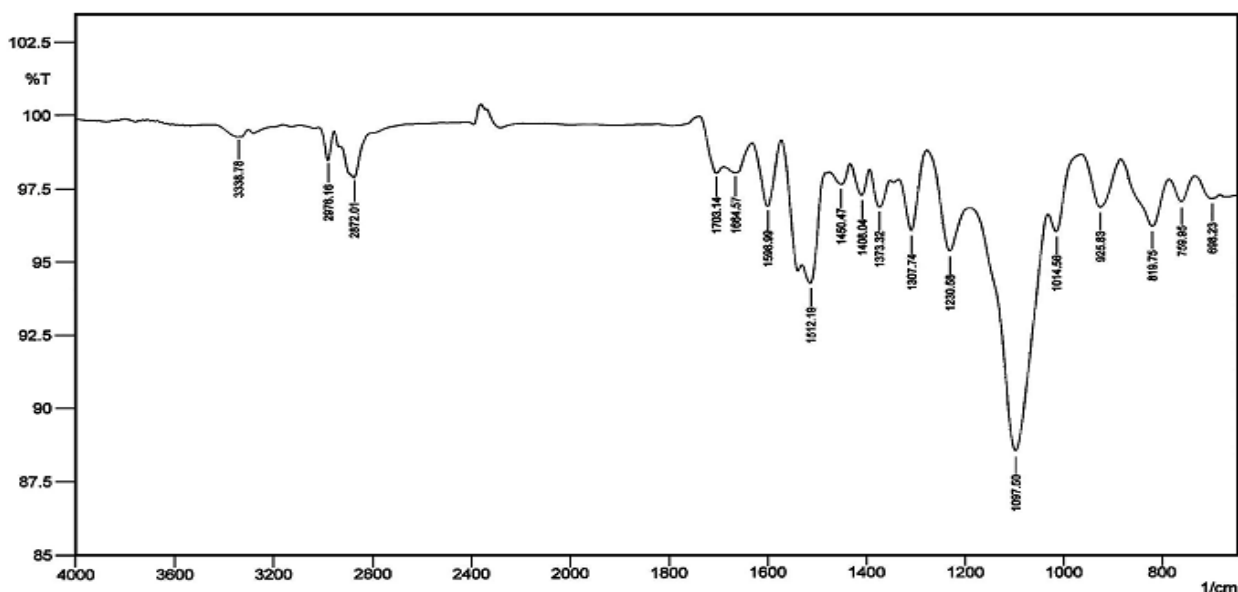


Figure 7: FTIR spectra of flexible foam (1<sup>st</sup> sample)

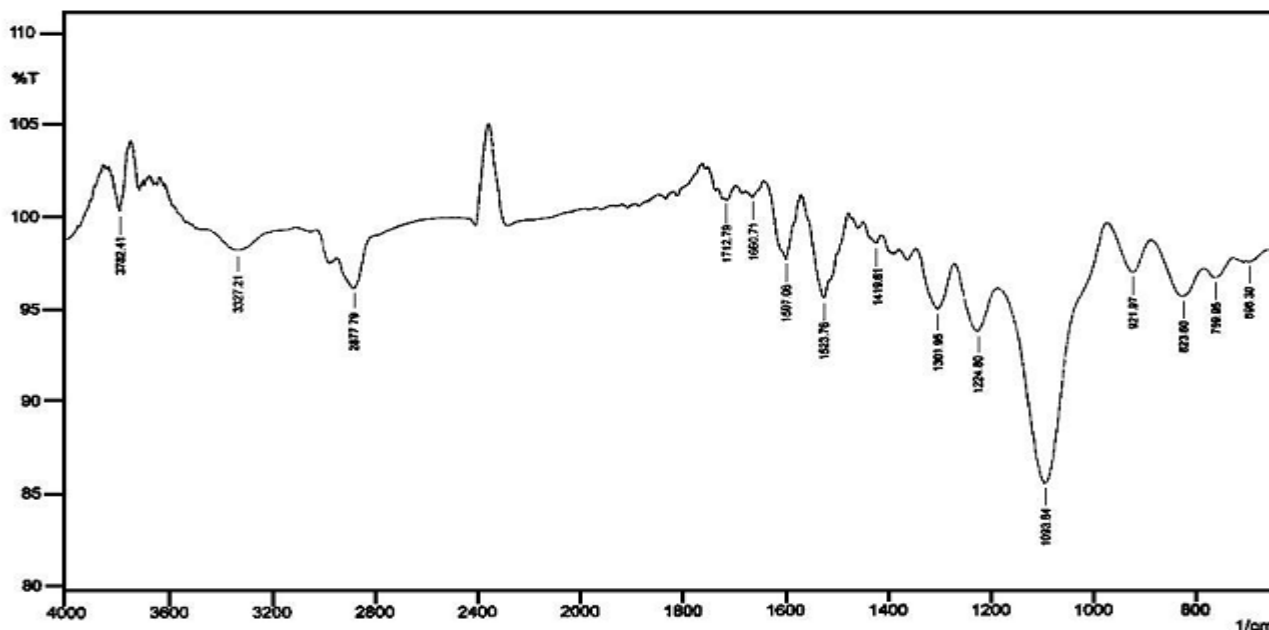


Figure 8: FTIR spectra of flexible foam (2nd sample)

#### 4.4 FTIR of Rigid foam

FTIR of rigid foam sample show peaks almost same as the spectra of flexible foam samples. It is due to the reason that the main ingredients of foam are same which are isocyanates and polyols. Only variation in their quantity makes the foam flexible or rigid. However some differences were observed in the peaks as compared to the spectra of flexible foam samples. In figure 9 Peak at  $3346.50\text{ cm}^{-1}$  indicates C-H stretch of alkynes and peak at  $2877.79\text{ cm}^{-1}$  indicates C-H stretch of aliphatic alkanes. Peaks at  $1597.06$  and  $1452.40\text{ cm}^{-1}$  show the presence of aromatic rings which are due to isocyanate structure. Peak at  $1242.16\text{ cm}^{-1}$  show aromatic ethers which are due to polyether polyol. Peaks at  $1097.50$  and  $923.90\text{ cm}^{-1}$  show C-C stretch and C-H. Peaks at  $840$  and  $690.52\text{ cm}^{-1}$  show C-H bend of aromatics.

Figure 10 shows spectra of second sample of rigid foam, the first peak at  $3338.78\text{ cm}^{-1}$  shows the C-H stretch of alkynes and peak at  $2976.16\text{ cm}^{-1}$  indicates alkanes having specific bond of  $\text{C}=\text{CH}_2$ . The peak at frequency  $2872.01\text{ cm}^{-1}$  shows C-H with specific methyl bond which indicates the presence of MDI. At frequency  $1703.14\text{ cm}^{-1}$  peak attributes to the presence of  $\text{C}=\text{O}$  carboxylic acid derivatives which are due to the structure of polyol. Peak at  $1598.99\text{ cm}^{-1}$  shows C-C dienes and at  $1512.19\text{ cm}^{-1}$  peak shows the presence of aromatic nitro compounds C-N. Peaks at  $1450.47$  and  $1408.04\text{ cm}^{-1}$  show aromatic rings which are due to isocyanate structures. At  $1373.32\text{ cm}^{-1}$  peak attributes to the presence of aliphatic nitro compounds N-O. Peak at  $1230.58\text{ cm}^{-1}$  shows alcohols or phenols. Peak at  $1097.50\text{ cm}^{-1}$  indicates C-C stretch of alkanes and peaks at  $925.83$ ,  $819.75$ ,  $759.95$  and  $698.23\text{ cm}^{-1}$  are showing C-H bend of alkenes.

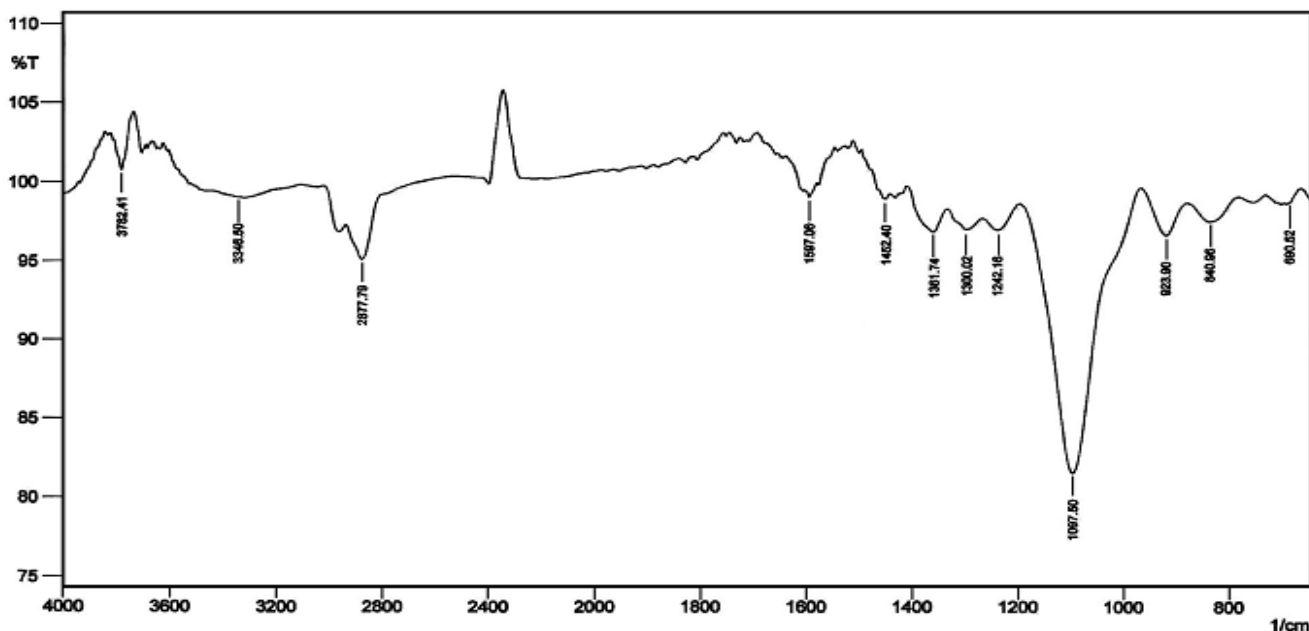


Figure 9: FTIR spectra of Rigid foam (1st sample)

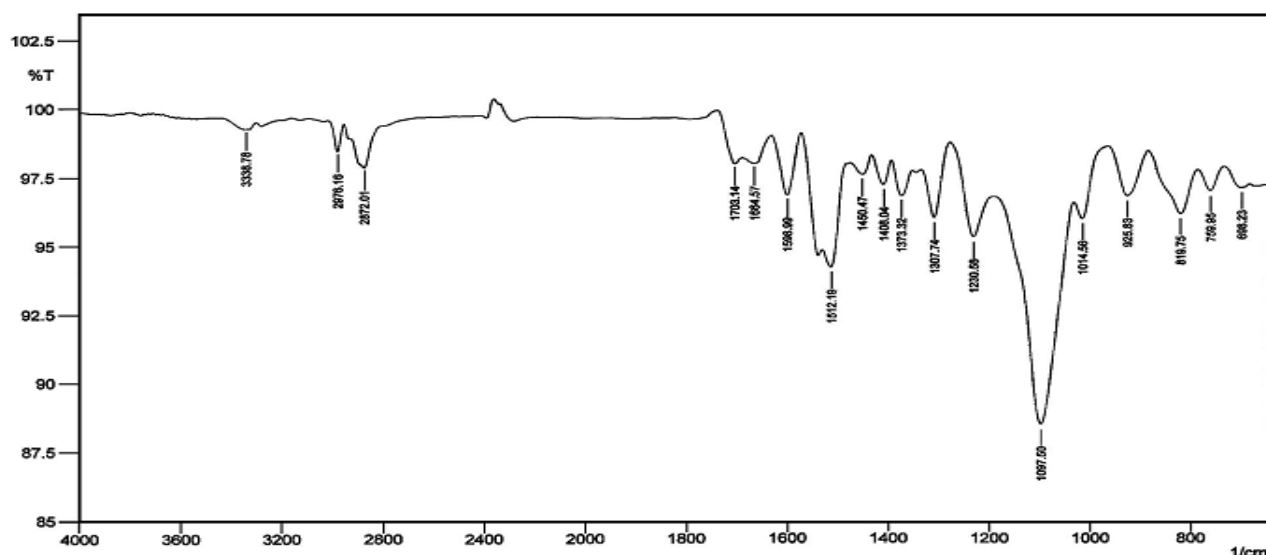


Figure 10: FTIR spectra of rigid foam sample (2nd sample)

## 5. CONCLUSIONS

- Little variation in chemicals and their quantities can change the product type from flexible to rigid.
- Difference in density values indicates the formation of both categories i.e soft and rigid foams
- Addition of catalyst in foaming processes enhances the reaction speed resulting in low rise time.
- Use of blowing agent results in slower rise time because blowing agent causes the mixture to blow rapidly and reaction gets complete in very less time.

## 6. ACKNOWLEDGEMENT

The authors would like to acknowledge the technical support from Department of Polymer Engineering and Technology, University of the Punjab. Authors are also thankful to Institute of Chemical Engineering and Technology, University of the Punjab for providing an opportunity to carry out this research.



## 7. CONFLICT OF INTEREST

The authors have declared no conflict of interest.

## 8. REFERENCES

- [1] Ashida, K., *Polyurethane and Related Foams: Chemistry and Technology*. 2006: Taylor & Francis.
- [2] Oertel, G.A.L., *Polyurethane handbook : chemistry - raw materials - processing - application - properties*. 1993, Munich; Cincinnati: Hanser Publishers ; Hanser/Gardner Publications.
- [3] Szycher, M., *Szycher's handbook of polyurethanes*. 1999, Boca Raton: CRC Press.
- [4] Matsumura, S., Y. Soeda, and K. Toshima, *Perspectives for synthesis and production of polyurethanes and related polymers by enzymes directed toward green and sustainable chemistry*. Applied Microbiology and Biotechnology, 2006. **70**(1): p. 12-20.
- [5] Begum, M. and Siddaramaiah, *Synthesis and characterization of polyurethane/polybutyl methacrylate interpenetrating polymer networks*. Journal of Materials Science, 2004. **39**(14): p. 4615-4623.
- [6] Molero, C., A. de Lucas, and J.F. Rodríguez, *Recovery of polyols from flexible polyurethane foam by “split-phase” glycolysis: Glycol influence*. Polymer Degradation and Stability, 2006. **91**(2): p. 221-228.
- [7] Rivera-Armenta, J.L., T. Heinze, and A.M. Mendoza-Martínez, *New polyurethane foams modified with cellulose derivatives*. European Polymer Journal, 2004. **40**(12): p. 2803-2812.
- [8] Krupers, M.J., et al., *Formation of rigid polyurethane foams with semi-fluorinated diblock copolymeric surfactants*. Polymer, 1998. **39**(10): p. 2049-2053.
- [9] Ligoure, C., et al., *Making polyurethane foams from microemulsions*. Polymer, 2005. **46**(17): p. 6402-6410.
- [10] Sonnenschein, M.F., R. Prange, and A.K. Schrock, *Mechanism for compression set of TDI polyurethane foams*. Polymer, 2007. **48**(2): p. 616-623.
- [11] Malak, S.F.F. and I.A. Anderson, *Orthogonal cutting of polyurethane foam*. International Journal of Mechanical Sciences, 2005. **47**(6): p. 867-883.
- [12] Dounis, D.V. and G.L. Wilkes, *Structure-property relationships of flexible polyurethane foams*. Polymer, 1997. **38**(11): p. 2819-2828.
- [13] Sarier, N. and E. Onder, *Thermal characteristics of polyurethane foams incorporated with phase change materials*. Thermochimica Acta, 2007. **454**(2): p. 90-98.
- [14] Everitt, S.L., O.G. Harlen, and H.J. Wilson, *Bubble growth in a two-dimensional viscoelastic foam*. Journal of Non-Newtonian Fluid Mechanics, 2006. **137**(1-3): p. 46-59.
- [15] Marsavina, L. and T. Sadowski, *Dynamic fracture toughness of polyurethane foam*. Polymer Testing, 2008. **27**(8): p. 941-944.
- [16] Singh, R., P. Davies, and A.K. Bajaj, *Identification of Nonlinear and Viscoelastic Properties of Flexible Polyurethane Foam*. Nonlinear Dynamics, 2003. **34**(3-4): p. 319-346.
- [17] Urgun-Demirtas, M., D. Singh, and K. Pagilla, *Laboratory investigation of biodegradability of a polyurethane foam under anaerobic conditions*. Polymer Degradation and Stability, 2007. **92**(8): p. 1599-1610.
- [18] Yick, K.-l., et al., *Study of thermal–mechanical properties of polyurethane foam and the three-dimensional shape of molded bra cups*. Journal of Materials Processing Technology, 2010. **210**(1): p. 116-121.

- [19] Yang, C.G., L. Xu, and N. Chen, *Thermal expansion of polyurethane foam at low temperature*. Energy Conversion and Management, 2007. **48**(2): p. 481-485.
- [20] Zhang, L., et al., *Substituting soybean oil-based polyol into polyurethane flexible foams*. Polymer, 2007. **48**(22): p. 6656-6667.
- [21] Tanaka, R., S. Hirose, and H. Hatakeyama, *Preparation and characterization of polyurethane foams using a palm oil-based polyol*. Bioresource Technology, 2008. **99**(9): p. 3810-3816.
- [22] Tan, S., et al., *Rigid polyurethane foams from a soybean oil-based Polyol*. Polymer, 2011. **52**(13): p. 2840-2846.
- [23] Abdel Hakim, A.A., et al., *Preparation and characterization of rigid polyurethane foam prepared from sugarcane bagasse polyol*. Materials Chemistry and Physics, 2011. **129**(1–2): p. 301-307.