## MAJOR PROJECT

# "SYNTHESIS AND CHARACTERIZATION OF RIGID POLYURETHANE FOAM WITH DIFFERENT FORMULATIONS OF BLOWING AGENT"

**A MAJOR PROJECT REPORT SUBMITTED IN THE PARTIAL FULLFILLMENT OF THE REQUIREMENTS OF**

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# CERTIFICATE

This is to certify that **Mr. Bipin Bihari Rai** had carried out his major project entitled “**Synthesis and Characterization of Rigid Polyurethane Foam with Different Formulations of Blowing Agent”** under my supervision and guidance during the session 2013. To the best of my knowledge and belief, this work has not been submitted to any other university or institutions for the award of any degree or diploma.

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**(BIPIN BIHARI RAI)**

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# ABSTRACT

Polyurethanes are the most important class of materials and their demand as an excellent performance industrial material is consistently growing. The broad applications of polyurethane includes as material for packaging; furniture; thermal insulation of buildings, refrigerators, deep freeze equipment, pipelines and storage tanks; buoyancy aids in boats and flotation equipment etc. The research and development of all kinds of domestic as well as international in polyurethane material industry have been revealed that the current situation of the polyurethane industry in the developing direction. Importance to understanding the chemistry and structural element that improve the thermal stability, mechanical strength, flame retardancy and biodegradability as these are important perquisites to obtain a high performance material for increasing applications. The scientific interest in using bio-based polyols in the manufacture of polyurethane products has increased significantly in recent years. In the present project rigid polyurethane foams have been prepared from natural oil like castor oil modified by glycerol and 4, 4-diphenylmethane diisocyanates. Castor oil was characterized in terms of moisture content, hydroxyl value, specific gravity, acid value, moisture contents and solid content. The results are within the range reported in literature. The studies had been carried out for different formulations of blowing agents on Castor oil based rigid polyurethane foams. For this purpose blowing agents used were n-Pentane and Water. The prepared rigid PU foams have characterized by using some sophisticated methods like FTIR, SEM, XRD, TGA, DSC, mechanical properties, flammability testing and biodegradability testing. The resulted castor oil based rigid polyurethane foams, due to their high strength and load bearing capacity are found suitable to replace petrochemical based Polyurethane Foam in commercial applications. It has been found that the foam with 10% concentration of n-Pentane as blowing agent was found to be best among all other formulations in its properties and structure. The foam obtained was found to be biodegradable to good extent.

**Key Words:** Rigid polyurethane foam, Castor oil, Glycerol, 4, 4-Diphenylmethane diisocyanates (MDI), FTIR, SEM, XRD, TGA, DSC, Mechanical properties.

# CHAPTER-1

# INTRODUCTION

## 1.1 Introduction

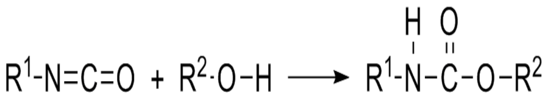
Polyurethanes (PUs) constitute one of the most useful commercial classes of polymers which are widely used in both industry and everyday life. With a global market of approximately six million tonnes per annum, the polyurethane industry covers a diverse business area with its multitude of applications. Polyurethanes are unique polymer materials with a wide range of physical and chemical properties. Polyurethanes can be manufactured in an extremely wide range of density and stiffness and have a broad range of applications. The densities of polyurethanes range from 6 to 1,220 kg/m$^3$ and polymer stiffness of polyurethanes range from elastomers to flexible, rigid, and hard plastics. A broad spectrum of properties gives polyurethanes their versatility. Polyurethanes are formed by the reaction of polyols and polyisocyanates (Figure 1). With well-designed combinations of monomeric materials, PUs can be tailored to meet diversified demands of various applications such as coatings, adhesives, fibres, thermoplastic elastomers and foams.

Polyurethanes vary from flexible to rigid and from solid to foam by suitable combination of the starting materials. In practice, the number of isocyanates used is limited to a few types of TDI, MDI, custom-formulated isocyanate components and in special cases aliphatic isocyanates. The broad spectrum of properties is achieved by the appropriate selection of polyols and additives. Variations of the chain length and the degree of branching or crosslinking determine the molecular structure of polyurethanes. The polyaddition of MDI with long chain diols and butanediol yields linear, segmented polymers typical of thermoplastic polyurethanes (TPU). Reversible crosslinking takes place by crystallization of the rigid segments consisting of MDI and butanediol. By reacting long-chain triols and water with isocyanates, wide-meshed, elastic networks are formed.Cross linking takes place both chemically (triols, polyfunctionalisocyanates) and physically by phase separation into generally amorphous urea rigid segments and flexible polyol segments. This structure is characteristic of flexiblepolyurethane foams.The reaction of low molecular weight polyols with three or more reactive centers (OH groups) with polyfunctionalisocyanates leads to a close-meshed, crosslinked polymer structures typical of rigid polyurethane foams. The high network density is usually futher increased by using excess isocyanate, which can react with one another to form macromolecules with isocyanurate structures (polyisocyanurate =PIR), thus results in additional crosslinking points through allophanate, biuret or isocyanurate groups (Figure 2).Reactions between isocyanates and polyols and isocyanates can take place simultaneously or in direct succession, forming macromolecules with urethane and isocyanurate structures (PIR-PUR).The resulted polyurethanes are demander when a high level of fire performance is required.

## 1.2 Chemistry of the Reaction

Polyurethane polymers are formed through step-growth polymerization reaction. In this process, a monomer containing at least two isocyanate functional groups reacts with another monomer containing at least two hydroxyl groups in the presence of a catalyst and other additives[1].

a) The generalized Polyurethane reaction is



$$R^1\text{-}N{=}C{=}O + R^2\cdot O\text{-}H \longrightarrow R^1\text{-}\overset{\overset{H}{|}}{N}\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}R^2$$

b) A urethane linkage is produced by reacting as isocyanate group, -N=C=O with a hydroxyl (alcohol) group, -OH.

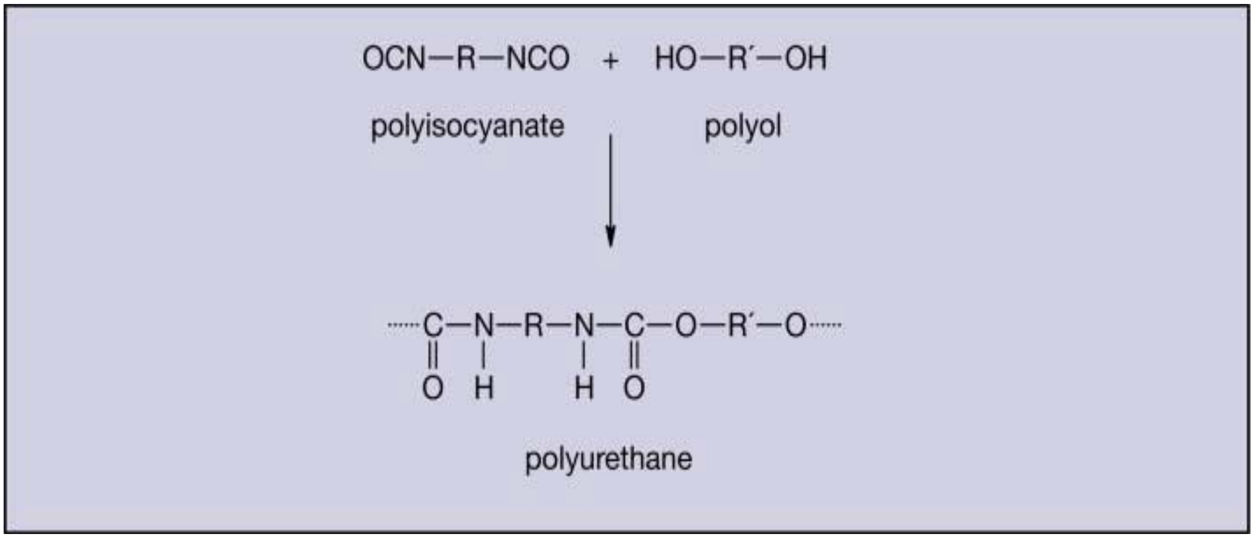


**Figure 1.1:** Generalized Polyurethane Reaction

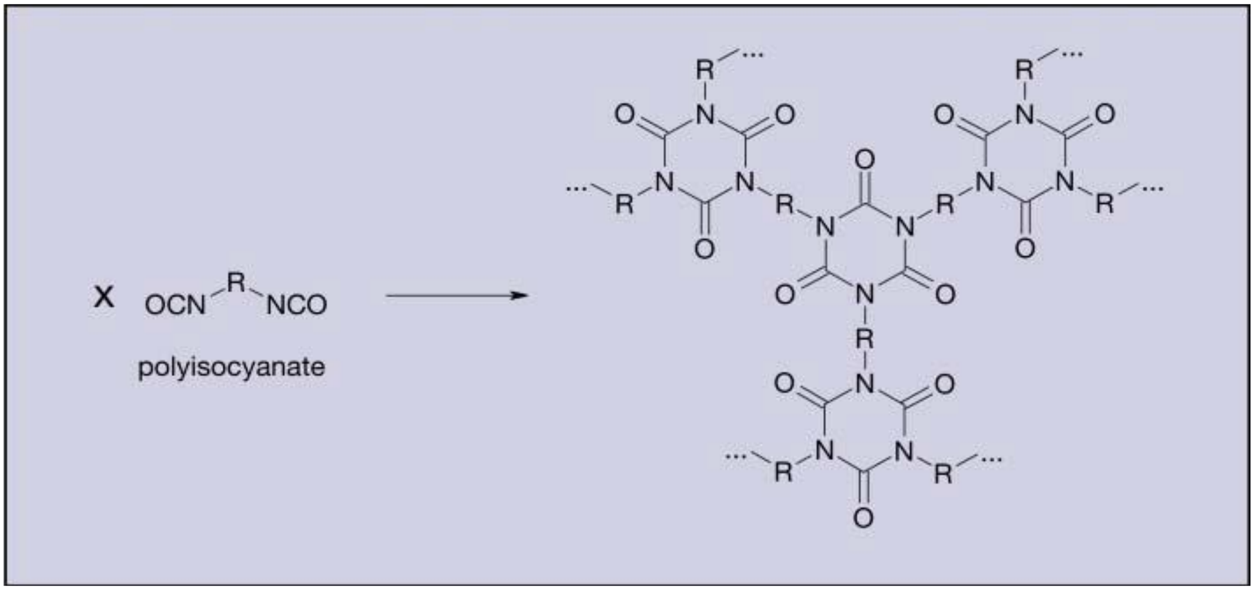


**Figure 1.2:** Reaction of Polyisocyanates in the presence of Trimerization Catalyst

## 1.3 Foams

Foams are cushiony materials formed by the creation of gas bubbles in a base material such as natural rubber, synthetic rubber or other elastomeric materials. A plastic or polymeric foam material consists of a gas phase dispersed in a solid plastic phase and derives its properties from both. The dispersed phase of the foam is usually called the internal phase (air or gases), whereas the continuous phase or the external phase is polymeric material. The solid plastic component forms the matrixwhile the gas phase is entrapped within the voids or cells.The matrix is made up of the base resin and other compounding ingredients that may include plasticizers, stabilizers, surfactants, dyes and pigments, fire retardants and fillers. The composition of the plastic matrix plays an important role in determining foam properties such as chemical resistance, thermal stability, flammability, specific heat, transition temperature and rigidity. With respect to the base resin of the matrix, plastic foams may be either thermoplastic or thermosetting. Thermoplastic foams are based on linear or slightly branched (non-cross-linked) polymers and thus have properties normally associated with thermoplastics. They exhibit a definite melting range and are generally susceptible to attack by organic solvents. With thermoplastic foam systems the polymerization of the base resin is generally completed first, and the polymer then compounded, melted and foamed. In contrast, thermosetting foams the matrix of these foams is based on cross-linked polymers so that, like the bulk plastics from which they are derived, they have generally good resistance to solvents and most chemicals. Although some show limited plastic flow at elevated temperatures, thermoset foams do not usually exhibit a melting range and can often be used at higher temperatures than thermoplastic foams.

Polymeric foams may be flexible, semi-flexible (or semi-rigid) and rigid, depending on chemical composition and the rigidity of the resin used as a matrix and the type of cross linking that exists between the molecules. Flexible foams have a glass transition temperature (Tg) below room temperature, whereas rigid foams have one above room temperature. Polyurethane foams represent the most important class and are further classified as flexible polyurethane foam and rigid polyurethane foam. PU foams have a remarkably broad range of applications including thermal insulation, cushioning, buoyancy, energy absorption (packaging) etc. Their low density also allows the design of light, rigid components such as aircraft-interior panels, structural shapes (transom cores, bulkhead core, stringers, motor mounts, etc.) in fiber-reinforced plastic (FRP) boat building, impact-limiters and crash-pads, composite foam cores, mold-patterns and plugs, sports-equipment core material, and composite tooling[2]. Khemani, 1997 and Kumar and Kaur, 2013 reviewed the background and history of urethane foams and elaborates on their potential future utility[3,4,5].

### 1.3.1 Foam Structure

The term cellular plastic generally used as a synonym for plastic foam and is derived from the structure of the material.The cell structure depends on the process used for the production of the foamed plastic. Generally, no foam has entirely one type of cell structure. Open- or closed-cell structure implies that the number of cells in the foam is predominantly open or closed; respectively.Open-cell structure foam {Figure 3 (b)} contains pores, which are connected to each other to form an interconnected network. This kind of foam has a comparatively lower density and a sponge-like appearance. Open-cell foams have sound absorbing properties and, when flexible, cushioning characteristics.Closed-cell structure foam {Figure 3 (a)} does not have a network of connected cells. It is a solid foam material. Normally this kind of foam has higher compressive strength due to its structure. It has a higher dimensional stability, absorbs less moisture and has higher strength as compared to open-cell foam. Its structure makes it have a harder surface feel and makes it better at absorbing impacts.

Rigid and flexible polyurethane foams, they do not only differ in molecular structure but also in the type of foam cell structure (closed cell or open cell).Closed-cell structures with discrete foam cells are typical of rigid foams. They are characterized by good thermal insulation properties. The reason for this comes, from the combination of a fine, closed-cell foam structure and enclosed cell gases, e.g. CO2, pentane and the long used CFC 11, which are poor heat conductors.Flexible foams generally have open-cell structure; i.e. during the last stage of the foaming operation, the cell walls rupture and the polymer material retracts to form a web of elastic bands. Suitable additives can promote the process of cell opening. This elastic web structure is what makes flexible polyurethane foams such excellent cushioning materials. Properties of flexible polyurethane foams can be controlled through a series of parameters. Flexibility (elongation) depends on the degree of crosslinking, which can be adjusted via the choice of starting materials. Indentation hardness (resistance of material to deformation) under compression increases with increasing NCO/OH equivalent ratio content. Content of urea linkages from the NCO/water reaction also raise the indentation hardness. The density of foam can be reduced within certain limits by increasing the water content in the polyol component. At the same time, urea content and hardness increase.In some cases, both flexible and rigid foams may be produced with either open or closed cells.For example, in case of rigid polyurethane foams, when an appropriate surfactant is selected, or when extreme internal pressures are produced, then the cells can open during foaming, which can lead to foams with a significant open-cell level or fully open-cell foam. Although not desired for conventional rigid foam applications, the properties of open-cell rigid foam can be beneficial in some specific applications (e. g. packaging).

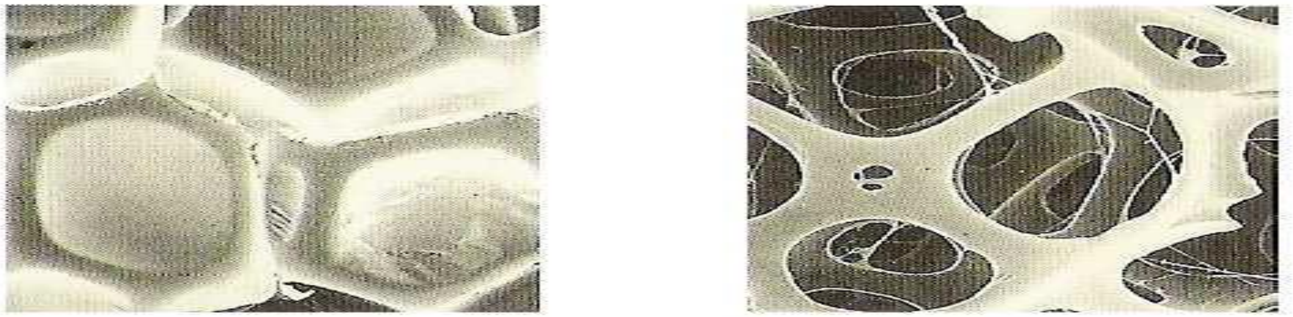


**Figure 1.3:** Foam Structure of Polyurethane (a) Closed-Cell, (b) Opened-Cell

### 1.3.2 Rigid Polyurethane Foam

Rigid polyurethane foams are very popular and highly energy-efficient materials of polyurethane product and are good at both through its physical strength and mechanical properties. Rigid polyurethane foam is currently one of the best thermal insulating materials available. As a result, thermal insulation is a key feature of almost all its applications.Additionally, rigid polyurethane foams are derived from highly functional starting materials; therefore, they are densely crosslinked and have high strength.By suitable choice of ingredients, the properties can be tailored to particular requirements through variation of molecular and phase structure. As density determines the mechanical property level of rigid polyurethane foams, density can be adjusted via the content of physical blowing agent and water in the PU system. The isocyanates used are generally polymeric MDI types (PMDI) with functionalities of 2.6 to 2.8. The main constituents of the polyol component are short-chain polyols with 2 to 8 hydroxyl groups.Common catalysts for rigid PU foam production are tertiary amines and they are chosen to ensure that the foaming process starts after 5 to 50 seconds and is completed after 20 to 400 seconds. The flame retardancy of the rigid polymer foams can be considerably improved by increasing the equivalent NCO/OH ratio. As a result isocyanatetrimers are formed which have very good thermal stability. However, this action leads to an increase in the brittleness if the foamed material. Consequently, flame retards are added to rigid polyurethane foams.The possibility of combining rigid polyurethane foam with different facing materials to produce composites also gives it an important role as a construction material.Rigid polyurethane foam has a number of advantages such as:

- It can be produced in a wide range of densities.
- It adheres to various facings without the use of adhesives.
- It can also be produced in complex cavities.

The principal areas of applications for rigid polyurethane foam are:

#### 1.3.2.1 Applications of Rigid Polyurethane Foam

***Domestic Appliances***

- Thermal insulation for domestic and commercial refrigerators and freezers, hot water tanks

***The Building industry***

- Sandwich panels with rigid facings as wall and roofing panels
- Insulating boards with flexible facings for roofs, walls, ceilings and floors
- Insulating and construction material as cut-to-size pieces from slab stock
- Spray-in-place foam for insulation and sealing
- As a polymeric concrete components

***Industrial Thermal Insulation***

- Insulation of tanks and containers, pipelines, district heating pipes and cold stores

***The Automotive Industry***

- Thermal insulation of refrigerated vehicles for road and rail including containers.

### 1.3.3 Blowing Agents

A blowing agent is a substance which is capable of producing a cellular structure via a foaming process. The formation of cellular polymeric products is possible only by the help of blowing agents[6].The production of rigid polyurethane foam mainly requires a polyol, a polyisocyanate and a blowing agent. The blowing agent is usually added to the polyol together with further auxiliary components such as activators or reaction accelerators, foam stabilizers and flame retardants. The polyaddition reaction that takes place when the polyol and polyisocyanate are mixed together results in macromolecules with urethane structures (polyurethanes). During the reaction a considerable amount of heat is released which is used partly to evaporate readily volatile liquids i.e. blowing agents. As a result, the reaction mix is expanded to form foam.

Blowing agents (also known as 'pneumatogens') create holes in a matrix producing cellular materials. The cellular structure in a matrix reduces density, increasingthermal and acoustic insulation, while increasing relative stiffness of the original polymer. Blowing agents can be classified as: Physical blowing agents e.g. CFCs, HCFCs, hydrocarbons such as pentane, isopentane, cyclopentane, liquid CO2 and Chemical blowing agents e.g. isocyanate and wate, azo-, hydrazine, sodium bi-carbonates and other nitrogen-based materials.Since the phaseout of CFC (because of ozone depletents), HCFC has become the blowing agent of choice in rigid polyurethane foam applications because it has desirable physical properties i.e. it has low flammability and it is a liquid at room temperature. Hence it is easy to handle and HCFC foam has excellent fire resistance and it is widely used in building insulations[7]. HCFC and n-pentane are the most utilized physical blowing agents (PBAs) but they cannot replace the CFCs because of their environmental impact and flammability respectively. Formic acid as a chemical blowing agent (CBA) other than water (CBA) can be used for polyurethane foam synthesis. The use of HCOOH creates some problems in connection with it chemical properties and in terms of toxicity. So, it must be handled with care. The more is the quantity of HCOOH (CBA) is used in foam production, the more is the speed of the ageing process increases as very similar to water blown foams. The water reacts with the polyisocyanate to form polyureaand carbon dioxide, which serves as a co-blowing agent but it cans also the sole blowing agent (Figure 4). N-pentane blown foam shows excellent mechanical performance due to the insolubility in the polymeric matrix. HCOOH shows better fire performance than only n-pentane or HCFC blown foams[8]. Hydrochlorofluorocarbons (HCFCs) like HCFC-141b (1,1-dichloro-1-fluoroethane), hydrocarbons like pentane and hydrofluorocarbons (HFCs) like HFC-245fa (1,1,1,3,3,-pentafluoropropane) and HFC-356mffm (1,1,1,4,4,4,-hexafluorobutane) are the blowing agents having low to zero ozone depletion potential (ODP). Compared to HFC-245a and HFC-365mfc, HFC-134a is less expansive. Fluorocarbon-11 is used for producing low density foams and water is preferred for producing high density foams. HFC-134a and HFC-365mfc are two zero ozone depletion potential non-flammable blowing agents. HFC-134a is used as both a blowing agent and a refrigerant gas. It is commercially available and offers an economical solution compared to other HFC alternatives. The disadvantages of HFC-134a are its limited solubility in polyurethane raw materials like polymeric MDI, polyols and its high vapour pressure continues to be a problem. In general, it is found that HFC-134a is more soluble in polyether polyols than polyester polyols. The vapour pressure of HFC-134a can be reduced by splitting the HFC-134a charge and distribute a small portion of it into the polymeric MDI. On the other hand, HFC-365mfc is a true liquid blowing agent. During thorough evaluations by many end users, HFC-365mfc has emerged to be a technically feasible and efficient blowing agent for rigid polyurethane foams[7]. N-Pentane, isopentane, cyclopentane and HFCs do not present any ozone environmental related problem due to their zero Ozone Depletion Potential (ODP)[6,8]. However, uncertainty about the cost and availability of HFCs has led the polyurethane foam industry to focus on pentane as the primary blowing agent, especially in construction[8].

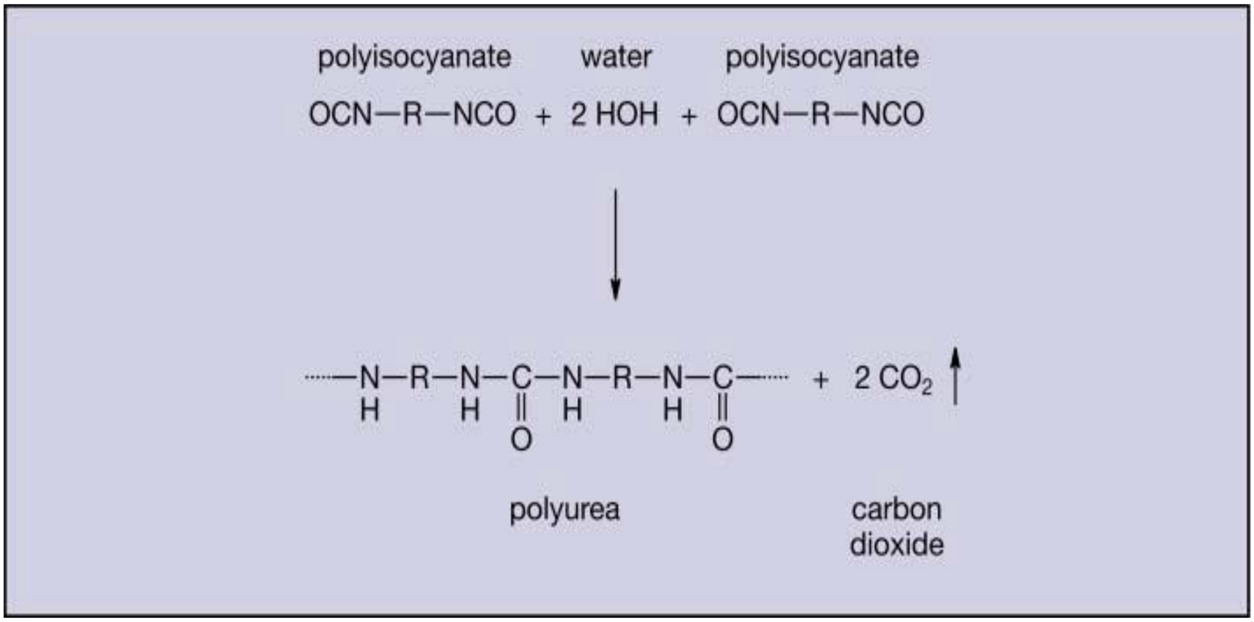


**Figure 1.4:** Polyurethane/water reaction

## 1.4 Polyurethanes from Castor Oil

The development of commodities derived from petrochemical polymers has brought many benefits to mankind. However, it is becoming more evident that the ecosystem is considerably disturbed and damaged as a result of pollution occasioned by discharge of heavy metals and the non-degradable materials used in disposable items. Therefore, the interest in polymers from renewable resources has recently gained exponential momentum and the use of biodegradable and renewable materials to replace conventional petroleum materials for disposable and other industrial applications is becoming popular and necessary[9,10]. To produce materials that are competitive with synthetic ones is gaining attention over the last decade, because of availability of materials, and low cost[11,12]. The potential for polyols derived from vegetable oils to replace petrochemical- based polyols began garnering attention around 2004, partly due to rising costs of petrochemical feedstock's and partially due enhanced public desire for environmentally friendly green products. There is a growing worldwide interest in the development of vegetable oil based polyurethane. This interest is economically driven because vegetable oils are relatively inexpensive and a renewable resource[13,14]. Moreover, these are renewable resources. Vegetable oils are composed of triglycerides of long chain fatty acids. The most common chain lengths in these fatty acids are 18 or 20 carbon atoms which can be either saturated or unsaturated, where unsaturation of the double bonds are located at the 9, 12 and 15 carbon. By using enzymes or chemicals to modify the unsaturated fatty acid and introducing hydroxyl functional groups, vegetable oils could be converted into polyols[15].Although many types of vegetable oils have been tested and reported for polyol and polyurethane applications for example soyabean oil, sunflower oil, castor oil, palm oil and rice-barn oil[16]. Castor oil is the most promising one to partially replacing petroleum to make polyols due to its volume and price stability. Castor oil differs from other oils from its high acetyl or hydroxyl value also; it is miscible with alcohol but only slightly soluble in petroleum ether at room temperature.

Castor oil is a vegetable oil obtained from the seeds castor bean (technically castor seed of the Castor plant (Ricinuscommunis), found in Nigeria. Castor oil is a colorless to very pale yellow liquid with mild or no odor or taste. Its boiling point is 313 °C (595 °F) and its density is 961 kg/m$^3$. It is a triglyceride which contains about 85% ricinoleic acid, Cis-1, 2-hydroxyoctadec-9-enoic acid[17]. Oleic and linoleic acids are the other significant components that can be used for many industrial applications. Ehrilich et al., 1959 and Leitheiser et al., 1969 reported that castor oil can be used to replace the petroleum-based polyol to make polyurethane foams [18,19].

## 1.5 Objective of Research Work

The formation of cellular polymeric products is possible only by the help of blowing agents. The properties and structure of the foam more or less depend upon the blowing agent used. Due to its zero ODP, n-Pentane is found a very promising physical blowing agent as a replacement of CFCs. N-pentane blown foam shows excellent mechanical performance due to the insolubility in the polymeric matrix. The water can also act as blowing agent, as it reacts with the polyisocyanate to form polyurea and carbon dioxide, which forms cellular polymers. Due to the harmful effects of chlorine based blowing agents, there is a need to develop and use environment friendly materials that could replace these non eco-friendly raw materials to fulfil our requirements, exhibiting similar or better properties.Moreover, in view of the environmental and sustainability aspects, raw materials are also needed to explore that could replace the existing synthetic petro-chemical materials with more eco-friendly bio-based materials. Raw materials based on vegetable oils are found promising because they have a number of excellent properties for producing polymers such as polyurethanes, polyesters, amides and epoxy resins. The potential for polyols derived from vegetable oils to replace petrochemical- based polyols is gaining attention, because

1) Petrochemicals based materials are expensive and the costs of petrochemical feedstocks are rising due to depleting fossil fuel resources.
2) Petrochemicals based materials require high technology processing systems and involves a huge amount of energy.

3) Polymers derived from petroleum sources do not undergo biodegradation on disposal, thus causing unnecessary waste which end up in landfills or create large amounts of pollution and greenhouse gases if incinerated.
4) Enhanced public desire for environmentally friendly green products.

In aim of this project is to: “Synthesis and Characterization of Rigid Polyurethane Foam with different formulations of Blowing Agent”. Castor oil is the most promising one to replace petroleum in the formation of polyols due to its volume and price stability. And it differs from other oils, as it is the only oil which bears hydroxyl groups naturally. The blowing agents used are n-pentane and water, both with zero ODP. Here I summarise my objectives of the research programme.

The objectives of the work are:

a) Determination of the properties of Castor Oil and Glycerol.
b) Modification of the Castor Oil for the synthesis of Polyol.
c) Characterization of Castor Oil based Polyol.
d) Development of Castor Oil based Rigid Polyurethane Foam with different formulations of Blowing Agents.
e) Characterization of Castor Oil based Rigid Polyurethane Foam.

# CHAPTER- 2

# LITERATURE

# REVIEW

## 2.1 History of Polyurethane

More than half a century ago, plastic industries were working with polymerization and polycondensation processes to produce plastics. In 1937 the German scientist Otto Bayer, also known as “father” of polyurethane, and his co-workers discovered a third process, called polyaddition reaction, where the polyaddition of a diisocyanate to a diol in the presence of a catalyst proceeds completely to a polyurethane under mild conditions without the formation of undesired byproducts.

**Figure 2.1:** Discovery of Polyurethane

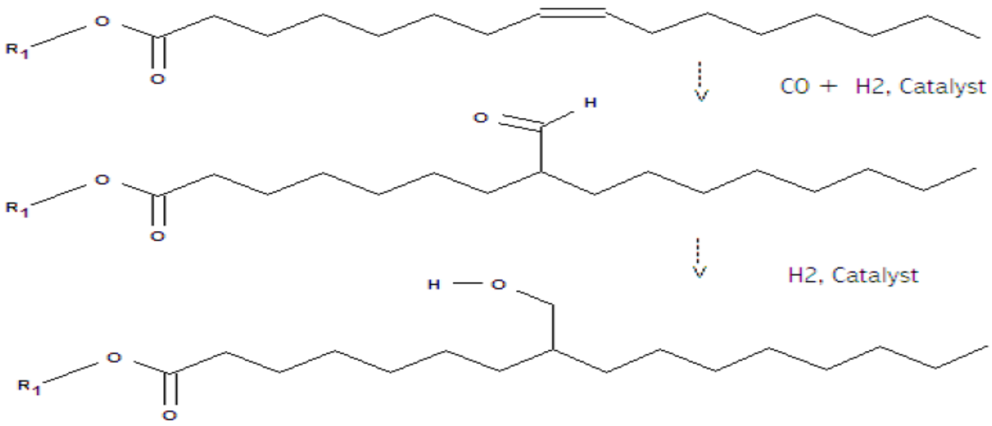
Initially, work focused on the production of fibres and flexible foams. With development constrained by World War II, when PUs were applied on a limited scale as aircraft coating it was not until 1952 that polyisocyanates became commercially available. Commercial production of flexible polyurethane foam began in 1954, based on toluene diisocyanate (TDI) and polyester polyols. The invention of the Polyurethane foams was the result of water accidentally introduced in the reaction mix. The first commercially available polyether polyol, poly (tetramethylene ether glycol), was introduced by DuPont in 1956 by polymerizing tetrahydrofuran. In 1957, BASF and Dow Chemical introduced less expensive polyalkylene glycols. These polyether polyols offered technical and commercial advantages such as low cost, ease of handling, better hydrolytic stability and quickly supplanted polyester polyols in the manufacture of polyurethane goods. And over the years a lot of successful achievements on polyurethanes were followed.

Polyurethane, usually referred to as PU, is actually another name for the family of chemicals known as the urethane polymers, which are composed of two principal raw materials: isocyanates and polyols, brought together with catalysts and a variety of additives as we will see further on[1]. This reaction produces a basic material whose variations can be stretched, smashed, or scratched, and remain indestructible. Depending on the different isocyanates and polyol constituents, the resulting polyurethane might take a liquid, foam, or solid form, each with advantages and limitations.Polyurethane might be hard, like fiberglass, squishy like upholstery foam, protective like varnish, bouncy like rubber wheels, or sticky like glue. Since its invention in the 40s, polyurethane has been used in everything from baby toys to airplane wings, and continues to be adapted for contemporary technology.

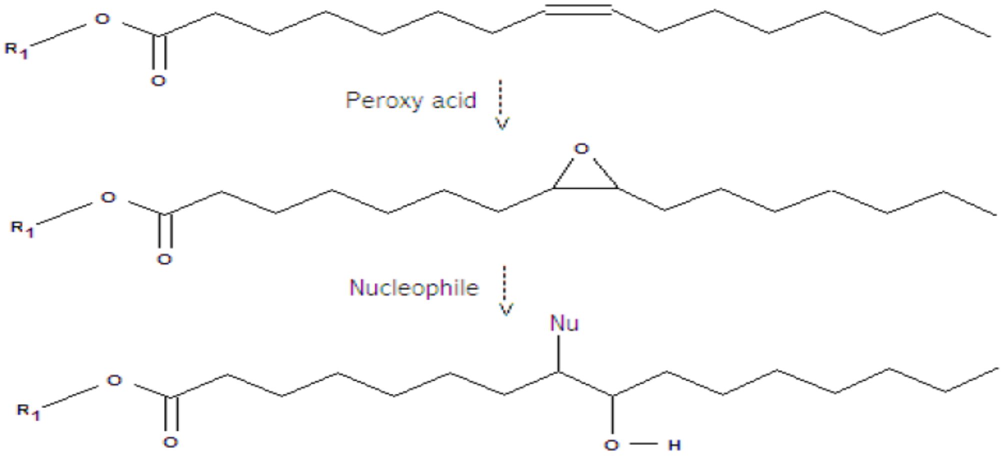
## 2.2 Polyurethanes from Bio-based Materials

The synthesis of vegetable oil based polymeric materials with excellent physical and chemical properties has drawn great interest in the recent times. Raw materials based on vegetable oils are important in our life because they have a number of excellent properties for producing valuable polymers such as polyurethane, polyester, amide and epoxy resins. There is a growing worldwide interest in the development of vegetable oil based polyurethane. This interest is economically driven because vegetable oils are relatively inexpensive and a renewable resource. Vegetable oils are composed of triglycerides of long chain fatty acids. The most common chain lengths in these fatty acids are 18 or 20 carbon atoms which can be either saturated or unsaturated, where unsaturation of the double bonds are located at the 9, 12 and 15 carbon. By using enzymes or chemicals to modify the unsaturated fatty acid and introducing hydroxyl functional groups, vegetable oils could be converted into polyols. Several methods are currently known to add hydroxyl at the unsaturated sites[20].

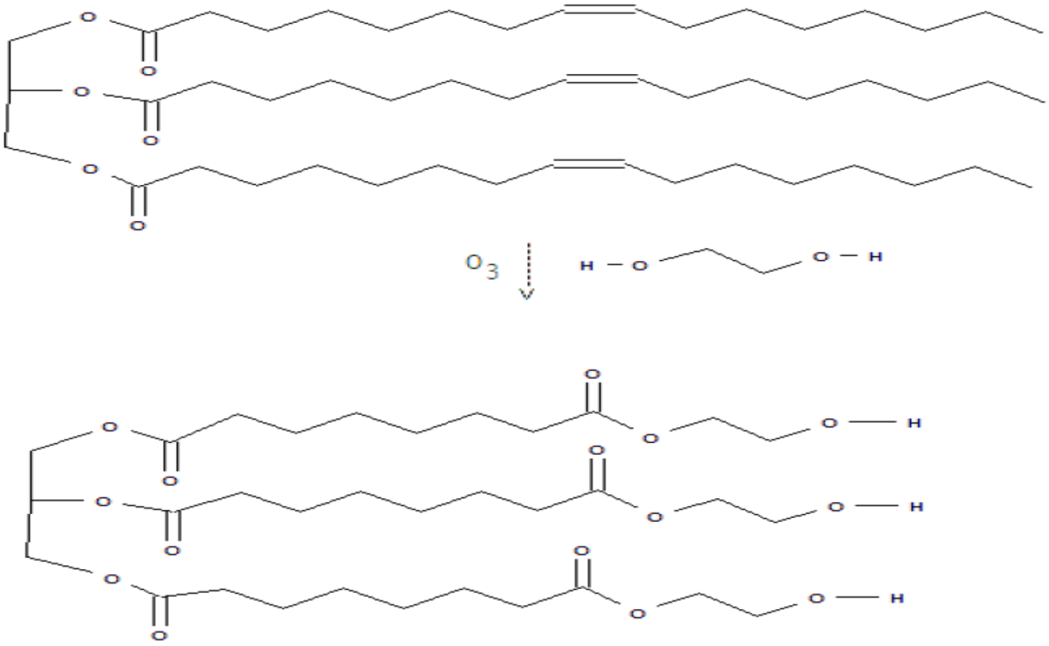
a) Hydroformylation followed by hydrogenation.



b) Epoxidation followed by oxirane opening.



c) Ozonolysis followed by hydrogenation.



All the above said methods produce polyols but with structural differences. Although many types of vegetable oils have been tested and reported for polyol and polyurethane applications for example soyabean oil, sunflower oil, castor oil, palm oil and rice-barn oil, Castor oil is the most promising one to partially replacing petroleum to make polyols due to its volume and price stability. Castor oil differs from other oils from its high acetyl or hydroxyl value also; it is miscible with alcohol but only slightly soluble in petroleum ether at room temperature. Ehrilich et al., 1959 and Leitheiser et al., 1969 reported that castor oil can be used to replace the petroleum-based polyol to make polyurethane foams[18,19]. Lu et al., 2005 used waterborne polyurethane made from rapeseed oil-based polyol to modify glycerol-plasticized starch and develop biodegradable films[21]. Chang et al., 2001a and 2001b added commercial soy flours into water-blown rigid polyurethane foams to improve the physical properties and lower the cost of these foams[22,23]. Rigid polyurethane foams had also been reported to be synthesized from rhodium catalyzed hydroformylated polyols. Petrovic et al[24], 2000.and Zlatanic et al., 2004[14], nvestigated the structure and properties of vegetable oil-based polyols, their applications in polyurethane foams, and the foam's biodegradation behaviour and thermal stability .Kumar and Kaur, 2013, reported the effect of NCO/OH ratio on the properties of Castor Oil based Rigid Polyurethane Foam[25].

**Table 2.1:** Work carried out by Different Researchers on Bio-based Polymers

| **Sr. No.** | **Author's Name** | **Year of Publication** | **Title** | **Outcome** |
|---|---|---|---|---|
| 1 | Ogunniyi, D. S. et al[26]. | 1996 | Preparation and Properties of Polyurethane Foams from Toluene Diisocyanate and Mixtures of Castor Oil and Polyol | Tensile strength of resulted PUF was found to be increased with increase in the concentration of castor oil. Compression set increase dramatically with increase in concentration of castor oil. |
| 2 | Guo, A. et al.[27] | 2002 | Polyols and Polyurethanes from Hydroformylation of Soybean Oil | The rhodium catalyzed reaction give a polyol with 95% conversion giving rise to rigid polyurethane. The cobalt catalyzed reaction gave a polyol with a 67% conversion, giving a hard rubber having lower mechanical strength. Glycerine was used as a cross- linker to improve the properties of PUs. |
| 3 | KendagannaSwamy, B. K. et al.[28] | 2003 | Structure-property relationship of castor | High density chain extended PUs were produced. 1,6-hexane diol |

| | | | | |
|---|---|---|---|---|
| | | | oil based diol chain extended polyurethanes (PUs) | system yields higher dimensional stability compared to 1,4-butane diol system. Higher tensile strength value are observed for 1,4-butanediol system than 1,6-hexane diol system. MDI based chain extended PUs show higher tensile strength of 1.10 and 1.29 MPa for 1,6-diol and 1,4-diol based PU system respectively. The variation of tensile strength with respect to diisocyanate is in the order: MDI > TDI > HMDI. |
| 4 | Badri, K. H. et al.[29] | 2004 | Rigid polyurethane foams from oil palm resources | The foam produced exhibited good mechanical properties. Silane was used as a coupling agent for surface modification. |
| 5 | Mythili, C. V. et al[30]. | 2004 | Synthesis, mechanical, thermal and chemical properties of polyurethane based on cardanol | The addition of commercial polyol, PPG-2000 along with cardanol formaldehyde resin introduces some degree of flexibility in the tough polyurethane. The TGA analysis |

| | | | | |
|---|---|---|---|---|
| | | | | of polyurethane showed higher thermal stability in RPUFs. The PUs were found to be stable in acid, alkali, 1 N sodium chloride, toluene, ether and ethanol. |
| 6 | Zhang, L. et al.[31] | 2007 | Substituting soybean oil-based polyol into polyurethane flexible foams | Compressive properties of the resulted PUs were found to be improved.. Substituting SAN copolymer filled polyol results in slightly smaller cell size and does not change phase separated morphology in the polymer phase. The use of crosslinker polyol alters polymer phase morphology, especially that of hard domains. |
| 7 | Lee, C. S. et al.[32] | 2007 | Rigid Polyurethane Foam Production from Palm Oil Based Epoxidized Diethanolamides | The increase in the isocyanate index from 1.0 to 1.4 had led to an increase in the density & compression strength. With further increase in NCO index, i.e. to 1.5, a decrease in the density & compression strength |

| | | | | |
|---|---|---|---|---|
| | | | | was recorded, which subsequently increased, but the brittleness increased as well. PUFs were produced with a higher percentage of close cell contents and exhibited lower thermal conductivity. |
| 8 | Chuayjuljit, S. et al.[33] | 2007 | Processing and Properties of Palm Oil-Based Rigid Polyurethane Foam | The obtained palm oil based polyol was a viscous yellowish liquid with much higher viscosity than that of the regular palm oil. This high viscosity was reported due to hydrogen bonding associated with the hydroxyl groups. The densities of the PUFs decreased with the increased amount of catalyst (DMCHA). Compressive strength of PUFs was found to be increased with an increase in DMCHA. Increased amount of surfactant showed negligible effect on the density and |

| | | | | |
|---|---|---|---|---|
| | | | | compressive strength of the PUFs. |
| 9 | Ogunleye, O. O. et al.[34] | 2007 | Effect of Castor Oil on the Physical Properties of Polyether Based Flexible Polyurethane Foam | Making a partial substitution of silicone oil by castor oil significantly increased density and hardness index. The tensile strength and elongation of samples declined with increased castor oil. |
| 10 | Narine, S. S. et al.[35] | 2007 | Physical Properties of Polyurethanes Produced from Polyols from Seed Oils: II. Foams | Canola PU was the most reactive system with the shortest cream, rising and gel times and Soybean PU was the least reactive one with the longest times. Castor oil PU has a cream time 50% larger, a rising time 35% larger and a gel time 25% larger than those of Canola PU. Canola PUF showed better compressive properties than Soyabean PUF but less than Castor oil PUF. |
| 11 | Ghosh, S. B. et al.[36] | 2010 | Synthesis of Soy-Polyol by Two Step | PUF produced from soybean polyol was found to have density |

| | | | | |
|---|---|---|---|---|
| | | | Continuous Route and Development of Soy-Based Polyurethane Foam | and compressive strength comparable to commercial polyols. The cellular microstructure of soy foam shows polygonal cell structure. |
| 12 | Corcuera, M. A. et al.[37] | 2010 | Microstructure and properties of polyurethanes derived from castor oil | Both melting temperature and enthalpy increased as hard segment content increases for both PUBD and PUPD polyurethane. Shore D hardness, tensile modulus and tensile strength and lower strain were measured by mechanical tests. As seen in mechanical tests, the higher hard segment crystallinity degree observed in PUBD polyurethanes at high hard segment contents did not improved the mechanical strength. The thermal decomposition mechanism followed the same behaviour in both synthesized polyurethanes. |

|  |  |  |  |  |
|---|---|---|---|---|
|  |  |  |  | PUs synthesized with PD as the chain extender structure showed a thermal stability comparable to that of synthesized from petroleum-derived chain extender. |
| 13 | Palanisamy, A. et al.[38] | 2011 | Development and Characterization of Water-Blown Polyurethane Foam from Diethanolamides of Karanja Oil | The two step synthesis involved hydroxylation followed by transamidation leading to a polyol with OH value of 225 mg KOH/g. The foams produced were found to have good mechanical properties such as compression and flexural strength as compared to semi-rigid PUFs. |
| 14 | Palanisamy, A. et al[39]. | 2011 | Diethanolamides of Castor Oil as Polyols for the Development of Water – Blown Polyurethane Foam | The density increased with hydroxyamide content and molecular weight of PPG while the reverse trend was observed in flexural strength measurements. The compression strength increased with the content of |

|  |  |  |  |  |
|---|---|---|---|---|
|  |  |  |  | hydroxyamide and the molecular weight of PPG. |
| 15 | Kashif, M. et al.[40] | 2011 | Synthesis and Characterization of Ricinoleamide – Based Polyurethane | The synthesized polymer showed moderate antibacterial activity. Thermal degradation of the resin was more or less similar to virgin polyurethane. |
| 16 | Tan, S. et al.[41] | 2011 | Rigid polyurethane foams from a soybean oil based Polyol | The Tg was found to be increased and foams had comparable foaming kinetics, density, cellular morphology, and initial thermal conductivity. Compressive strength of the soy-based RPUFs were superior to those of petroleum-based foams possibly due to smaller cell size. Foams with 50% SBOP showed thermal conductivity comparable to those of commercially available PUFs.Foams with 100% SBOP showed more aging. |
| 17 | Kong, X. et al.[42] | 2012 | Novel polyurethane | Foams were produced using |

|  |  |  |  |  |
|---|---|---|---|---|
|  |  |  | produced from canola oil based poly(ether ester) polyols: Synthesis, characterization and properties | Liprol 270 and Liprol 320 MDI. Both Liprol 270-MDI PU and Liprol 320-MDI PU networks were found highly cross-linked. Compared to Liprol 320-MDI PU, Liprol 270-MDI PU displays shorter gelation time and better initial thermal degradation properties, whereas Liprol 320-MDI PU have a higher Tg, higher cross-linking density. |
| 18 | Pawlik, H. and Prociak, A.[43] | 2012 | Influence of Palm Oil Based Polyol on the Properties of Flexible Polyurethane Foams | The palm oil polyol upto 15 wt% in the polyol premix resulted in more uniform cell size, increased density, compressive strength and resilience, but slightly decrease of $T_g$ was observed. |
| 19 | Cardoso, G. T. et al.[44] | 2012 | Rigid foam polyurethane (PU) derived from castor oil (Ricinus communis) for thermal insulation in | The TGA showed that PUFs had higher resistance to degradation by heat. |

|  |  |  |  |  |
|---|---|---|---|---|
|  |  |  | roof systems |  |
| 20 | Yang, L. T. et al.[45] | 2012 | Thermal and Mechanical Properties of Polyurethane Rigid Foam Based on Epoxidized Soybean Oil | The mass fraction of the soybean oil-based polyol at 60% presents higher compressive strength and density. Two glass transition temperatures of each foam were reported and $Tg_1$ increased with OH value. |
| 21 | Silva, V. R. D. et al.[46] | 2013 | Polyurethane foams based on modified tung oil and reinforced with rice husk ash I: Synthesis & physical chemical characterization | Rice husk ash filled RPUF showed a higher thermal conductivity than that of the unfilled samples. TGA analysis showed that thermal stability was almost unaffected by ash content. |
| 22 | Silva, V. R. D. et al.[47] | 2013 | Polyurethane foams based on modified tung oil and reinforced with rice husk ash II: Mechanical Characterization | Both unreinforced and RHA filled samples exhibited a density gradient in the foam rise direction due to the free rise method selected for the preparation. The addition of rice husk ash led to reduced compression modulus, |

|  |  |  |  |  |
|---|---|---|---|---|
|  |  |  |  | compressive strength, thermal transitions and storage modulus respect to the unfilled foam. |
| 23 | Kumar, M. and Kaur, R.[25] | 2013 | Effect of Different Formulations of MDI on Rigid Polyurethane Foams based on Castor Oil | Glycerol modification of castor oil results in more cross-linked and stiffer polymer. The tensile and compressive strength of RPUF were found to be increased with MDI content. The highest values were obtained for the high MDI: Polyol ratio. SEM studies had revealed more closed packing with increased MDI content. |

# CHAPTER-3

# EXPERIMENTAL WORK

## 3.1 Raw Materials

Castor oil (99.9%) and 4, 4’-diphenylmethane diisocyanate (AR grade) was obtained from Shivathene Linopack ltd. Parwanoo, Himachal Pardesh. Stannous octoate (99%), n-Pentane (99.5%), and Silicon oil, were purchased from Standard Chemicals (ISO 9001:2008 certified), Chawari Bazar, Delhi. Glycerol (99%) was supplied by Sisco Industries Pvt. Ltd, Mumbai. The other chemicals used for analysis purpose i.e. Acetone, Amido sulphonic acid, Methanol, Mono methyl glycol, Ethyl methyl ketone, Ethylene diamine, Triethyl phosphate (flame retardant), Triethyl amine, Dibutyl amine, Toluene, Phenolphthalein, Bromophenol blue, Pyridine, Acetic anhydride, Sodium hydroxide, Ethanol, Diethyl ether, Hydrochloric acid, Potassium hydroxide, Hexane1,6-diol (crosslinker). All the reagents were of A.R. grade.

### 3.1.1 Analytical Testing of the Raw Materials

The precision of the results is not only dependent on the instrument and experiment performed, but also to some extent to the purity of the substance/materials used. The properties of the raw materials determine the characteristics of the final product. The characterization of the raw materials is thus essential to control the quality as well as properties of the product. The commercially available Castor Oil, Glycerol and 4, 4-diphenylmethane diisocyanate (MDI) had been tested for their properties. The properties of Castor Oil and Glycerol as determined by various experimental procedures are reported in Table 3.1 and Table 3.2 respectively. The values obtained are almost similar to that available in literature[48,49]. Characterization of available Castor Oil and Glycerol for the determination of these properties is as given in Appendix-1.

**Table 3.1:** Properties of Castor Oil

| **Property** | **Value** |
|---|---|
| Color and Appearance | Clear/ Dark Yellow |
| OH value (mg KOH/g) | 161.98 |
| Viscosity (cP at 25 °C) | 600-650 |
| Water content (%) | 0.5 |
| Acid number | 0.96 |
| Specific gravity (25 °C) | 0.95 |
| Solubility in Alcohol | Completely Soluble /Mixing |

**Table 3.2:** Properties of Glycerol

| **Properties** | **Value** |
|---|---|
| Color and Appearance | Clear/ Natural Transparent |
| OH value (mg KOH/g) | 1795.61 |
| Viscosity (cP at 25 °C) | 875 |
| Water content (%) | 0.02 |
| Acid number | 0.37 |
| Specific gravity (25 °C) | 1.25 |

### 3.1.2 Characterization of 4, 4-Diphenylmethane Diisocyanate (MDI)

4.4-Diphenylmethane diisocyanate (MDI) was purchased from market in pure form and Characterized for its properties. The properties of MDI as determined by various experimental procedures are reported in Table 3.3. Characterization of 4.4-Diphenylmethane diisocyanate (MDI) for the determination of these properties is as given in Appendix-1.

**Table 3.3:** Properties of 4.4-Diphenylmethane Diisocyanate (MDI)

| Properties | Value |
|---|---|
| % of NCO | 33.12 |
| Viscosity (cP at 25 °C) | 240 |
| Water content (%) | NIL |
| Specific gravity (25 °C) | 1.2 |
| Solid content (%) | 98.97 |

#### 3.1.2.1 FTIR Analysis of 4, 4-Diphenylmethane Diisocyanate (MDI)

FTIR spectra of the MDI were recorded in A Nicolet 380 FTIR spectrophotometer. Small quantities of the liquid samples were spread in pure dried KBr for analysis. The characteristic absorptions peaks and respective bonds are observed at 3694.95 $cm^{-1}$(O-H stretch, free strong, sharp intensity), 3396.19 $cm^{-1}$(N-H stretching frequency), 3027.36 $cm^{-1}$(C-H aromatic stretching medium), 2917.78 $cm^{-1}$(C-H stretching strong intensity), 2593.69 $cm^{-1}$(O-H acid stretching strong, very broad), 2277 cm$^{-1}$(--N=C=O isocyanate stretch), 1731.8 cm$^{-1}$(C=O stretch strong), 1577.92 cm$^{-1}$(-NO$_2$ aliphatic nitro group), 1609.01 cm$^{-1}$(N-H amides bend), 1524.96 cm$^{-1}$(N-H bend 1$^0$), 1435.74 cm$^{-1}$(C=C aromatic stretch medium-weak, multiple bands), 1376.49 cm$^{-1}$(-C-H alkane bending variable), 1296.32 cm$^{-1}$ (C-O anhydrides stretch), 1206.02 cm$^{-1}$(C-C stretch), 1018.57 cm$^{-1}$(C-O stretch), 945.85 cm$^{-1}$ (C-H bend), 802.06 cm$^{-1}$ (C-H bend trisubstituted), 756.03 cm$^{-1}$(C-H bend mono aromatic), 694.21 cm$^{-1}$(C-H bend disubstituted-z), 658.89 cm$^{-1}$(C-Cl stretch), 621.9 cm$^{-1}$(C-Br stretch), 564 503.39- cm$^{-1}$(C-I stretch) frequency in the FTIR for 4, 4-Diphenylmethane Diisocyanate.

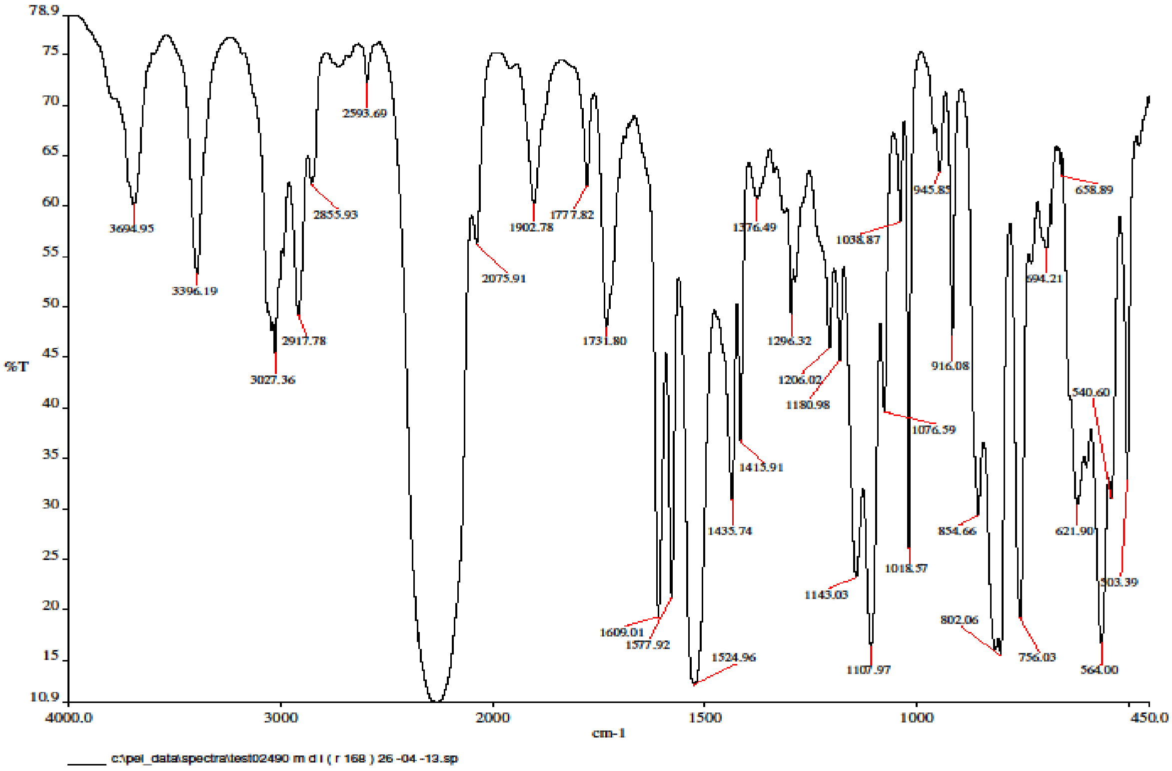


**Figure 3.1:** FTIR for 4, 4-Diphenylmethane Diisocyanate (MDI)

## 3.2 Modification of Castor Oil/Formation of Polyol

### 3.2.1 Experimental Setup and Procedure

The modification of castor oil was carried out under the inert atmosphere i.e in the presence of nitrogen. The setup consisted of a four necked round bottom flask of 500 mL capacity equipped with a mechanical stirrer. The stirrer was mounted on an overhung shaft, i.e. shaft supported from above, along the axis of the reactor, with a clearance from the bottom equal to one third of the diameter of the reactor. The shaft was driven by a 1/8 H P motor which was controlled through a dimmerstat.  Heating was carried out by means of a heating mentle. Nitrogen was supplied at a constant flow rate to avoid any oxidation reaction within the reactor. One of the necks of the reactor was equipped with a reflux condenser, to minimize the carry over losses.

**Figure 3.2:** Arrangement for Modification of Castor Oil

## 3.2.2 Procedure

The reaction kettle was charged with castor oil and Glycerol 6:1. The reacting contents were heated to a temperature of $220\pm10^0$C. The stirring speed is kept constant at 600 rpm. The progress of condensation reaction and its stability were confirmed by checking its hydroxyl value. For this purpose, the samples at regular intervals were taken out and checked for hydroxyl value, acid value, viscosity and water content. The heating was carried out till a hydroxyl value of 350-410 mg KOH/g is achieved. The time required to complete the reaction was 3-4 hrs. The resulted polyol was stored in dark bottles away from direct sun light. The properties of Modified Castor Oil or Modified Polyol as determined by various experimental procedures are reported in Table 3.4. Characterization of Modified Polyol for the determination of these properties is as given in Appendix-1.

**Table 3.4:** Properties of Modified Polyols

| **Properties** | **Value** |
|---|---|
| OH number (mg KOH/g) | 386.87 |
| Viscosity (cP at 25 °C) | 900 |
| Water content (%) | 0.01 |
| Acid number | 0.97 |
| Specific gravity (25 °C) | 0.98 |
| Solid content (%) | 98.67 |

These above properties shown in table are suitable for synthesis of polyurethane rigid foam.

### 3.2.3 FTIR Analysis of Modified Polyol

FTIR spectra of the modified polyols were recorded in A Nicolet 380 FTIR spectrophotometer. Small quantities of the liquid samples were spread in pure dried KBr for analysis. FTIR spectra of polyols are well known to be sensitive to hard domain organization. The characteristic absorptions peaks of the modified polyols are observed. Peaks ore obtained at frequency 3400.43 cm$^{-1}$(N-H stretching frequency), 3008.5 cm$^{-1}$(C-H stretching frequency), 2855.2 cm-$^{1}$(C-H stretching strong frequency), 1745.07 cm$^{-1}$(C=O stretching strong ester group), 1524.18 cm$^{-1}$(N-H amide bending), 1464.58 cm$^{-1}$(C=C aromatic stretch), 1377.73 cm$^{-1}$(-C-H alkane bending variables), 1165.77 cm$^{-1}$(C-N amine medium- weak stretch), 858.15 cm$^{-1}$(=C-H alkene bending strong intensity), 566.27 cm$^{-1}$(C-Br alkyl halide stretching strong intensity) respective to the bonds present. It is significant for the identification of the source of an absorption band is intensity, shape and position in the FTIR spectra.

**Figure 3.3:** FTIR for Modified Polyol

## 3.3 Preparation of Castor Oil Based Rigid Polyurethane Foams with Different Formulations of Blowing Agents

The rigid polyurethane foams were obtained by a two step method. In the first step, the castor oil was modified to obtain polyol of desired hydroxyl value. The Calculated amount of modified polyol is mixed with other ingredients as such as Catalyst: Stannous Octoate, Surfactant: Silicon Oil, Anti-flaming agent: Triethyl phosphate and Blowing Agent: 1,6-Hexanediol were added in the reaction kettle and thoroughly mixed under controlled temperature conditions at 35±2$^{0}$C to form Polyol-premix. In the subsequent step, this Polyol-premix was mixed with calculated amount of MDI by means of a high speed mechanical stirrer operating at 1000 rpm. The resulting reaction mixture was poured into a metal mould, coated with releasing agent i.e. silicon oil. The mould was thus closed and kept under a load of about 10 kN. To ensure complete curing, the moulds were left to stand for 24 hours. After demoulding, the resulted Castor Oil based Rigid Polyurethane foam was cut into desired dimensions and tested for its visual colour, tensile strength, compression strength, flexural strength, density, water absorption, morphology structure and biodegradability. Different formulation of blowing agents was used to study the effect of blowing agent on the properties of the foam. The experiment had been conducted by using two types of blowing agents: 1) Physical blowing agent: n-Pentane and 2) Chemical blowing agent: Water. Different formulations (10 %, 15%, and 20% w/w $_{\text{Polyol}}$) of the blowing agents had been used to study their effect on the properties of the foam. Both of the blowing agent used are having ODP value equal to zero, so are environmental friendly. To insure that a complete reaction takes place, the raw material formulation had NCO Index equal to 105. Different formulations of raw materials used in these studies are given in Tables 3.5 to 3.10. The procedure for the calculation of NCO Index is as given in Appendix-2.

**Table 3.5:** Formulations-A

| | | |
|---|---|---|
| Formulation-A | Polyol-premix | |
| | Modified polyols (OHV=373.5) | 100 pbw |
| | n-pentane | 10 pbw |
| | Triethyl phosphate | 10 pbw |
| | Stannous octoate | 2 pbw |
| | Silicon oil | 3 pbw |
| | Hexane 1, 6 diol | 2 pbw |
| MDI (R-168) | | Index = 105 |

**pbw=Parts By Weight.**

**Table 3.6:** Formulations-B

| | | |
|---|---|---|
| Formulation-B | Polyol-premix | |
| | Modified polyols (OHV=373.5) | 100 pbw |
| | n-pentane | 15 pbw |
| | Triethyl phosphate | 10 pbw |
| | Stannous octoate | 2 pbw |
| | Silicon oil | 3 pbw |
| | Hexane 1, 6 diol | 2 pbw |
| MDI (R-168) | | Index = 105 |

**pbw=Parts By Weight.**

**Table 3.7:** Formulations-C

| | | |
|---|---|---|
| Formulation -C | Polyol-premix | |
| | Modified polyols (OHV=373.5) | 100 pbw |
| | n-pentane | 20 pbw |
| | Triethyl phosphate | 10 pbw |
| | Stannous octoate | 2 pbw |
| | Silicon oil | 3 pbw |
| | Hexane 1, 6 diol | 2 pbw |
| MDI (R-168) | | Index = 105 |

**pbw=Parts By Weight.**

**Table 3.8:** Formulations-X

| | | |
|---|---|---|
| Formulation -X | Polyol-premix | |
| | Modified polyols (OHV=373.5) | 100 pbw |
| | Water | 10 pbw |
| | Triethyl phosphate | 10 pbw |
| | Stannous octoate | 2 pbw |
| | Silicon oil | 3 pbw |
| | Hexane 1, 6 diol | 2 pbw |
| MDI (R-168) | | Index = 105 |

**pbw=Parts By Weight.**

**Table 3.9:** Formulations-Y

| | | |
|---|---|---|
| Formulation -Y | Polyol-premix | |
| | Modified polyols (OHV=373.5) | 100 pbw |
| | Water | 15 pbw |
| | Triethyl phosphate | 10 pbw |
| | Stannous octoate | 2 pbw |
| | Silicon oil | 3 pbw |
| | Hexane 1, 6 diol | 2 pbw |
| MDI (R-168) | | Index = 105 |

**pbw=Parts By Weight.**

**Table 3.10:** Formulations-Z

| | | |
|---|---|---|
| Formulation -Z | Polyol-premix | |
| | Modified polyols (OHV=373.5) | 100 pbw |
| | Water | 20 pbw |
| | Triethyl phosphate | 10 pbw |
| | Stannous octoate | 2 pbw |
| | Silicon oil | 3 pbw |
| | Hexane 1, 6 diol | 2 pbw |
| MDI (R-168) | | Index = 105 |

**pbw= Parts By Weight.**

# CHAPTER-4

# RESULTS AND DISCUSSION

Polyurethane foams are one of the most important classes of cellular plastics. Rigid Polyurethane foams had been produced from the castor oil. As the properties and structure of the foam more or less dependent on the blowing agent used. Studies had been carried out for the effect of ddifferent formulation of blowing agents on the properties of the Castor Oil based Rigid Polyurethane foam. The experiments were conducted using two types of blowing agents with different formulations i.e.10 %, 15% and 20% of basic polyol. The resulted Castor Oil based Rigid Polyurethane foam was characterized for its visual colour, tensile strength, compression strength, flexural strength, density, water absorption, morphology structure and biodegradability.

## 4.1 Foaming Time

For foam production, the Polyol-premix and MDI are thoroughly mixed together under controlled temperature conditions. The reaction starts and progresses with heat evolution. The reaction mix continually expands by the blowing gases released, till the reaction product reaches the solid state (because of progressive crosslinkage) and attain its structure. The foaming process progresses with the following stages:

- The **mixing time** or **stirring time** that indicates the time needed for mixing the reactants.

- The **cream** and **foaming time** is the time which elapses from the start of mixing of the reactants to the visible start of foaming of the mix. In many cases this can be seen clearly by a color change. With slow reacting mixes this requires practiced observation.

• The **string or fiber time** is the transition of the reaction mix from the liquid to the solid state. It roughly corresponds to the gel point. When this point in time is reached the reaction is about 50 % complete. The fiber time is measured by, for example, a wooden rod being repeatedly immersed in and removed from the already well expanding reaction mix, and it is determined when the rod draws fibers. Time measurement begins with mixing.

•**Full rise time** and **tack-free time**: After fiber time, the speed at which the foam rises slows down. The time from the start of mixing till the end of the optically perceptible rise is called the rise time. The surface of the foam is still tacky when the rise process is complete. By repeatedly testing the foam surface with a wooden rod, the moment of freedom from tack is determined. The time elapsing from the start of mixing to the moment when the surface is no longer tacky is called **tack-free time**.

• **Gas release time**: Open-cell foams can open their surface after a certain time and release excess blowing gas. The time elapsing from the start of mixing to the start of gas release is called the **gas release time.**

Reaction times are dependent on the temperature of the reaction components, i.e. the reaction mix. The reaction times decrease as the temperature rises. The foam reaches its final structure at the end of fiber time. The forming stages for different formulation of raw materials are given in Table 4.1.

**Table 4.1:** The Forming Stages for Different Formulations

| **Processing Stage** | **Formulation A** | **Formulation B** | **Formulation C** | **Formulation X** | **Formulation Y** | **Formulation Z** |
|---|---|---|---|---|---|---|
| Cream Time | 40 sec | 37 sec | 36 sec | 35 sec | 35 sec | 34 sec |
| Gel Time | 135 sec | 125 sec | 120 sec | 50 sec | 46 sec | 45 sec |
| Tack Free Time | 230 sec | 218 sec | 215sec | 70 sec | 65 sec | 57 sec |
| Mold Temp. | ambient | ambient | ambient | ambient | ambient | ambient |
| Demold Time | 15 min. | 15 min. | 15 min. | 15 min. | 15 min. | 15 min. |

From the results obtained for the different formulations, it is clear that with increase in the content of blowing agent, the processing time decreases. It is clearly evident from the Table 4.1 that the cream times get reduced from 40 seconds for formulation A to 37 and 36 seconds respectively for formulation B and C for n-Pentane as blowing agent. Similarly the gel time and tack free time had shown decrease in values, for formulation A to C. Similar trend was observed for the system, with water as blowing agent. Although the cream time did not show a significant fall, but tact free time, the time get reduced with increase in the water content. It clearly indicates that with increase in quantity of blowing agent, the foaming process becomes more rapid. Much difference had been observed in the values of get time and tact free time for the n-pentane blown foam and water blown film. Although no significant difference had been observed in the cream time for both blowing agent system, but gel time and tact fee time became almost 2.5 to 3.5 times for n-pentane system (formulation A, B,C) as compared to water blown system (formulation X, Y, Z). From the results obtained as given in Table 4.1, for the water blown foams, the reaction progresses at much faster rate as compared to the n-Pentane blown foams. With increase in the concentration of blowing agent the process progresses faster even when the temperature is kept constant.

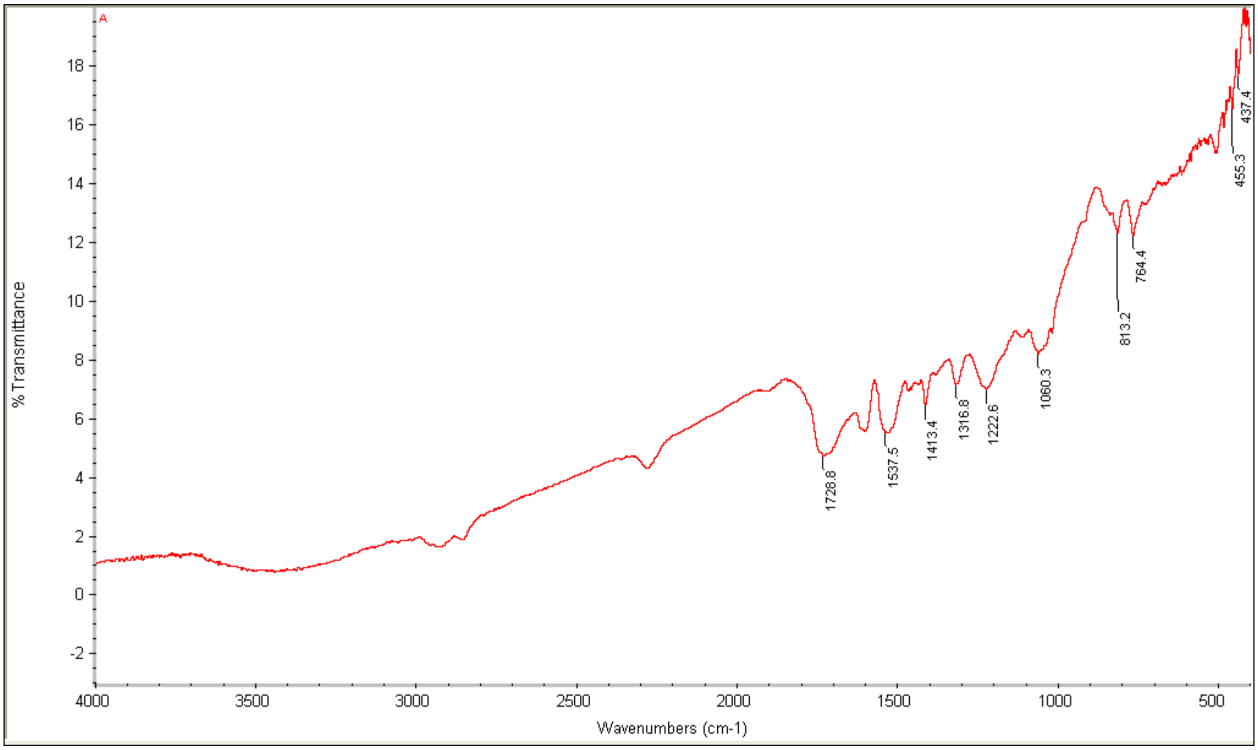
## 4.2 Visual Studies for Appearance and Color

It was observed that in all the products obtained, the intensity of the yellow colour was more. The reason behind this is that of the yellow colour of natural castor oil itself. However, if castor oil is bleached prior to the formation of foams, the resulted foam produced would range from colourless to white. In addition, the foam can be made coloured by the addition of dyes or pigments during the processing itself.

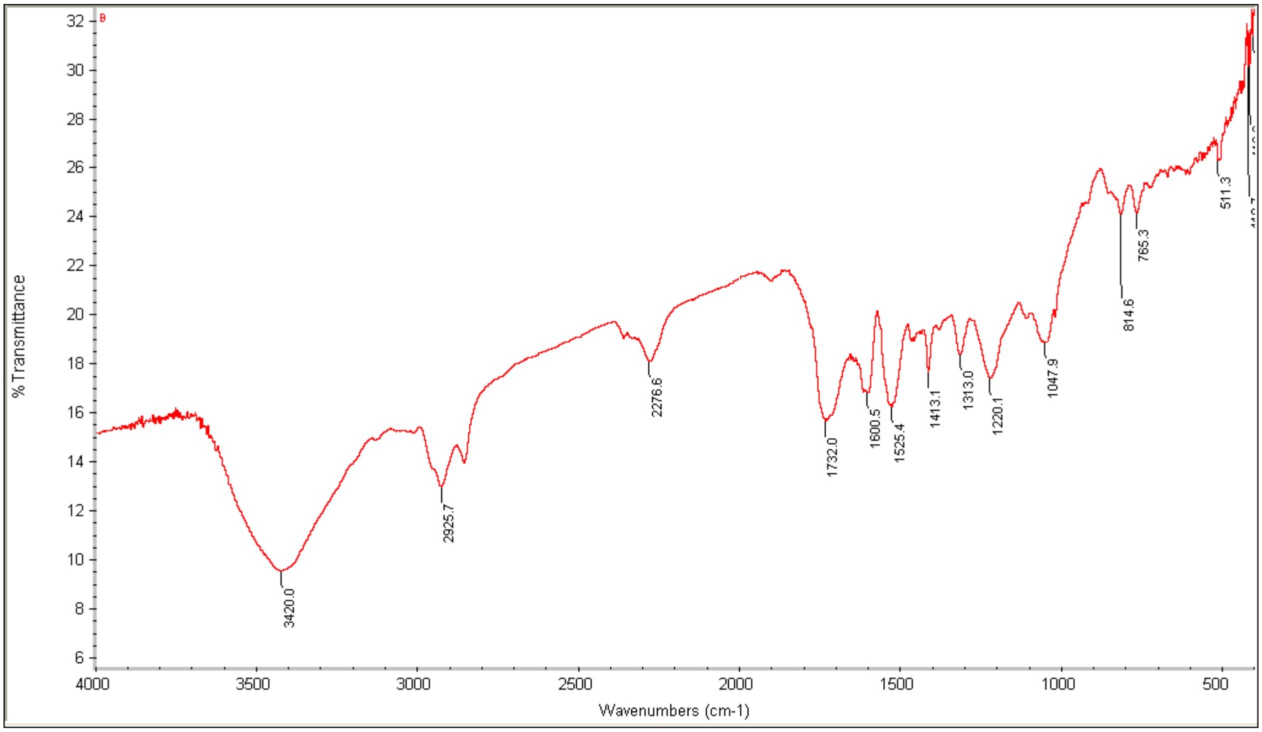
## 4.3 FTIR Analysis

To understand the possible reactions that may occur among the reactants i.e. modified polyols and MDI with different formulations of blowing agents, Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 380 spectrometer (Figure 4.1), in the range 400–4,000 cm-1. KBr pellets were used to verify the completion of the resin curing reaction and the presence of free isocyanate groups (NCO) in cured Rigid Polyurethane Foam. FTIR spectra of PUs (and modified polyol-based polyurethanes) are well known to be sensitive to hard domain organization and the urea and urethane hydrogen bonding. The characteristic absorptions peaks of the PU rigid foam blown with n-Pentane are as shown in Figure 4.2 (a) to (c). For formulation-A, with 10% concentration of n-Pentane, the absorption peaks, with corresponding bonds were observed at 1728.8 cm$^{-1}$ (C=O carbonyl urethane stretching, strong), 1537.5- 1413.4 cm$^{-1}$ (C=C stretching frequencies), 1316.8 cm$^{-1}$ (C-N stretching), 1222.6- 1060.3 cm$^{-1}$ (coupled C–N and C–O stretching), 813.2 cm$^{-1}$ (C-H bend (trisubstituted)), and 764.4 cm$^{-1}$ (C-H bend, ortho). For formulation-B with n-Pentane Concentration 15%, as clear from Figure 4.2 (b), peaks are observed at 3420 cm$^{-1}$ (N-H stretch), 2925.7 cm$^{-1}$ (C-H stretch), 2276.6 cm$^{-1}$ (-N=C=O stretch), 1732 cm$^{-1}$ (C=O stretch), 1600.5 cm$^{-1}$(C=C stretch), 1525.4 cm$^{-1}$(N-H bend 1$^{0}$), 1413.1 cm$^{-1}$ (O-H bend), 1313 cm$^{-1}$ (C-N stretch, aryl), 1220.1-1047.9 cm$^{-1}$ (C-O stretch), 814.6 cm$^{-1}$ (C-H bend, trisubstituted), 765.3 cm$^{-1}$(C-H bend, ortho), 511.3 cm$^{-1}$(C-Br stretch with strong intensity) more interested peaks observed. Similarly for formulation-C (20% concentration of n-Pentane), as clear from Figure 4.3 (c), absorption peaks are at frequency 3420.1cm$^{-1}$ (N-H stretch with unsubstituted have two bands intensity), 2924.8 cm$^{-1}$(C-H alkane, stretch strong intensity ), 1736.8 $cm^{-1}$ (C=O aldehyde, stretch with strong intensity), 1600.6 $cm^{-1}$(N-H amide, bending), 1528.9 $cm^{-1}$(N-O nitro, stretch strong two bands), 1413.1 $cm^{-1}$ (-C-H alkane, bending, variable intensity), 1314.2 $cm^{-1}$ (C-N amine, stretch, medium weak intensity), 1220.1 $cm^{-1}$ (C-O acid, stretch, strong), 1060.3 $cm^{-1}$ (C-O ether, stretch, strong), 816.1 $cm^{-1}$ (=C-H alkene, bending, strong intensity)observed . In the similar manner FTIR spectra for formulations blown with water is as given in Figure 4.3 (a) to (c). In formulation X, with 10% concentration of water, as in Figure 4.3 (a), absorption peaks are observed at frequency 1711.9 $cm^{-1}$ (C=O, stretch, strong), 1533.7 $cm^{-1}$ (C=C aromatic stretch, medium weak, multiple bands), 1043.6 $cm^{-1}$(C-O, ether, stretch, strong intensity), 925.7 $cm^{-1}$(C-H, alkane bend), 863.4 $cm^{-1}$(C-H, phenyl ring, substitution band), 803.7 $cm^{-1}$ (=C-H, bonding stretch), 509.6 $cm^{-1}$(C-Br, stretch), for formulation Y with 15% water concentration in Figure 4.3 (b) at 3433.8 $cm^{-1}$ (N-H, amine, stretch), 1735.5 $cm^{-1}$(C=O, aldehyde, stretch, strong intensity), 1654.8 $cm^{-1}$(C=C, stretch, variable intensity), 1261.5 $cm^{-1}$(C-O, ester, stretch, two band intensity), 1095.4 $cm^{-1}$ (C-O, alcohol, stretch, strong intensity), 804.3 $cm^{-1}$(C-H, aromatic ring, band ) and for formulation-Z (20%) water concentration, as in Figure 4.3 (c). are at 3384 $cm^{-1}$(N-H, amine, stretch), 2928.5 $cm^{-1}$(C-H, alkane, stretch, strong), 2278.5 cm-$^{1}$ (CN, nitrile, stretch), 1712.9 $cm^{-1}$(C=O, acid, stretch, strong intensity), 1597.8 $cm^{-1}$(N-H, amide, bending, two band), 1538.6 $cm^{-1}$(N-O, nitro, stretch, strong band), 1454.3-1413.7 $cm^{-1}$ (C=C, aromatic, stretch , medium weak multiple band), 1315.7-1226.6 $cm^{-1}$(C-N, amine, stretch, medium weak), 1050.2 $cm^{-1}$(C-O, alcohol, stretch, strong), 916.7 $cm^{-1}$(C-H, band), 813.5-761.7 $cm^{-1}$(C-Cl , stretch), 511.3 $cm^{-1}$(C-Br, stretch). It has been observed that with increase in concentration of blowing agent, number of peaks got increased. Also the number of peaks observed in water blown rigid polyurethane systems is more as compared to n-Pentane blown systems. Thus, from the observed FTIR spectra, the absorption peaks obtained are as according to that of characteristic peaks observed for polyurethane foams.

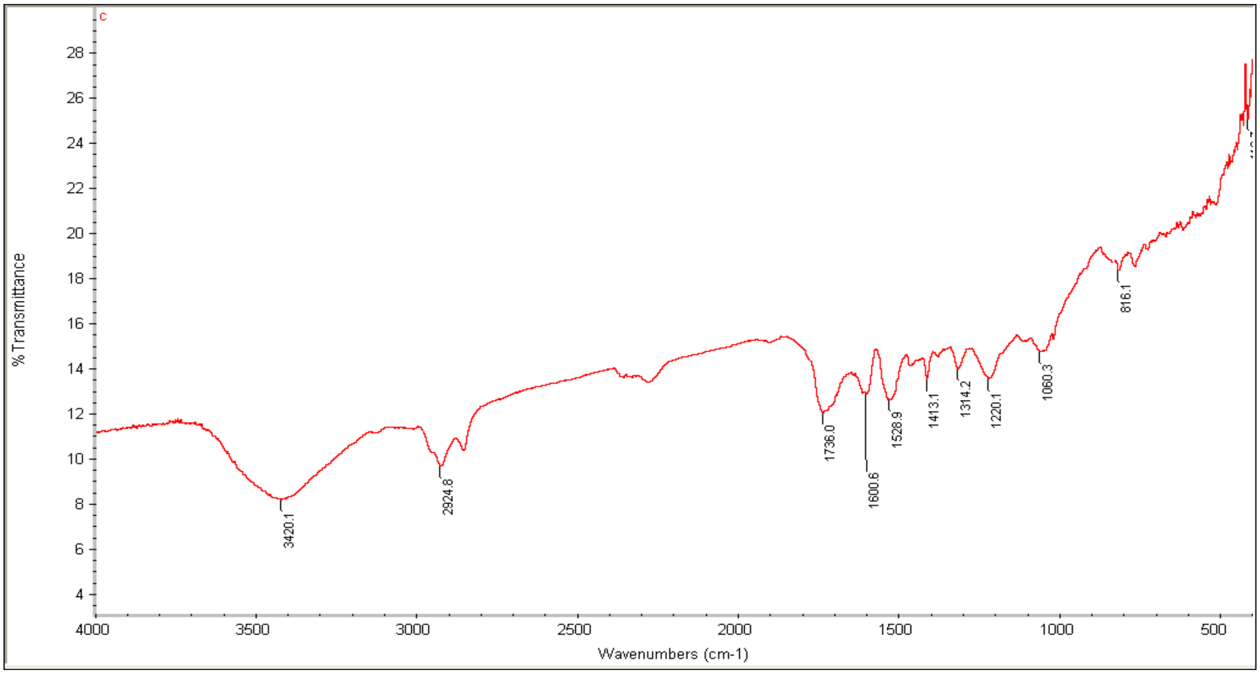
**Figure 4.1:** FTIR (Nicolet 380) Spectrometer



(a)



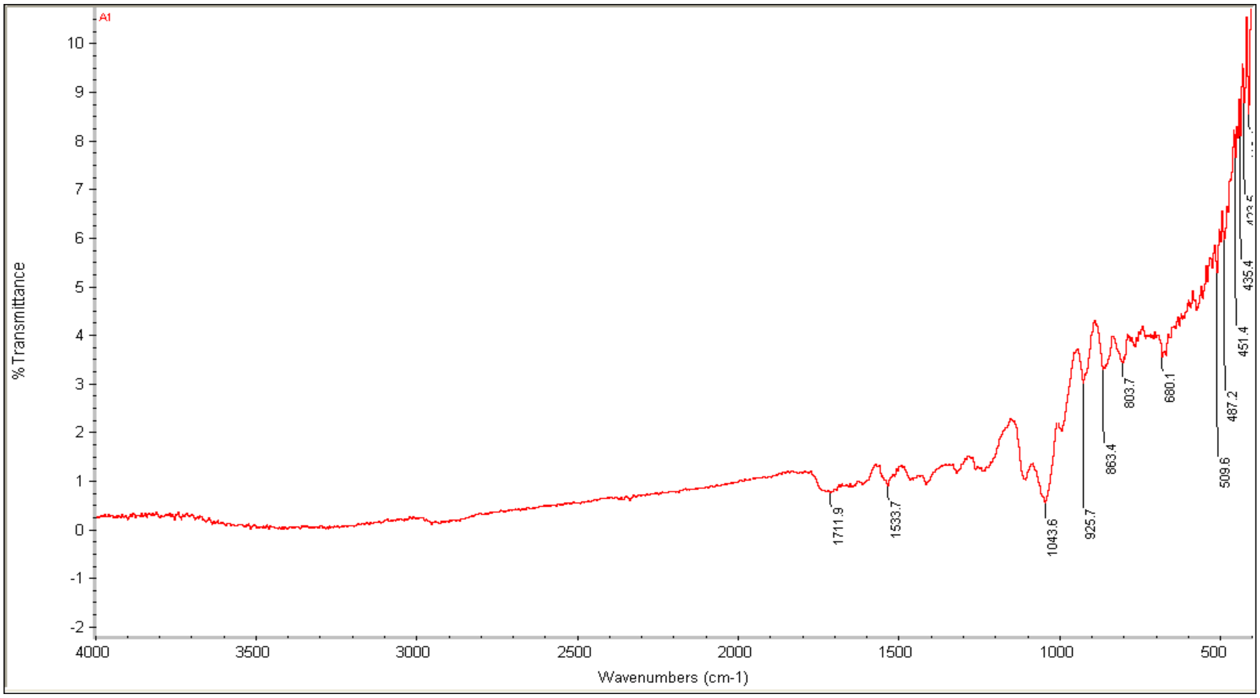
(b)



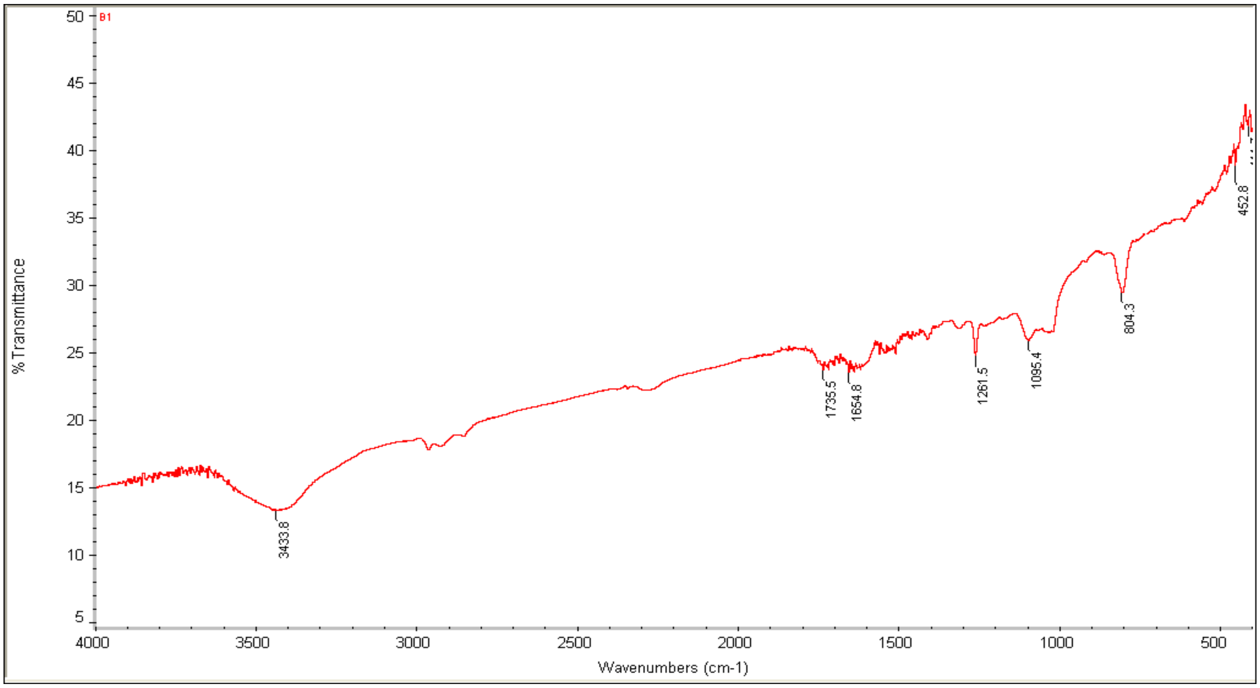
(c)

**Figure 4.2:** FTIR Spectra of Castor Oil based of Rigid Polyurethane Foam for

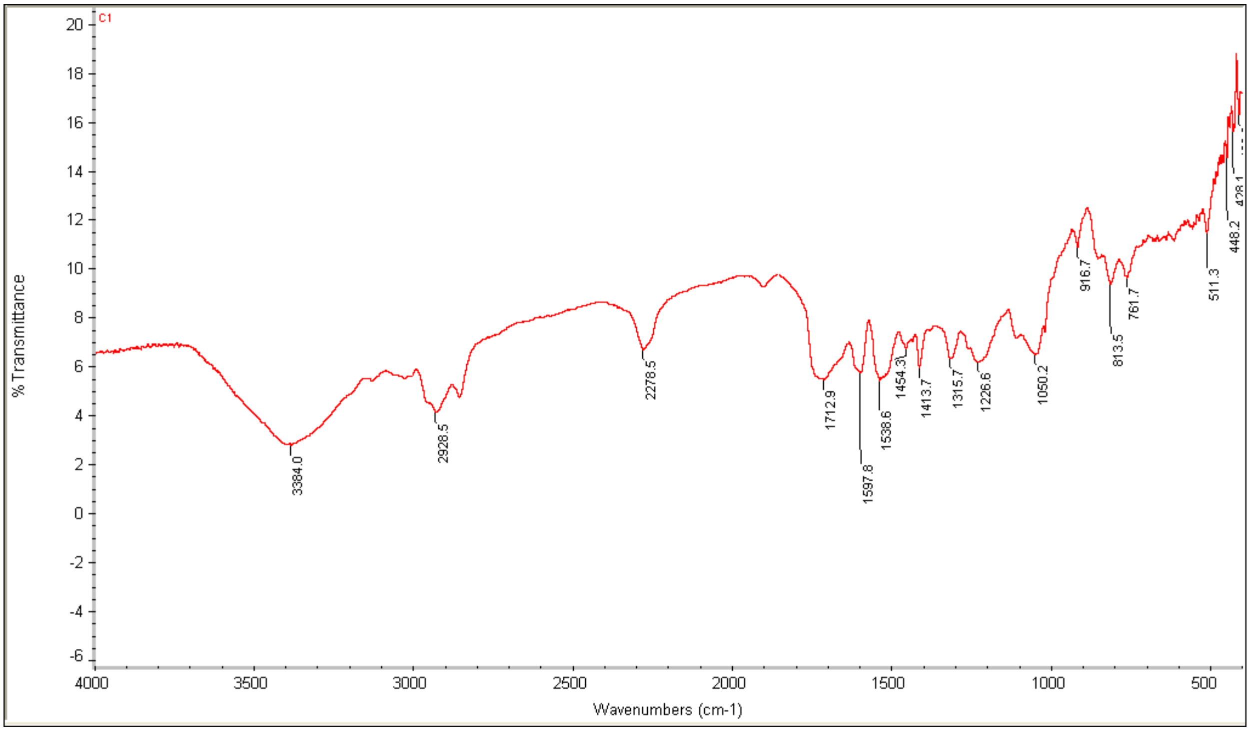
(a) Formulation-A (b) Formulation-B and (c) Formulation-C


A1
% Transmittance
10
9
8
7
6
5
4
3
2
1
0
-1
-2
1711.9
1533.7
1043.6
925.7
863.4
803.7
680.1
509.6
487.2
451.4
435.4
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

(a)


B1
% Transmittance
50
45
40
35
30
25
20
15
10
5
3433.8
1735.5
1654.8
1261.5
1095.4
804.3
452.8
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

(b)



(c)

**Figure 4.3:** FTIR Spectra of Castor Oil based of Rigid Polyurethane Foam for

(a) Formulation-X (b) Formulation-Y and (c) Formulation-Z

## 4.4 Thermogravimetric Analysis (TGA)

TGA is most important technique to measure thermal properties of the materials. The thermal degradation pattern of the Castor Oil based Rigid Polyurethane with different formulation of n-Pentane as blowing agents were determined by Thermogravimetric Analysis Instrument (Universal V4.5A, TA) under a nitrogen atmosphere. The TGA Analysis Instrument is shown in Figure 4.4. The thermal degradation studies of n-Pentane blown Castor Oil based Rigid Polyurethane samples were carried by heating the samples from room temperature to 300 ºC at a rate of 10ºC/min. The weight change of each sample was recorded as a function of temperature and the results were compared to pure clay. The thermal degradation of polyurethane occurs in two stages: the first stage is mainly governed by the degradation of the hard segment and the second stage correlates well with the degradation of the soft segment. Thermogravimetric Analysis Curves for Castor Oil based Rigid Polyurethanes with different formulations of n-Pentane are as shown in Figure 4.5 (a) to (c). From the Figure 4.5, it has been observed that the first degradation temperatures (T1), i.e. the temperatures at 5% weight loss of the PU rigid foam for formulation A (10% N-Pentane) was in the very close range for that of formulation B (15% n-Pentane) and formulation C (20% n-Pentane). The first degradation is mostly dominated by the degradation of organic modifier present in the foam. The derivative of the weight loss curves gave distinct degradation temperature peak (T2), where the effect of blowing agent is clearly seen. The T2 values of the PU rigid foam for formulation A were higher than those of formulation B and Formulation C hence showing less degradation in comparison. This result indicates that increased concentration of blowing agent makes the polymer a bit less prone to degradation. Generally, it is said blowing agents can enhance the thermal stability of polymer by acting as thermal insulator and mass transport barrier to the volatile products generated during decomposition. In the case of all the polyurethanes, a small % weight loss observed in the temperature range 100ºC - 200ºC is apparently associated with adsorbed water. At higher temperatures (200° C and 300° C), the weight loss observed in polyurethanes are 2%, 15% (Figure 4.5 (a), 3%, 17 % ((Figure 4.5 (b)) and 3%, 18% (Figure 4.6 (c)) respectively at the same temperature there by proving the higher thermal stability of the rigid polyurethane foam.

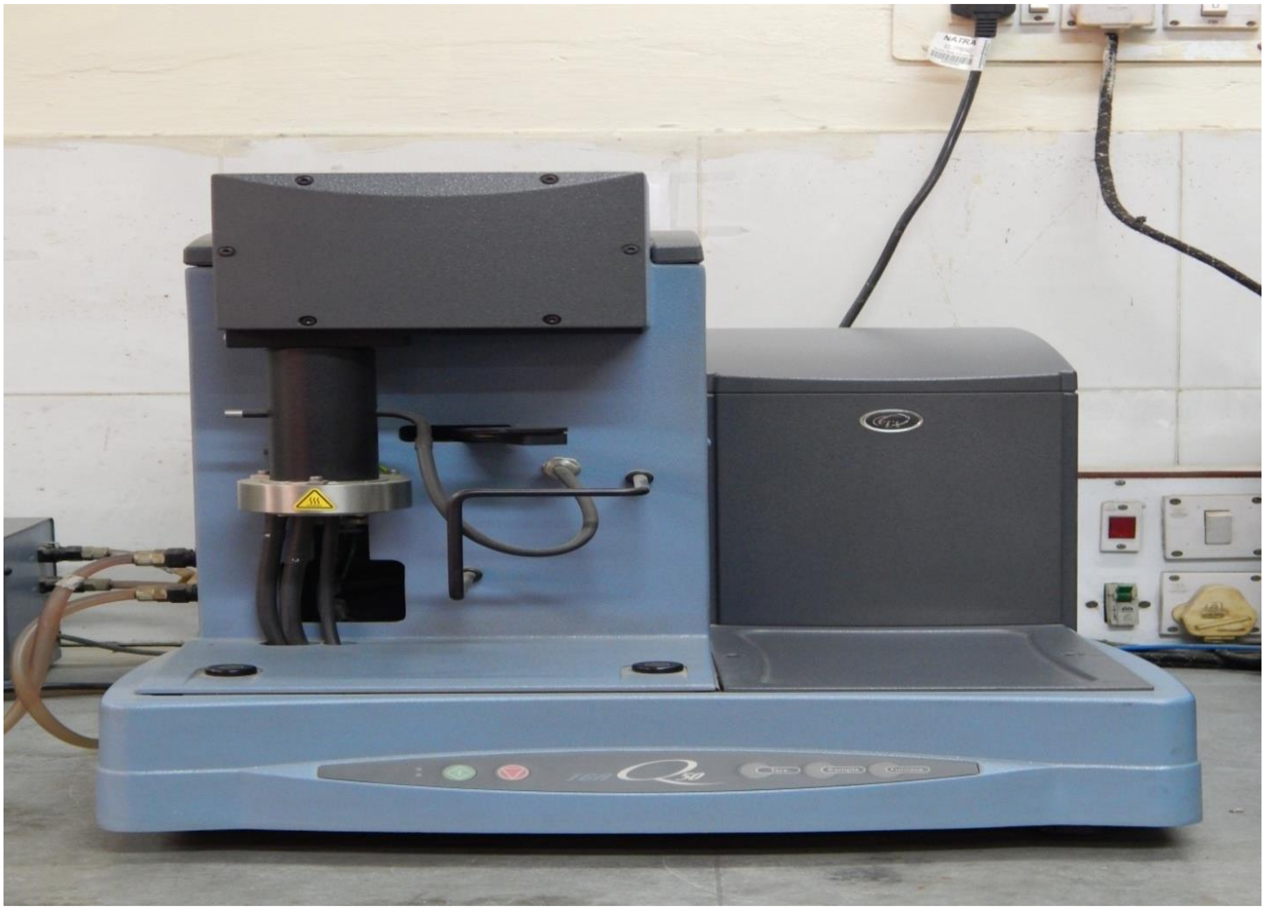
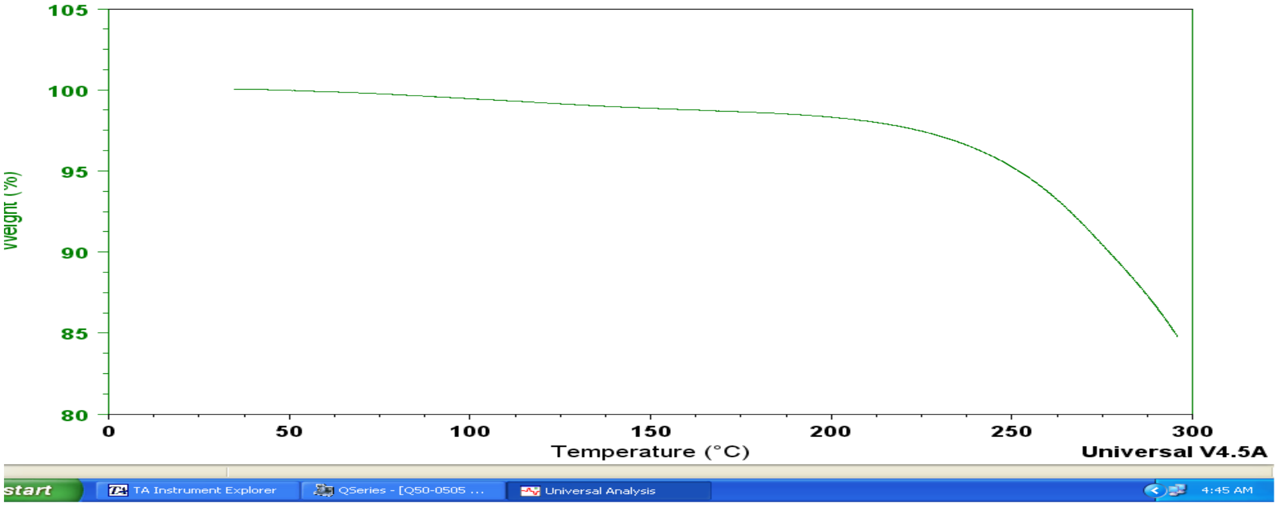
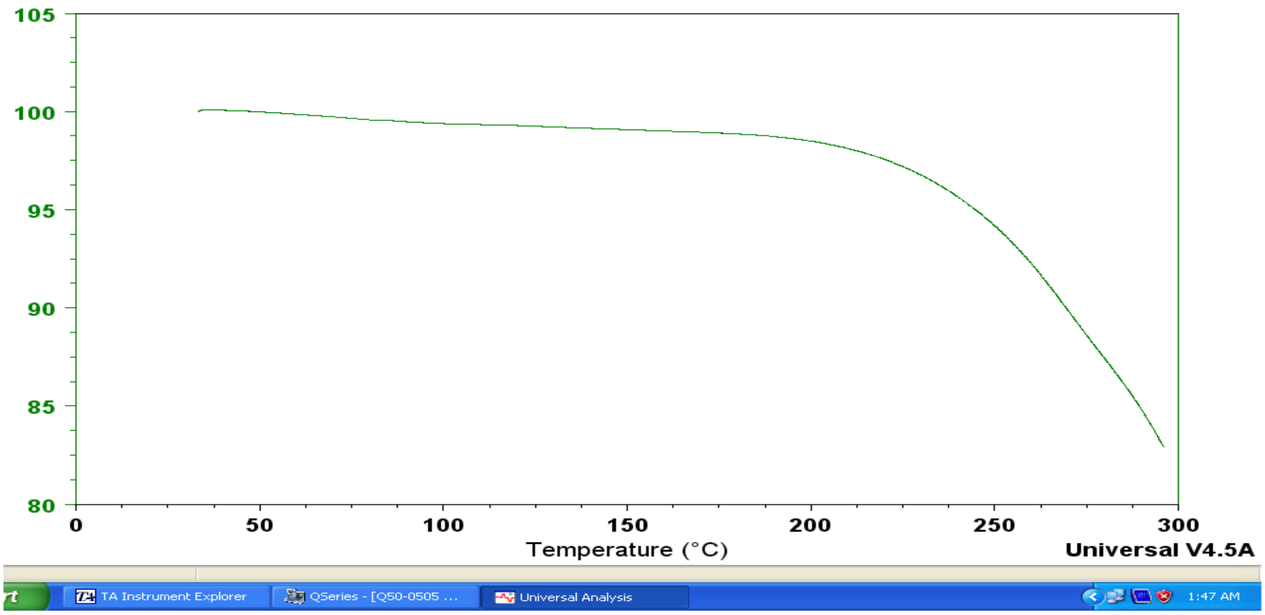


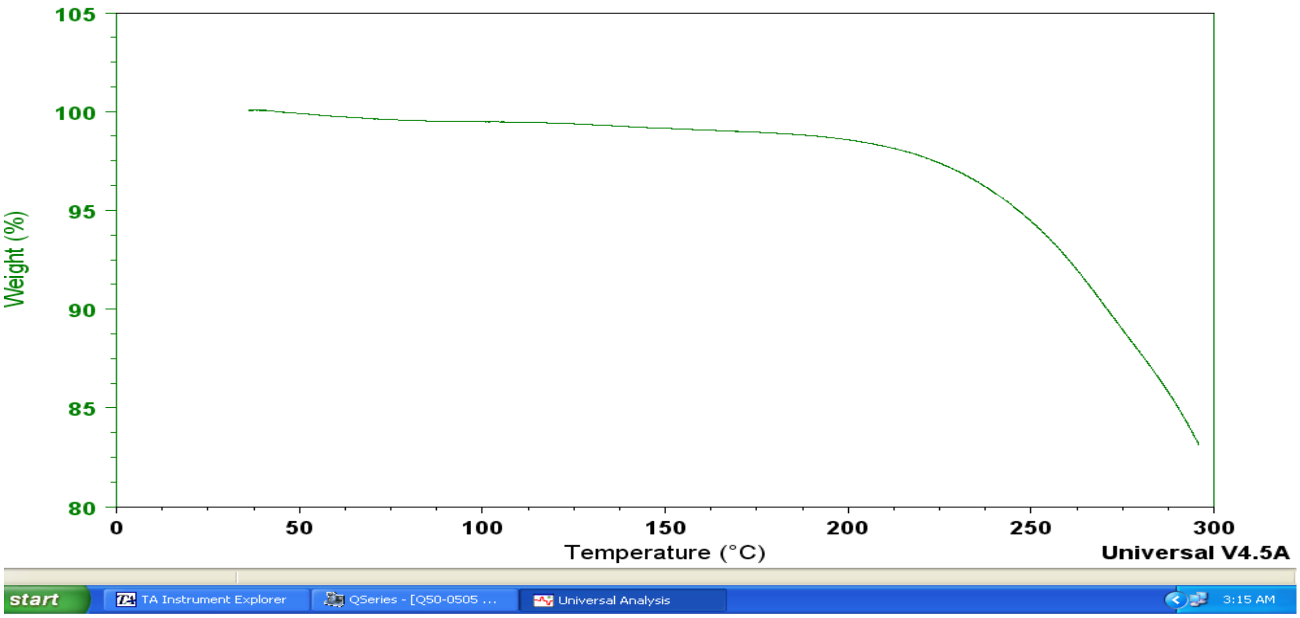
**Figure 4.4:** Thermogravimetric Analysis Instruments (Universal V4.5A, TA)



(a)



(b)



(c)

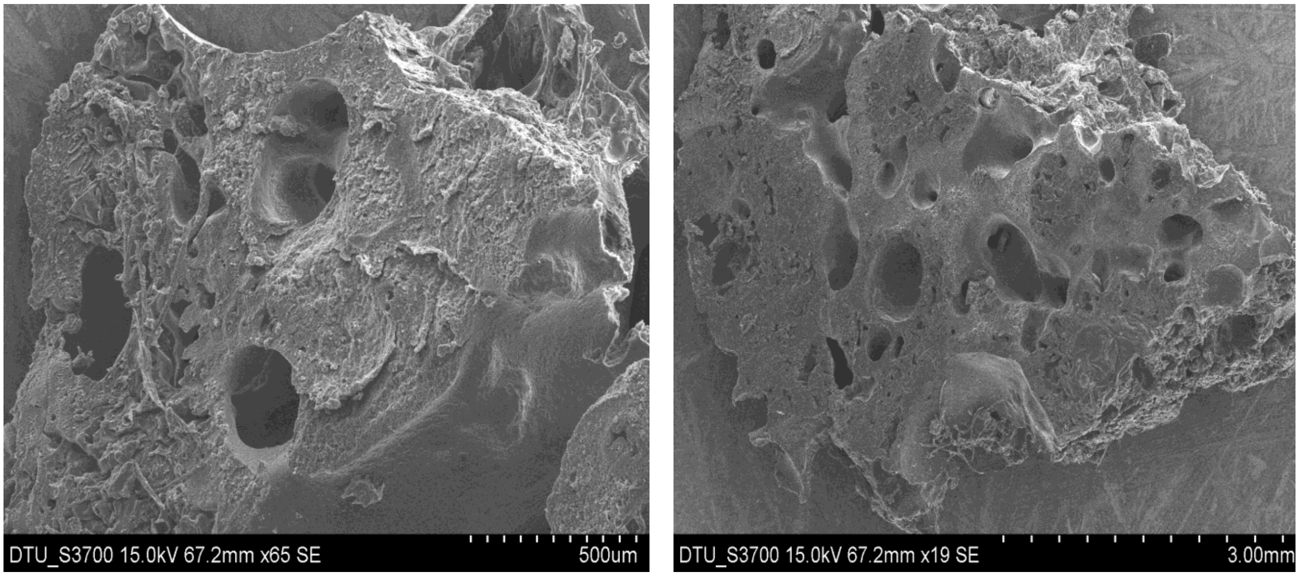
**Figure 4.5:** Thermogravimetric Analysis (TGA) of Castor Oil based Rigid Polyurethane foam with (a) Formulation- A (b) Formulation-B and (c) Formulation- C

## 4.5 Scanning Electron Microscope (SEM) Studies

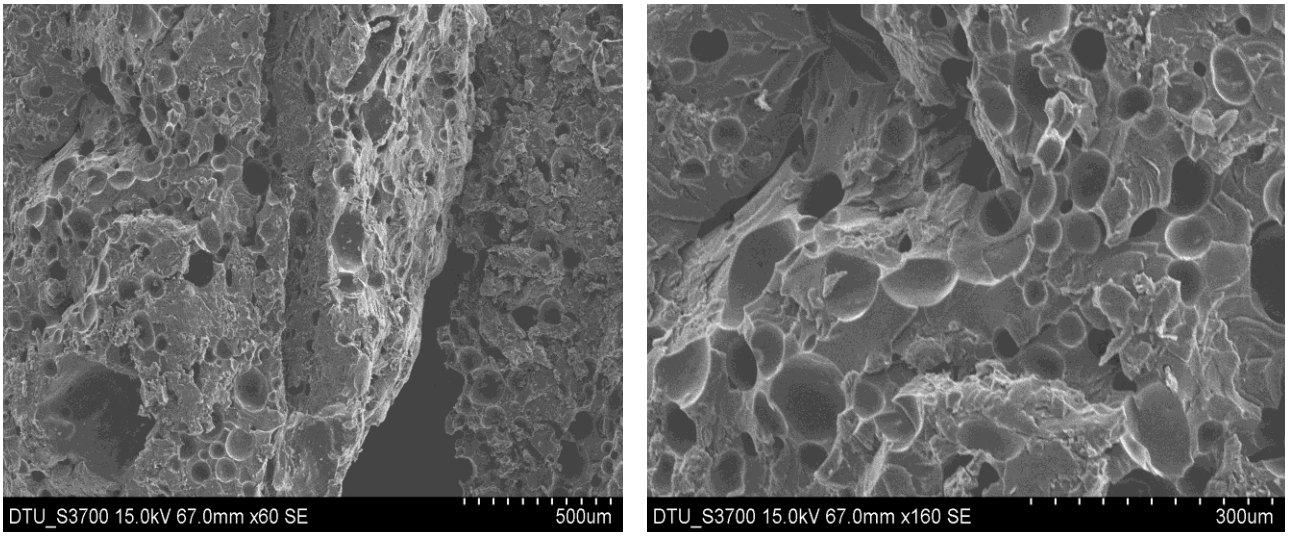
In general, the physical properties of foams do not only depend on the rigidity of the polymer matrix, but are also related to the foam cell structure.  Thus, it is of interest to observe the structure of the foam specimen using SEM. The cell structures of the samples were characterized with a Hitachi S 3700 SEM (Scanning Electron Microscope) using an acceleration of 15 kV (Figure 4.6 (a) and (b). Figure 4.7(a) to (c) and Figure 4.8 (a) to (c) shows the scanning electron micrographs of the castor oil based rigid polyurethane foams with different formulation of n-pentane and water respectively. As seen in Figure 4.7 (a), for the formulation-A, i.e. for blowing agent 10%, the foams present a higher cell density with a smaller pore size. The size of pores is mostly in range of 200 µm and a few are in the range of 150-250 µm, with an average pore size equal to 180 µm. The pore size is found to be subsequently increased for other two formulations, with more % age of blowing agent.  For formulation-B (n-pentane, 15%), in Figure 4.7 (b), it is clearly indicated that pore size is increases to an average pore size of 350 µm. And, with further increase in n-pentane contents, i.e. for formulation-C with ratio of n-pentane, 20%, average pore size was reported to be 400 (Figure 4.7(c)). Thus, the pore size nearly becomes double when the concentration of pentane is increased for 10% to 20%. The increases in pore size have been observed for foams blown with water.  From the observed pore size, as in case of formulation–X (water,10%), from Figure 4.8 (a), formulation–Y (water, 15%) from Figure 4.8 (b) and formulation-Z (water,20%), from Figure 4.8 (c), it is clearly indicated that the structure of foam was less  packed. This may be due to the chemical blowing action of water, leading to higher expansion efficiency thus resulting in the less packed foam molecules. The less packed structure of the water blown Castor Oil based Rigid Polyurethane foam, leaded to low density and decreased compressive strength, as discussed in subsequent sections. This may be due to the chemical blowing action of the water, resulting in the blow of the foam molecules.

(a) (b)

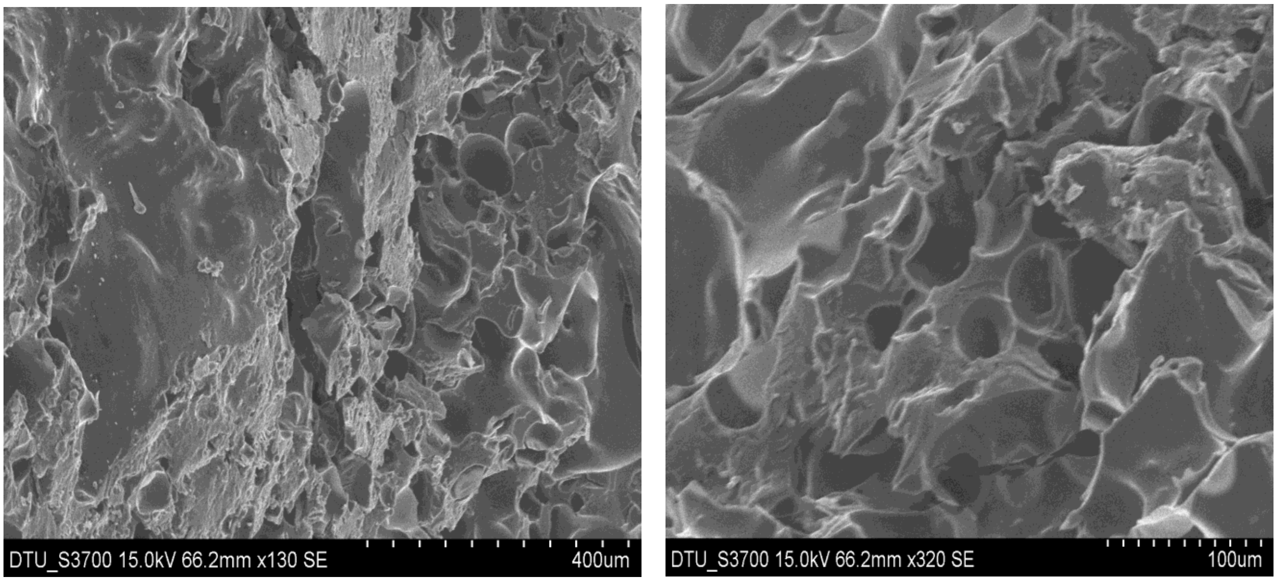
**Figure 4.6:** Scanning Electron Microscopic (Hitachi S-3700N), (a) front view, (b) side view



(a) 500 & 300µm magnificatio

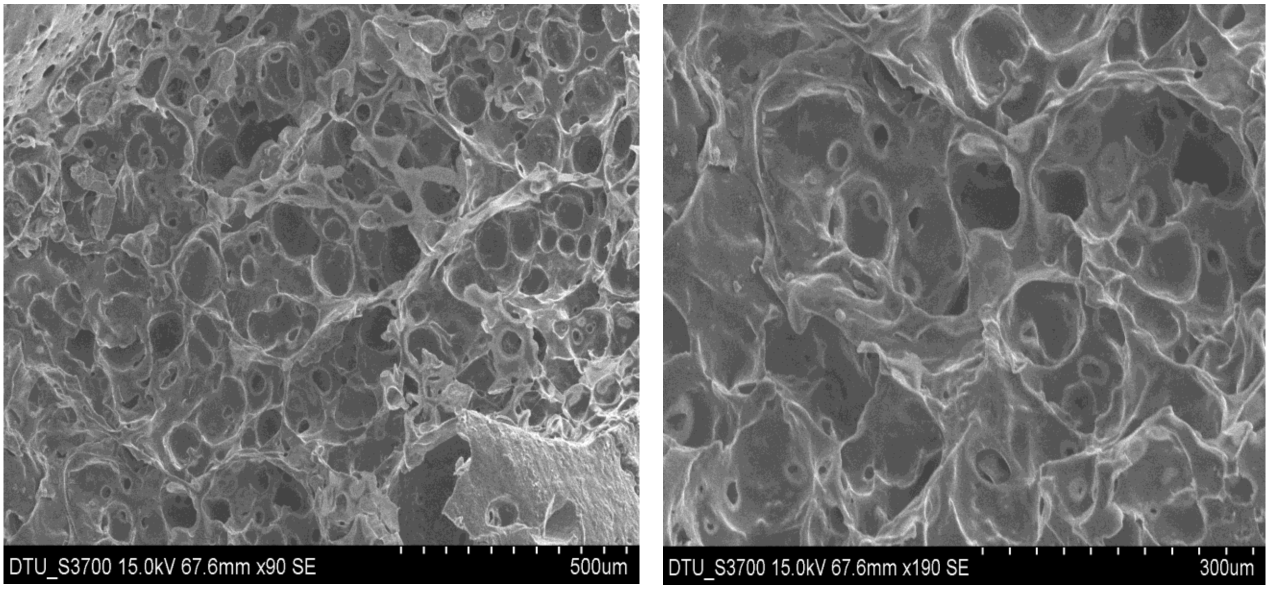


(b) 500 & 300µm magnification

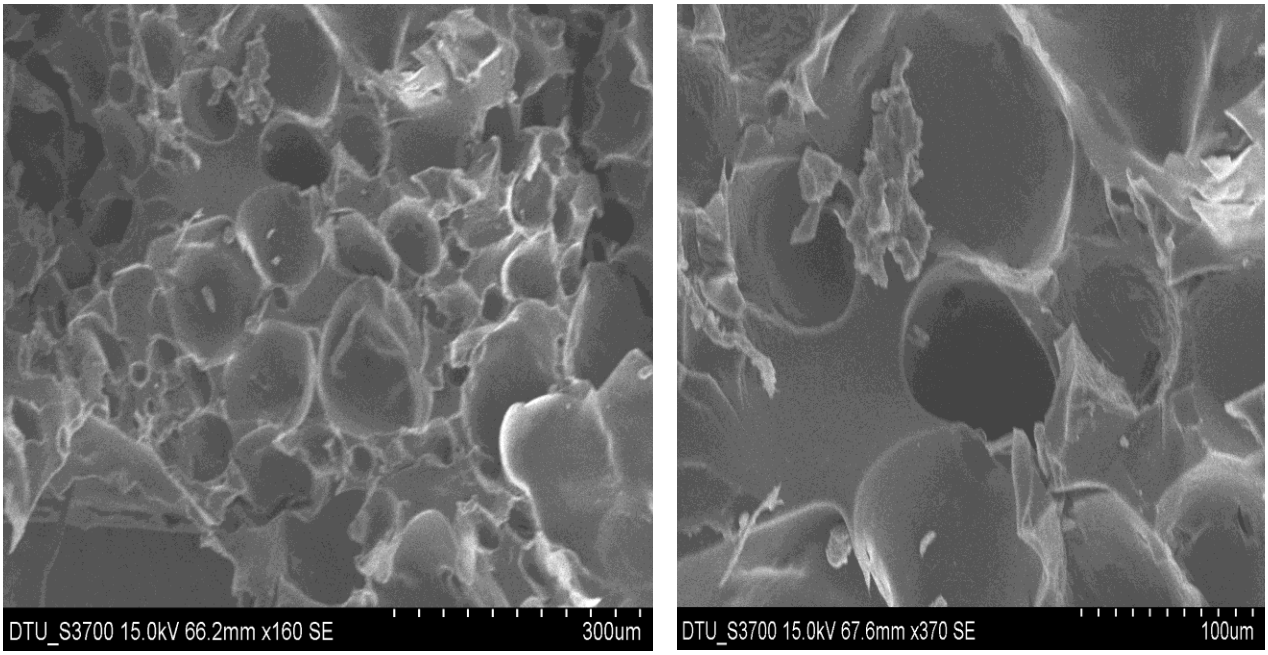


(c) 400 & 100µm magnification

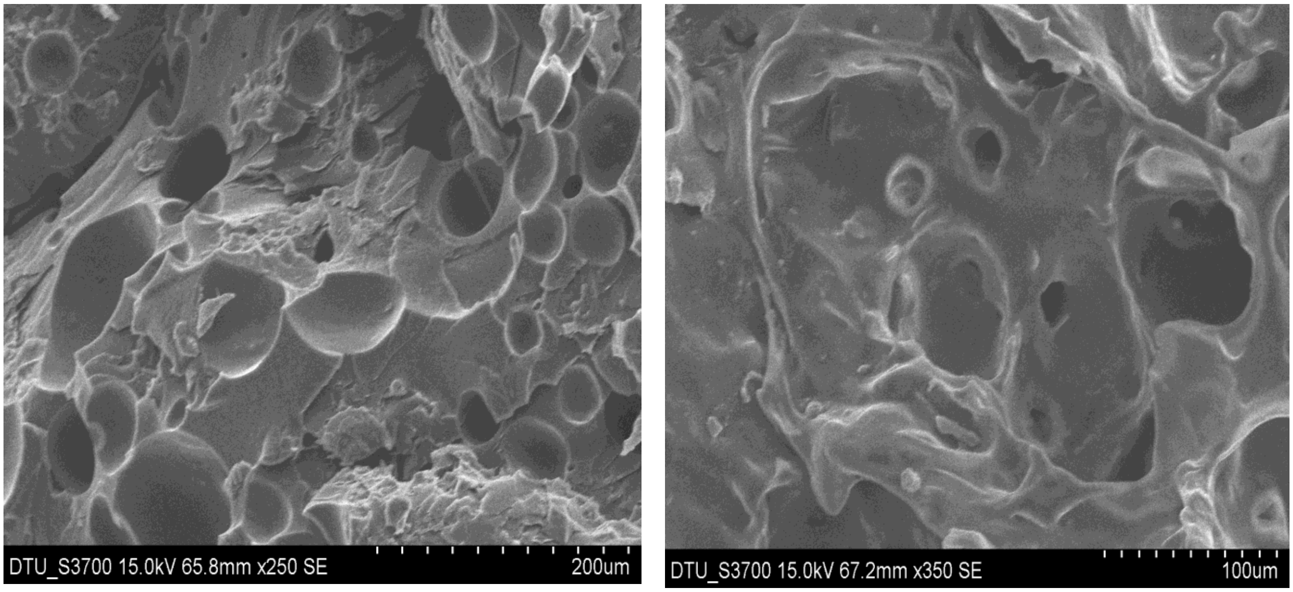
**Figure 4.7:** SEM of Caster oil based Rigid Polyurethanes Foam for (a) Formulation-A, (b) Formulation-B and (c) Formulation-C



**(a)** 500 & 300µm magnification



(b) 300 & 100µm magnification



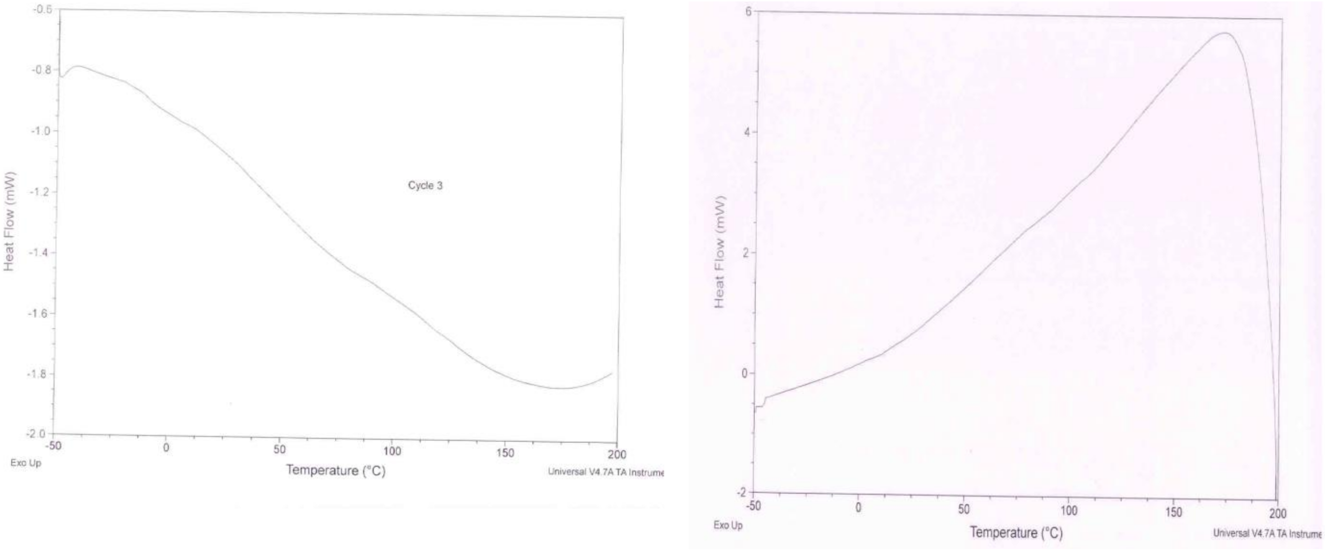
(c) 200 & 100μm magnification

**Figure 4.8:** SEM of Caster oil based Rigid Polyurethanes Foam for (a)Formulation-X, (b) Formulation-Y and (c) Formulation-Z

## 4.6 Differential Scanning Calorimeter (DSC)

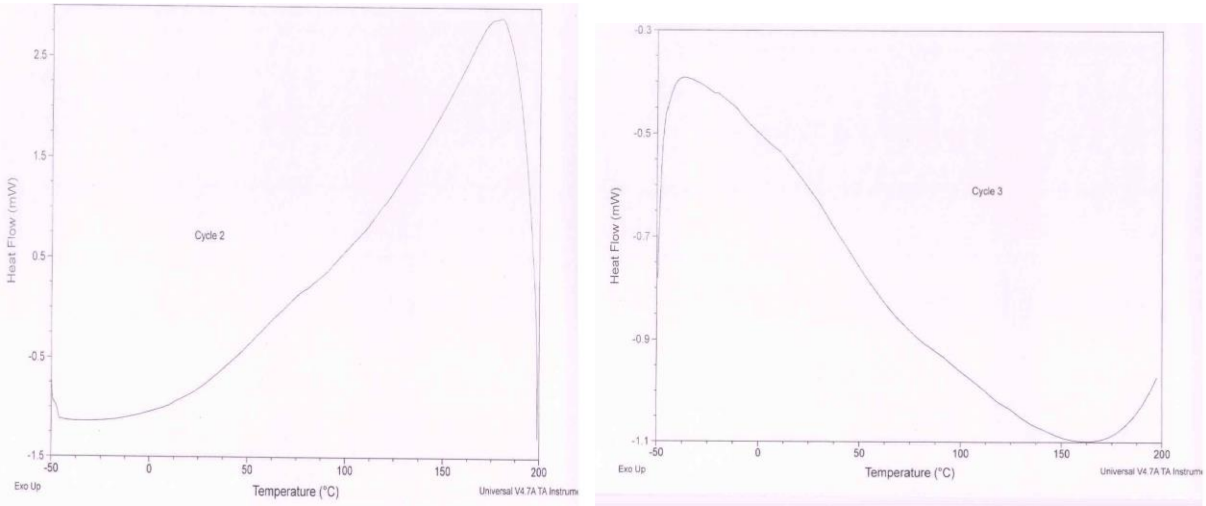
A Differential Scanning Calorimeter (DSC 7, Perkin-Elmer, Waltham, MA) was used to determine the glass transition temperatures (Tg) and specific heat change ($\Delta c$p) of polyurethane rigid foam (Figure 4.9). Approximately 6 to 7 mg of polyurethane film was loaded into an aluminium sample holder and sealed. The sample was cooled to -50°C and equilibrated for 5 min first and then heated to 200°C at 10°C/min. The DSC heating curves of rigid polyurethane foams containing n-pentane and water as blowing agents with different concentrations at temperature range from -50 to 200°C are as shown in Figure 4.10 (a) to (c) and 4.11 (a) to (c) respectively. All curves show a discontinuity in specific heat indicating a second-order transition. The glass transition temperature, Tg, of the rigid polyurethane foams were determined by taking the middle of the change in base line which is the inflection point. The specific heat changes at Tg, *Δc*p, of the rigid polyurethane foams are shown in graph itself.

**Figure 4.9:** Differential Scanning Calorimeter (Perkin-Elmer, Waltham, MA)



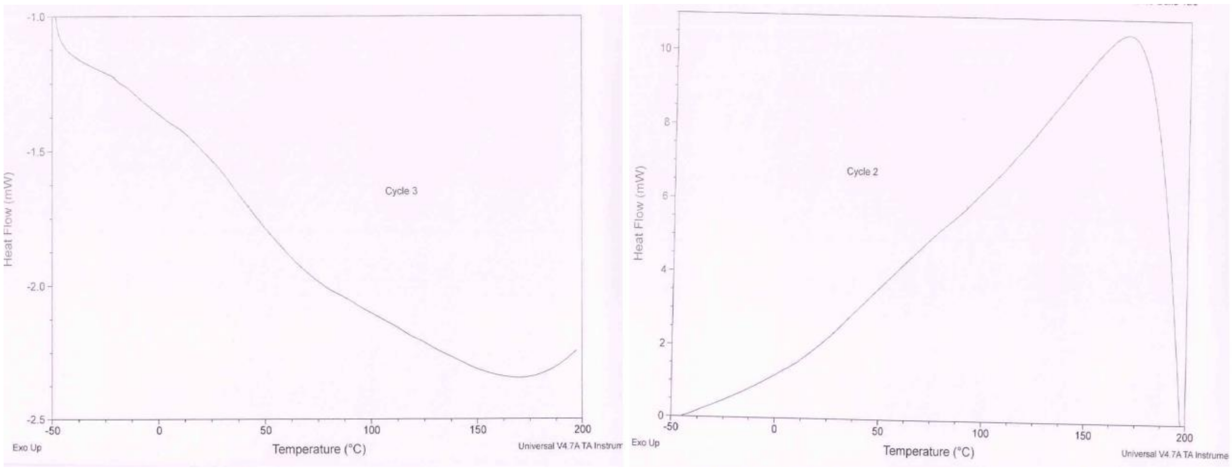
(a) (b)

**Fig. 4.10 (A):** DSC of Caster oil based Rigid Polyurethanes Foam for Formulation-A in (a) cycle 3 and (b) cycle 2



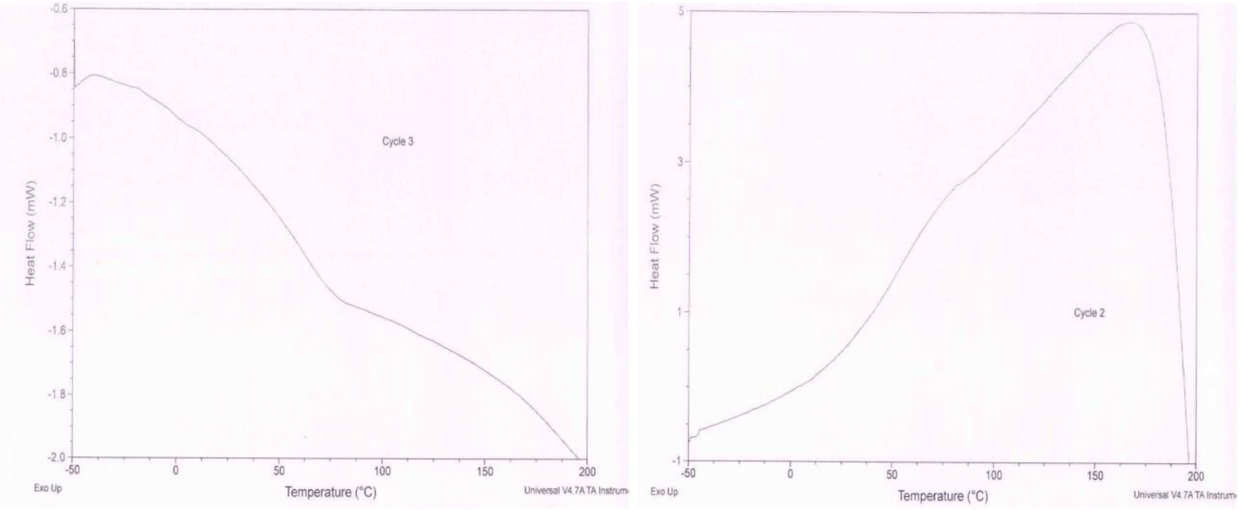
(a) (b)

**Figure 4.10(B):** DSC of Caster oil based Rigid Polyurethanes Foam for Formulation-B in (a) cycle 3 and (b) cycle 2



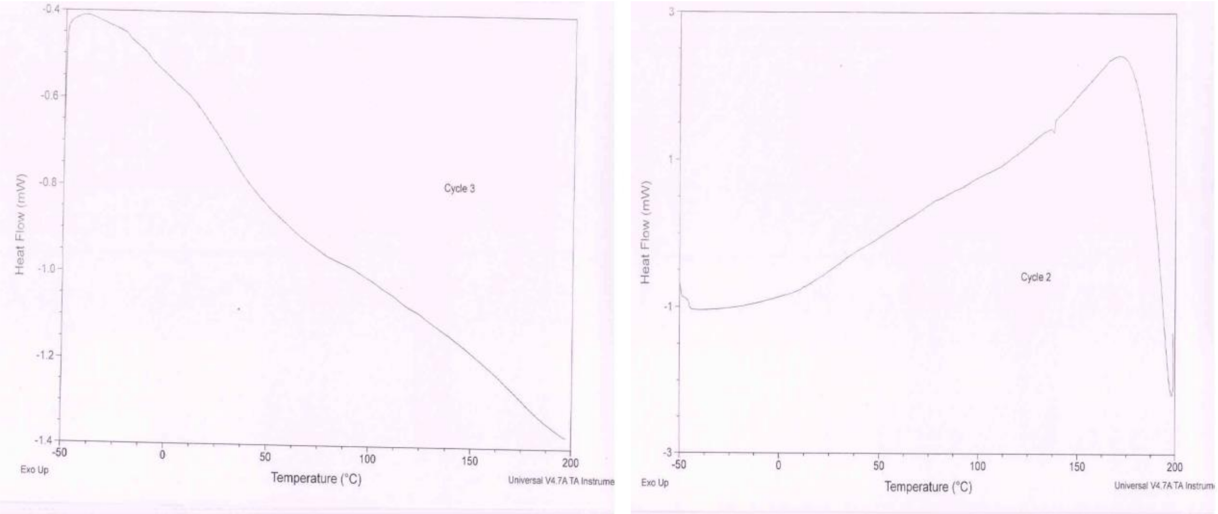
(a) (b)

**Figure 4.10 (C):** DSC of Caster oil based Rigid Polyurethanes Foam for Formulation-C in in (a) cycle 3 and (b) cycle 2



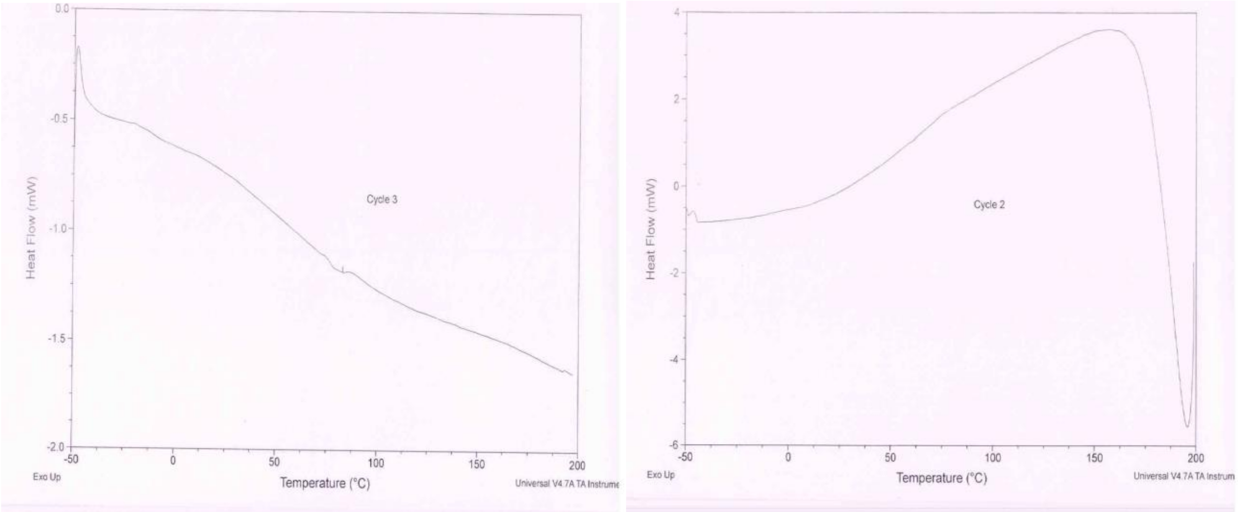
(a) (b)

**Figure 4.11 (A):** DSC of Caster oil based Rigid Polyurethanes Foam for Formulation-X in (a) cycle 3 and (b) cycle 2



(a) (b)

**Figure 4.11(B):** DSC of Caster oil based Rigid Polyurethanes Foam for Formulation-Y in (a) cycle 3 and (b) cycle 2



(a) (b)

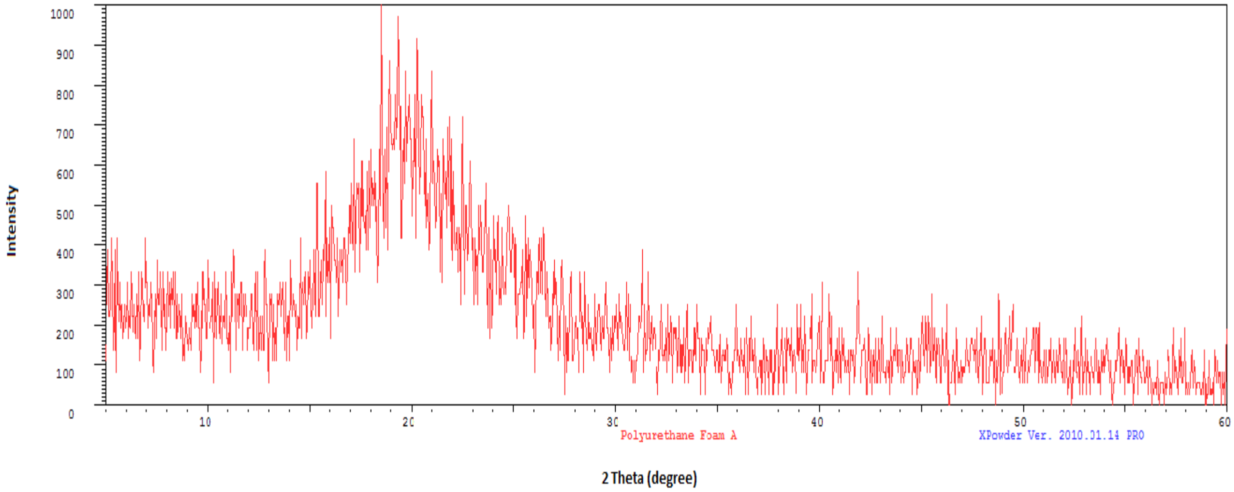
**Figure 4.11 (C) :** DSC of Caster oil based Rigid Polyurethanes Foam for Formulation-Z in (a) cycle 3 and (b) cycle 2

## 4.7 X-ray Diffraction (XRD) analysis

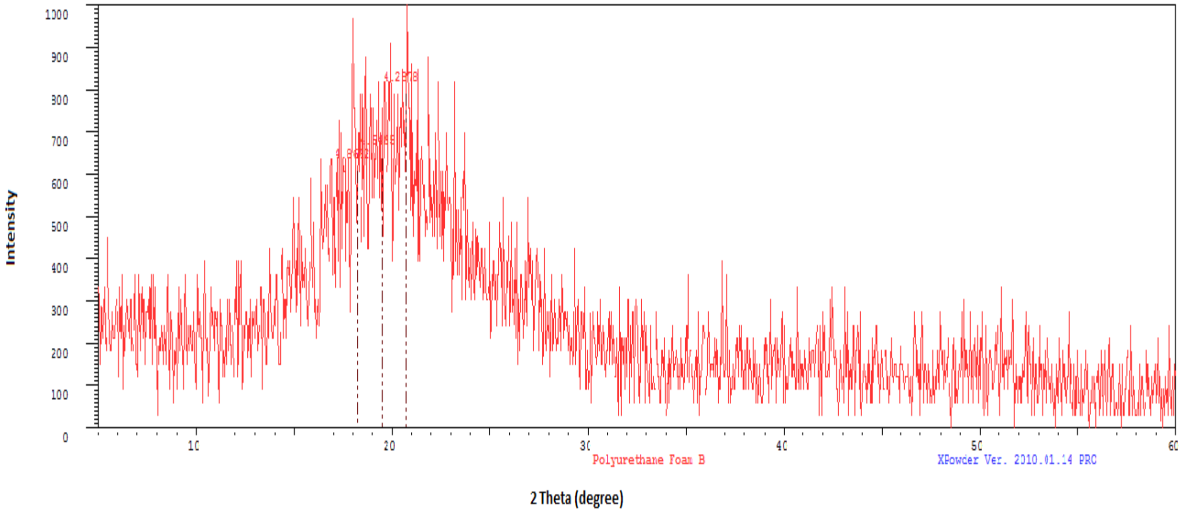
Powder XRD patterns were obtained using D-8 Advance, Bruker diffraction, with monochromatic Cu Ka radiation (k = 0.15418 nm). Scans were obtained in the 2h range = 20–60_, with a step sizes of 0.02_ every 1 s.

**Fig.4.12:** X-ray diffraction (D-8 Advance, Bruker)

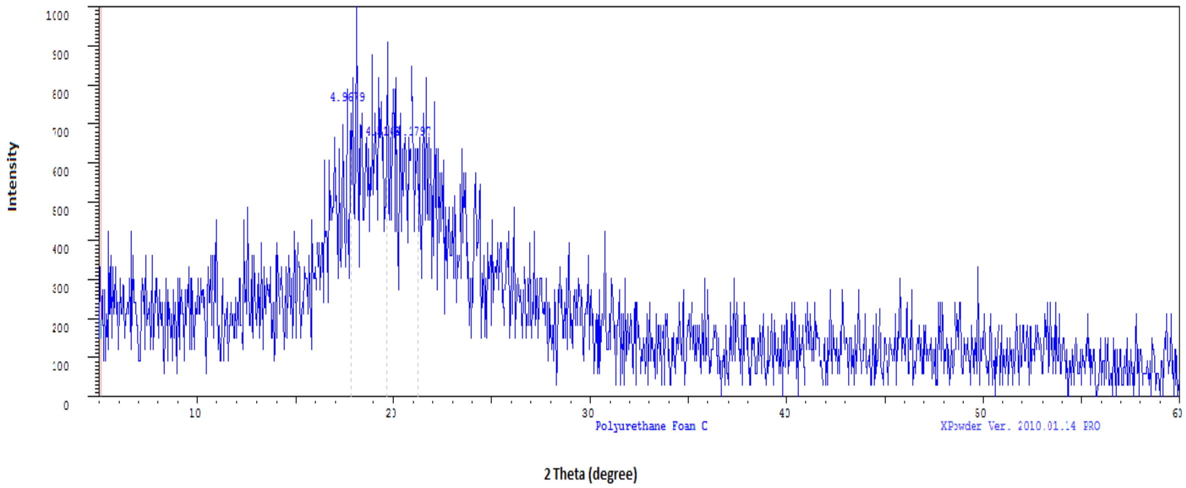
As a result, the XRD result indicates that the foam is highly exfoliated. XRD is generally employed to characterize the interlayer spacing in rigid foam particles, which is correlated with their extent of intercalation. As the polymer chains are intercalated, the gallery height increases, resulting in the shift of characteristic, reflection to lower angles. If complete exfoliation takes place, no peak would be seen in the XRD pattern. The XRD of Figure 4.13 (a) to (c) and Figure 4.14 (a) to (c) where it can be seen that the diffraction peak. Figure 4.13 (a) shows diffraction peak 2 theta 19.338 degree, 4.59031 d- spacing and 972.2 intensity, Figure 4.13 (b), 2 theta 19.843 degree, 4.48035 d-spacing and 818.2 intensity and Figure 4.13 (c), 2 theta 20.014, 4.43292 d-spacing and 787.9 intensity diffraction peaks observed. Figure 4.14 (a), 2 theta 19.757 degree, 4.48996 d-spacing and 588.2 intensity, Figure 4.14 (b), 2 theta 19.457 degree, 4.55842 d-spacing and 734.4 intensity and Figure 4.14 (c), 2 theta 20.399 degree, 4.35006 d-spacing and 666.7 intensity observed in peak. Thus sharp peak shown in Formulation-A, high intensity 19.3 $A^{0,}$ it shows sharp peak at high intensity.


Intensity
0
100
200
300
400
500
600
700
800
900
1000
10
20
30
40
50
60
Polyurethane Foam A
XPowder Ver. 2010.01.14 PRO
2 Theta (degree)

(a)

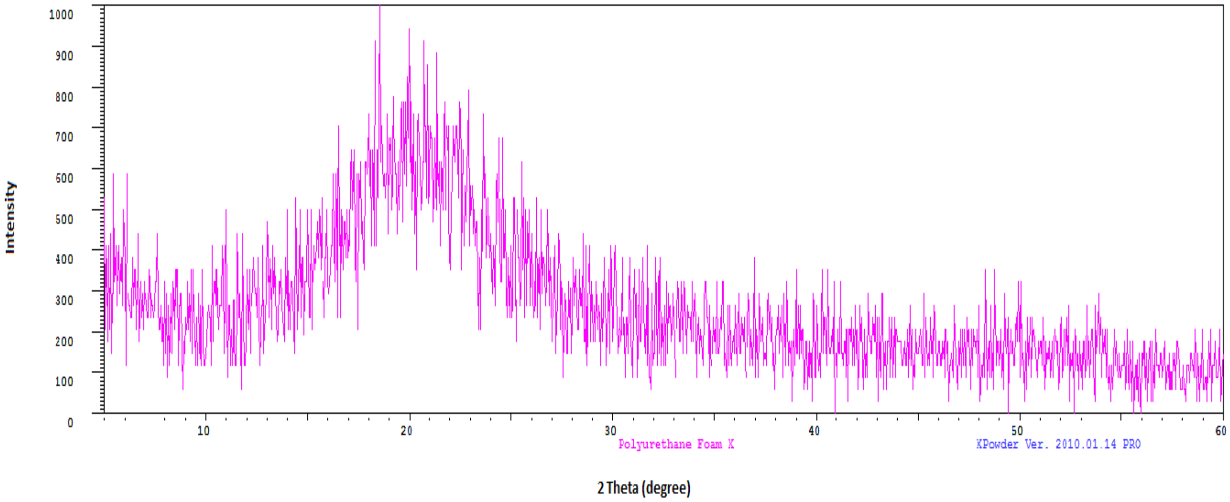

Intensity
0
100
200
300
400
500
600
700
800
900
1000
4.2878
10
20
30
40
50
60
Polyurethane Foam B
XPowder Ver. 2010.01.14 PRO
2 Theta (degree)

(b)

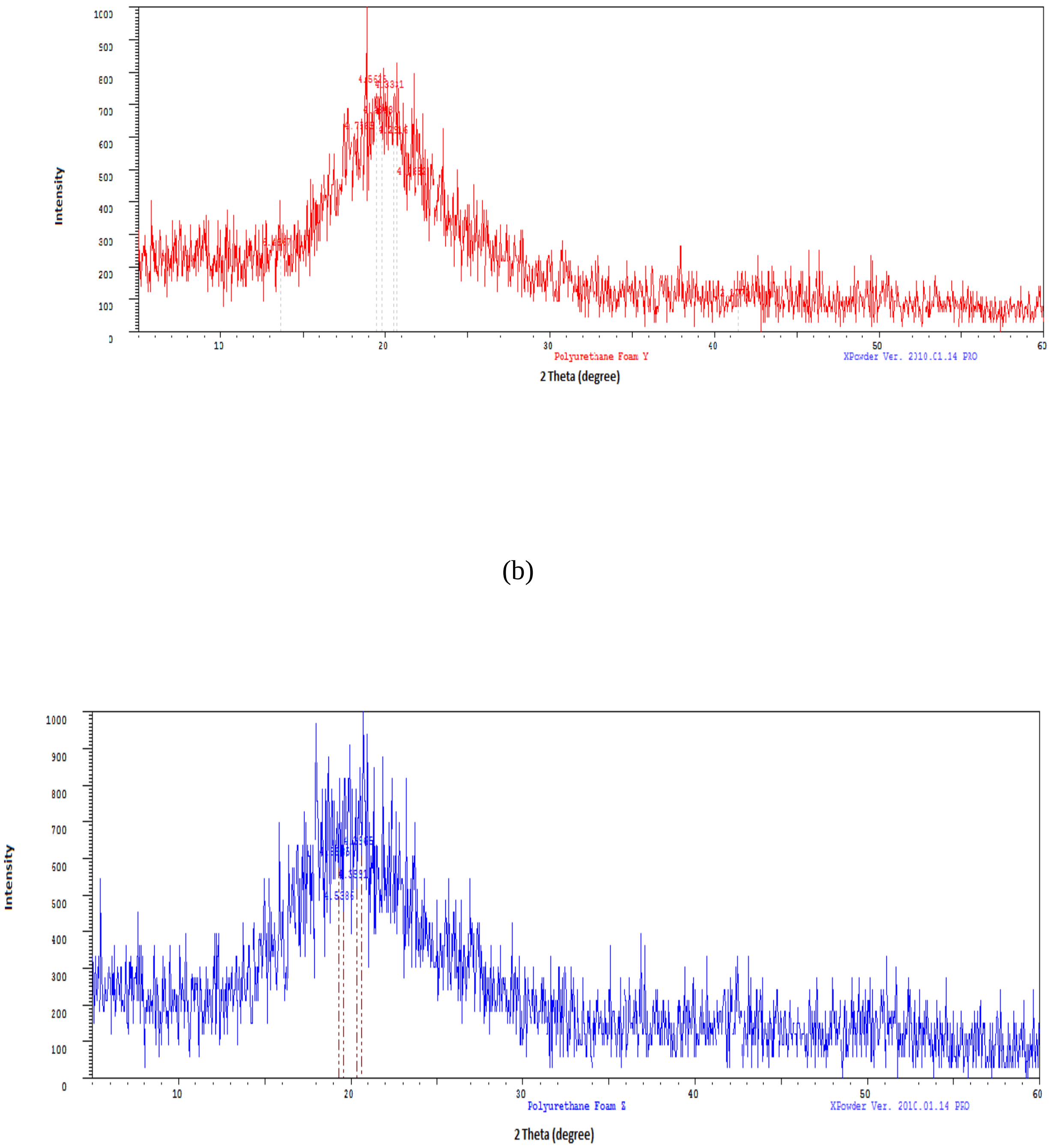


(c)

**Figure 4.13:** XRD graph (a) Formulation-A, (b) Formulation-B and (c) Formulation-C



(a)



(b)

(c)

**Figure 4.14:** XRD graph (a) Formulation-X, (b) Formulation-Y and (c) Formulation-Z

## 4.8 Mechanical Properties

The mechanical properties of the castor oil based rigid polyurethane samples were determined according to the standard procedures. Samples were cut at ambient temperature to the required dimensions. Tensile, compressive and flexural properties of the resulted foams were measured at room temperature using Instron (model No. 3369) universal testing machine (Figure 4.12) as per ASTM D-638, ASTM D-695and ASTM D-790 method respectively.

**Figure 4.15:** Instron (model No. 3369) Universal Testing Machine

### 4.8.1 Tensile strength

Tensile strength and Tensile Modulus of the n-Pentane blown Castor Oil based Rigid Polyurethane Foams is as given in Table 4.2. The tensile strengths of the resulted foam samples were found good and was first found to be increased with increase in the concentration of the blowing agent from Formulation-A(10%) to Formulation-B(15%). With further increase in Concentration of blowing agent to 20% i.e. for formulation-C, the tensile strength value was decreased. The relationship between tensile stress and tensile strain for the n-pentane blown castor oil based rigid polyurethane rigid foams is as shown in Fig 4.16 (a) to (c). From the graph, it is clear that tensile strength increases with increase in the concentration of blowing agent from 10 to 15%, but with further increase, tensile strength decreases. The curve for formulation-A is somewhat irregular and there is no sharp breaking point. This may be due to some flexible segment present within the foamed structure.

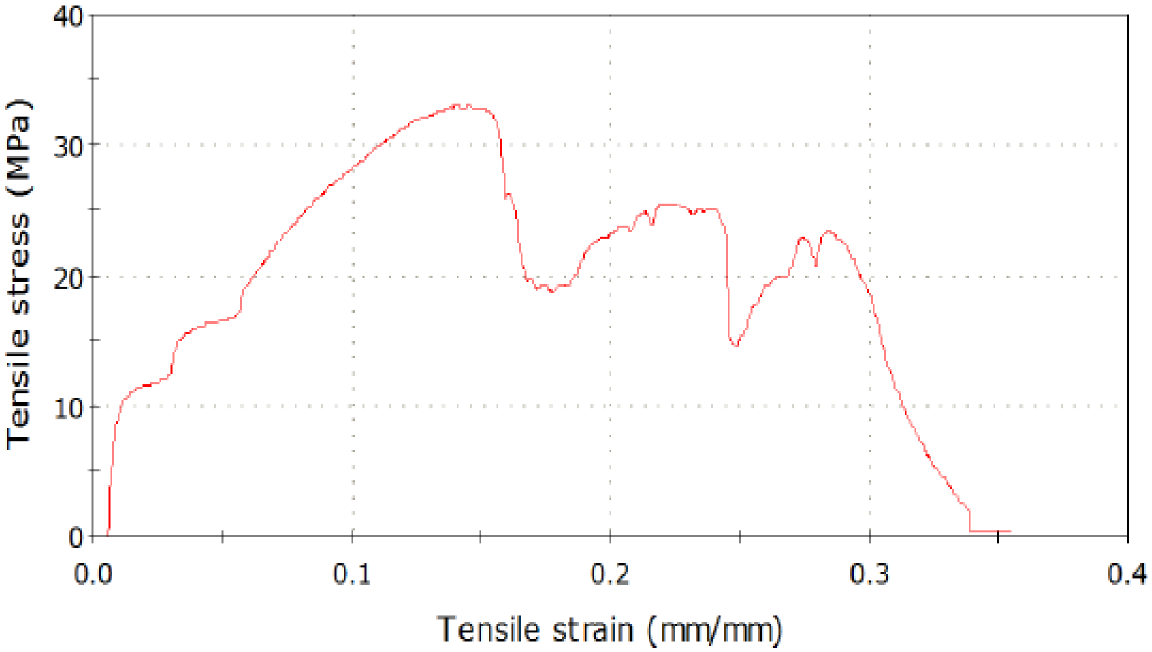
The tensile properties for the water blown rigid foams are as given in Table 4.3. The Tensile strength of the water blown foams is very less comparable to that of n-Pentane blown films. The similar behaviour is reflected from the curves obtained for water blown Castor oil based Rigid Polyurethane foams, as shown by Figure 4.17(a) to 4.17 (c). For formulation -X, with 10% water content, Tensile strength is 0.25191 MPa, which got increased with increase in water content, both for formulation-Y (15% water) and Formulation -Z(20% water ). The low tensile strength of the water blown systems is due to less packed structure of the foam as observed earlier, in SEM studies. The n-pentane is found more suitable blowing agents in as compared to the water as blowing agent in the concentration 10% by weight of base polyol.

**Table 4.2**: Tensile Properties of Castor Oil based Rigid Polyurethane Foams with DifferentConcentrations of n-Pentane as Blowing Agent

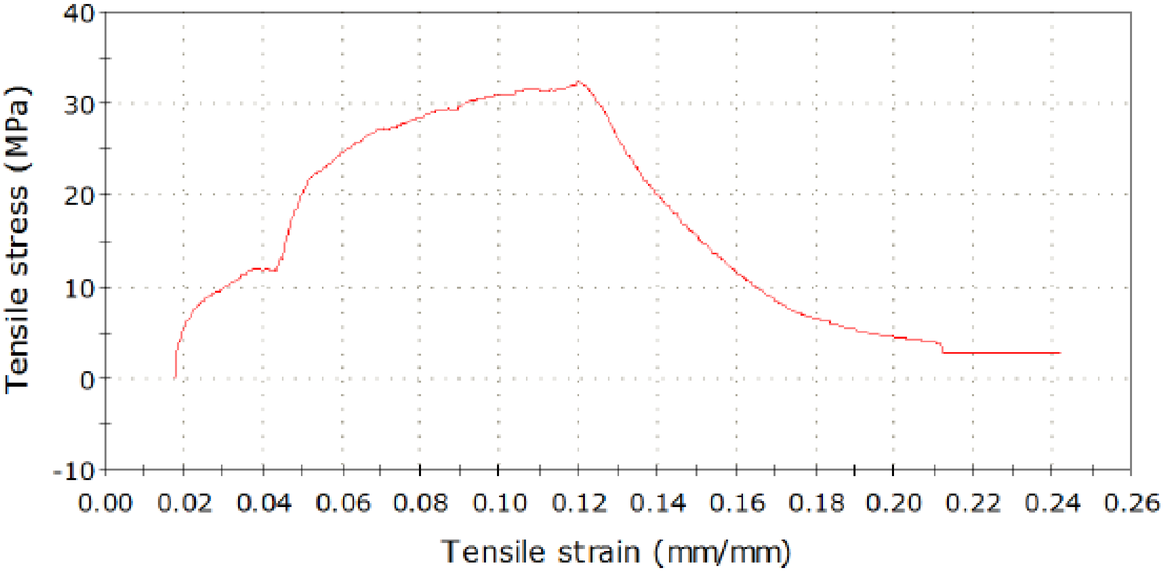
| **Formulation** | **Tensile stress at Tensile Strength (MPa)** | **Tensile strain at Tensile Strength (mm/mm)** |
|---|---|---|
| Formulation A | 32.68509 | 0.13473 |
| Formulation B | 31.34387 | 0.10545 |
| Formulation C | 20.51491 | 0.05815 |

**Table 4.3**: Tensile Properties of Castor Oil based Rigid Polyurethane Foams with Different Concentrations of Water as Blowing Agent

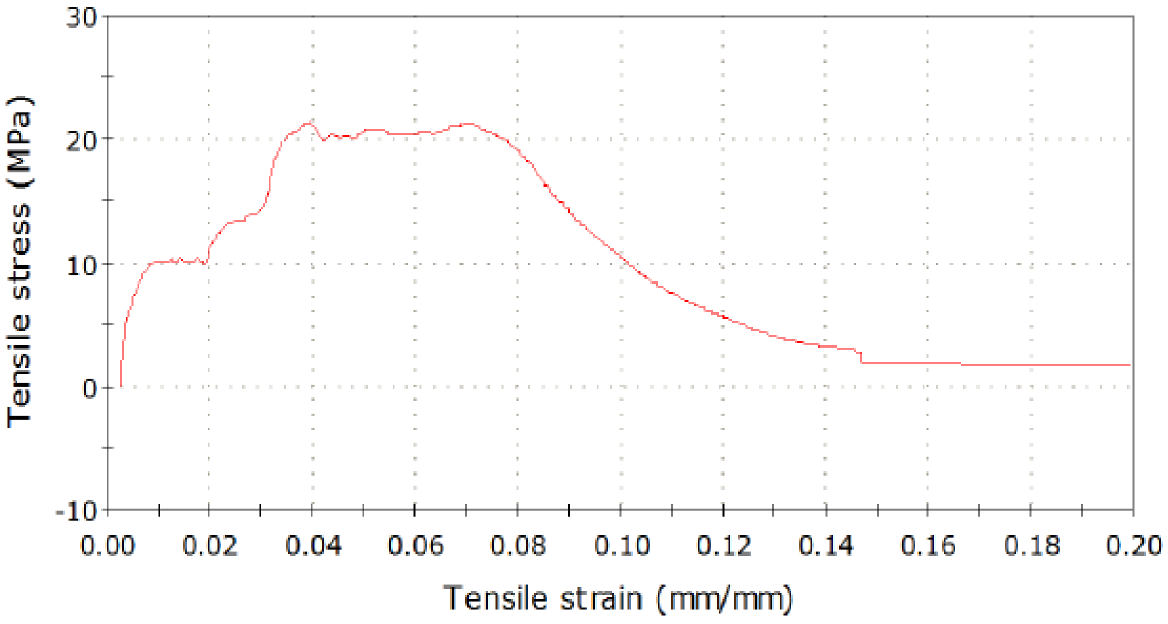
| **Formulation** | **Tensile stress at Tensile Strength (MPa)** | **Tensile strain at Tensile Strength (mm/mm)** |
|---|---|---|
| Formulation X | 18.43563 | 0.04751 |
| Formulation Y | 2.51574 | 0.03135 |
| Formulation Z | 1.98097 | 0.02070 |


Tensile stress (MPa)
40
30
20
10
0
0.0
0.1
0.2
0.3
0.4
Tensile strain (mm/mm)

(a)

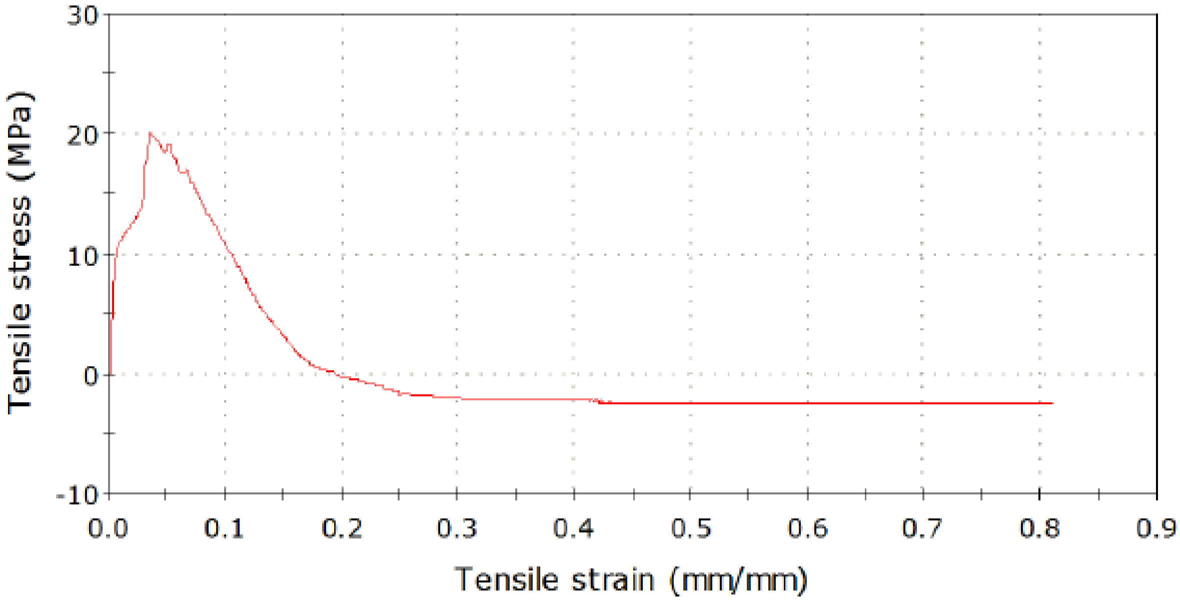

Tensile stress (MPa)
40
30
20
10
0
-10
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
0.18
0.20
0.22
0.24
0.26
Tensile strain (mm/mm)

(b)

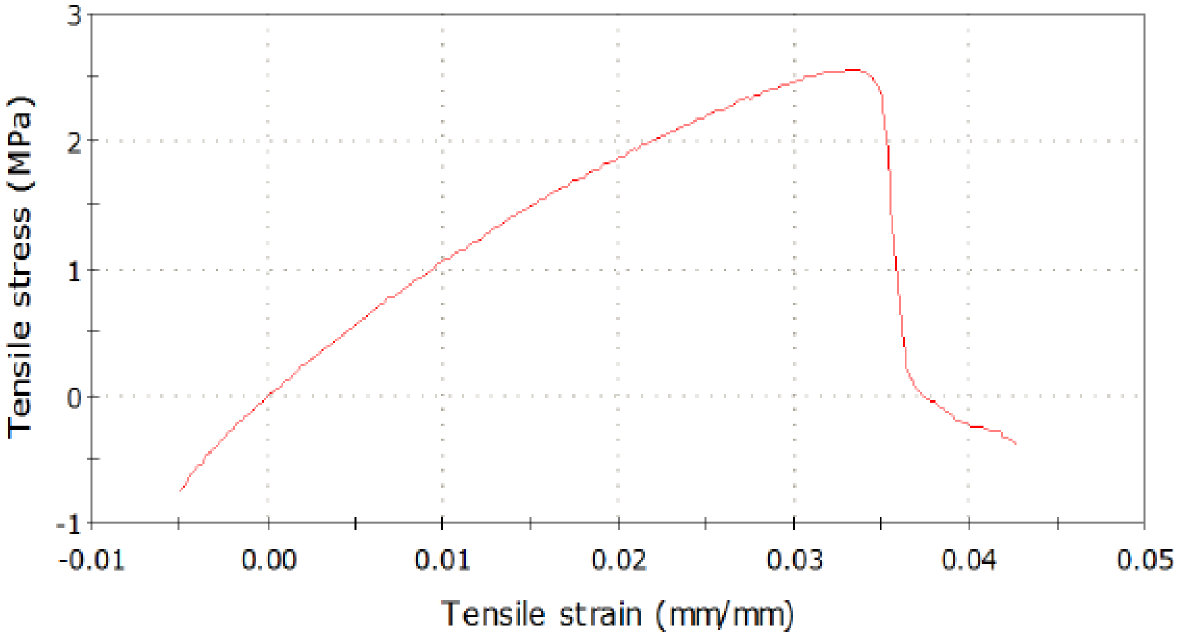


(c)

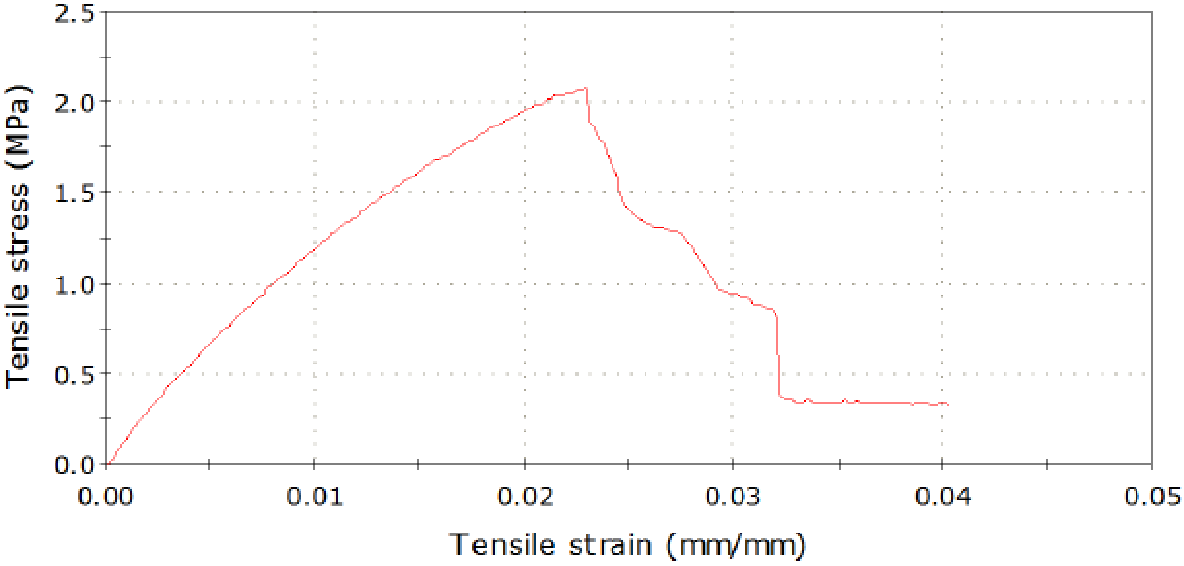
**Figure 4.16:** Relationship between Tensile stress and Tensile strain for (a) formulation-A, (b) formulation-B, (c) formulation-C



(a)



(b)

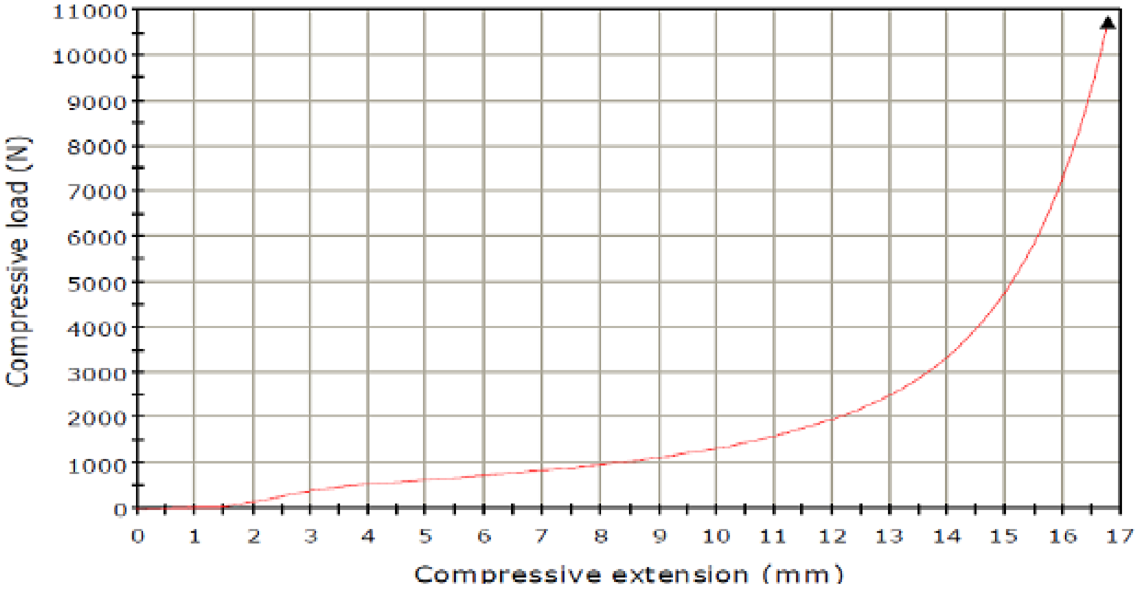


(c)

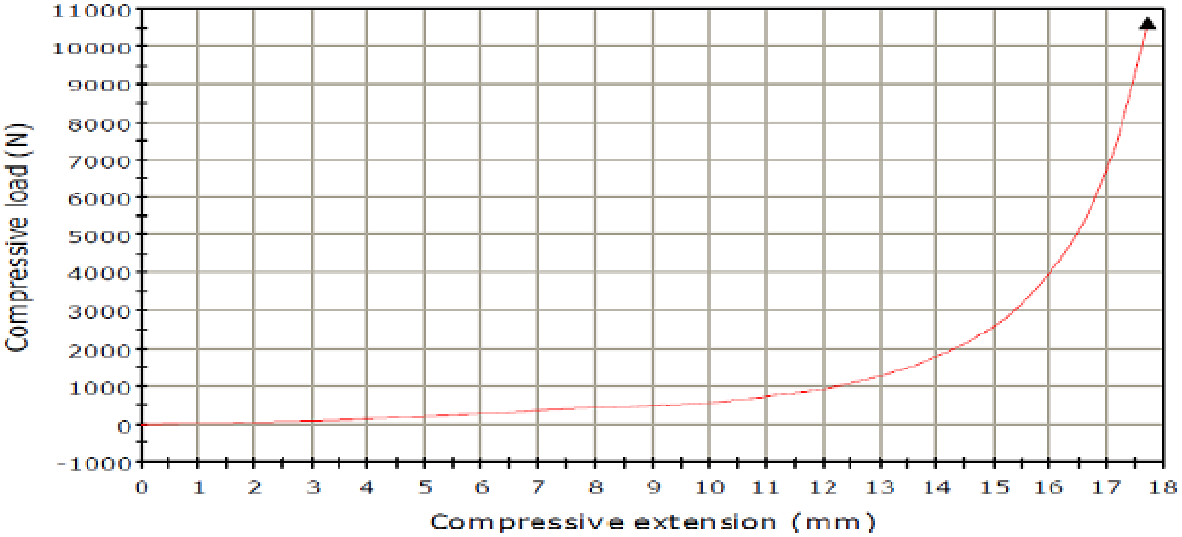
**Figure 4.17:** Relationship between Tensile stress and Tensile strain for (a) formulation-X, (b) formulation-Y, (c) formulation-Z

### 4.8.2 Compressive strength

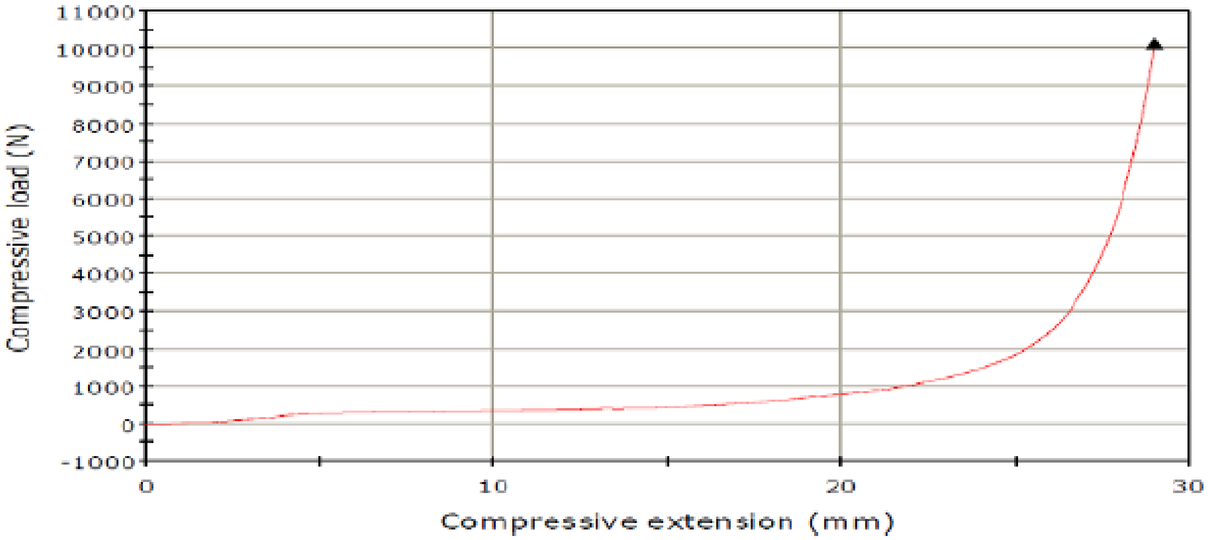
The compressive strengths of the n-Pentane blown rigid polyurethane samples were found very good. The relationship between compressive load and compressive extension for the castor oil based rigid polyurethane rigid foams with different formulation of n-Pentane and water are shown in Figure 4.18 (a) to (c) and Figure 4.19 (a) to (c) respectively. For formulation A, for a maximum compressive load of 1085.64752 kgf, an extension of 15-16 mm was observed. For formulation-B is a maximum compressive load of 1077.10801 kgf gives an extension up to 17 to 18 mm and for formulation-C for a maximum compressive load of 1020.13814 kgf, an extension up to 26-27 mm had been observed. The compressive strength is found to be decreased with increasing the content of n-Pentane, but this decrease is not much significant and overall compressive strength of the prepared foam is good. The similar results had been reported by Modesti et. al, 1998, for the n-Pentane blown films[50].It was reported that n-Pentane blown foams have excellent mechanical performance due to insolubility in the polymeric matrix. The relationship between compressive load (kgf) and compressive extension (mm) for water blown castor oil based rigid polyurethane rigid foams is as shown in Figure 4.19 (a) to (c). For water blown rigid polyurethane foams, for formulation-X (Water=10%) for a maximum compressive load of 1021.54095 kgf the extension observed was 1.52 mm. For formulation-Y(Water=15%), a maximum compressive load of 454.22746 kgf gives an extension of 9 mm and for formulation – Z (Water=20%) for a maximum compressive load of 365.01999 kgf and extension was 7.58 mm only. The water blown PU foams are weak and shows brittleness in behavior specially in the formulation X. The compressive properties have shown a decline in value with increase in content of water. Modesti et. al, 1998, reported the same i.e. increasing the water content leaded to decline in performance[50]. This decline is due to the disubstituted urea content which leads to a more rigid polymeric structure, making it brittle.



(a)



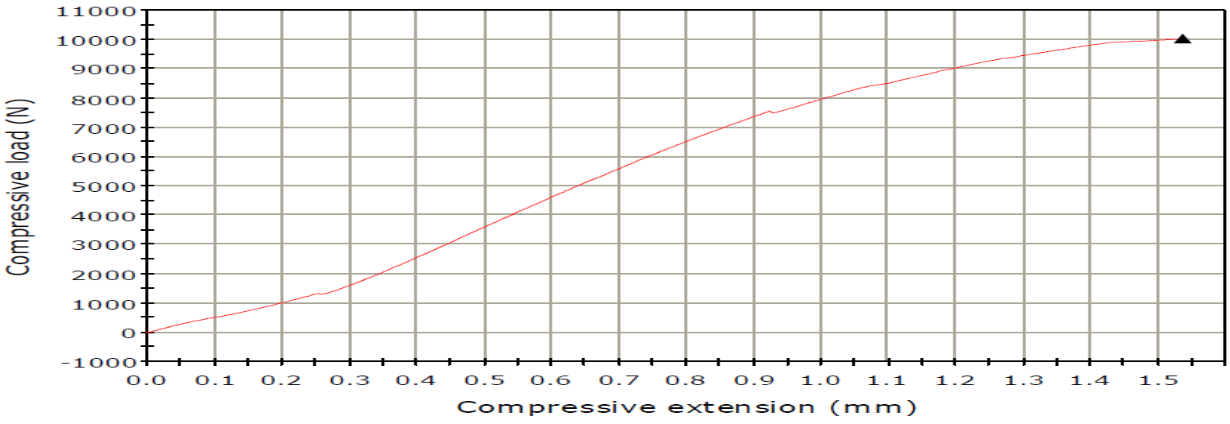
(b)



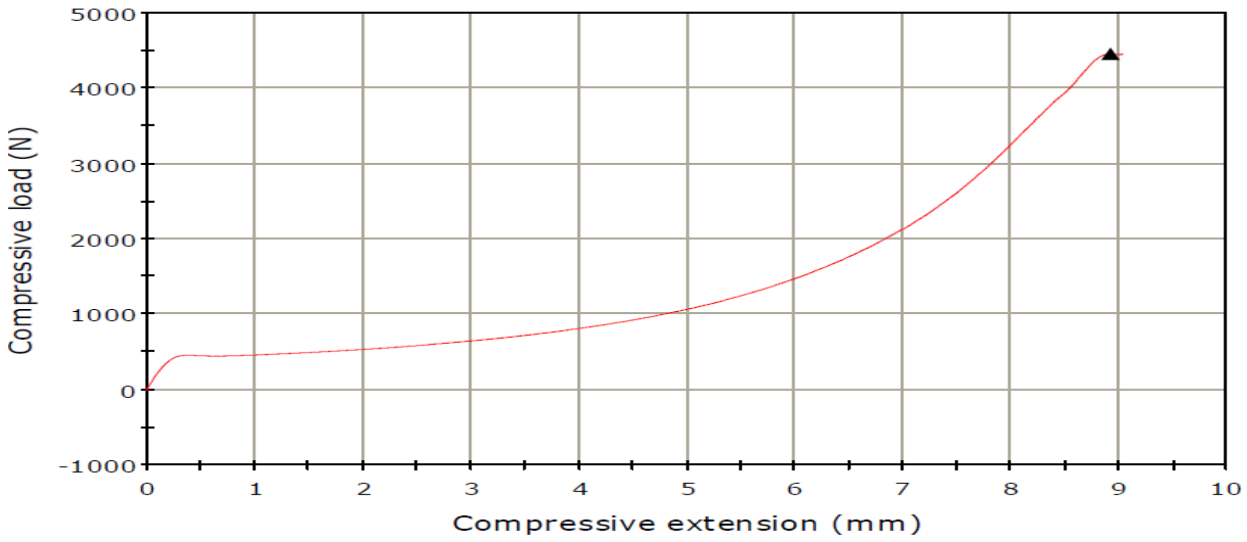
(c)

**Figure 4.18** Relationship between Compressive load and Compressive extension for

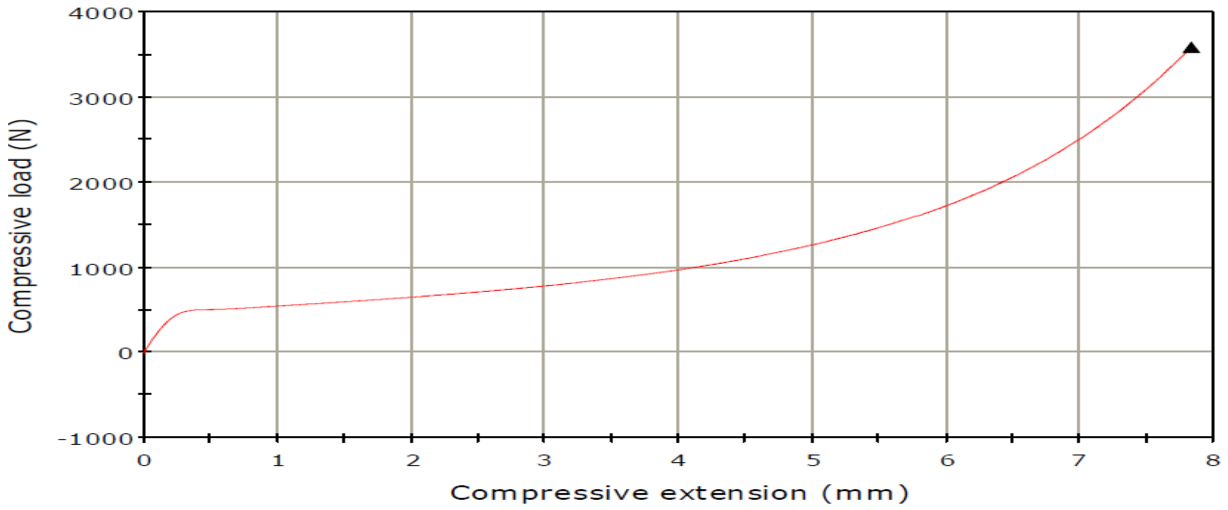
(a) formulation-A, (b) formulation-B and (c) formulation-C



(a)



(b)



(c)

**Figure 4.19:** Relationship between Compressive load and Compressive extension for

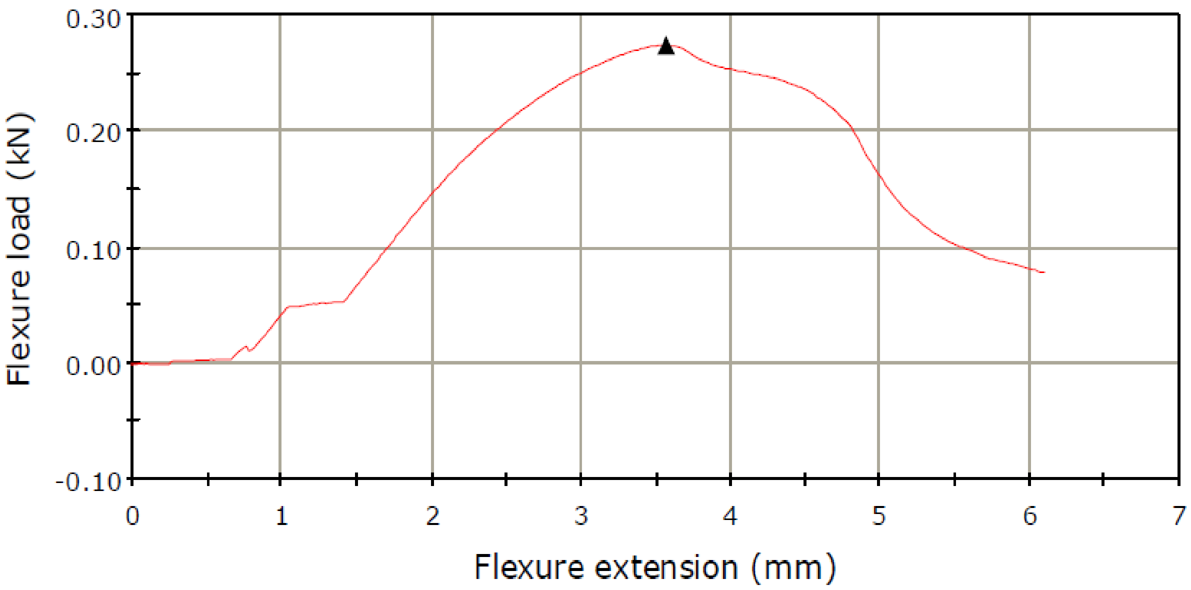
(a) formulation-X, (b) formulation-Y and (c) formulation-Z

### 4.8.3 Flexural strength

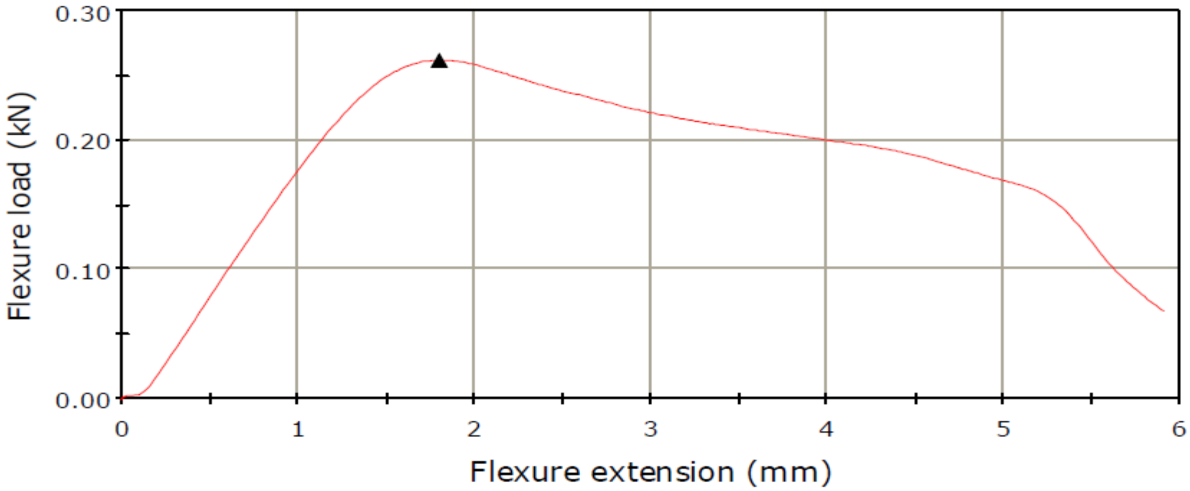
Flexural strength is the ability of the material to withstand bending forces applied perpendicular to its longitudinal axis. The stresses induced by the flexural load are a combination of compressive and tensile stress[51]. The relationship between flexure load (kN) and flexure extension (mm) for the castor oil based rigid polyurethane rigid foams with different formulation of n-Pentane are as shown in Figure 20 (a) to (c) and different formulation of water shown in Figure 20 (d) to (f). Initial linear portion of three curves is due to linear elastic deformation of the cell structures. As the cell begins to rupture due to stretching, the slope of the load-deflection curve changes and the foam almost uncontrollably deforms and finally fail at maximum load. It was found that flexure stress at maximum flexure load (MPa) for formulation 1 Flexural strength and flexural extension is excellent in the modified castor oil based polyurethane rigid foam. The flexural strength is represented in Figure 20 (a) to (f) for formulation-A, B, C, X, Y and Z. The observation of the flexural strength is maximum in formulation-A, lower strength in formulation –Z. This formulation –A is more useful in several applications due to achieve more strength. The flexural strength and extension is represented in summarized Table 4.4.

**Table 4.4:** Flexural strength and extension of castor oil based rigid polyurethane foam in formulation-A, B, C, X, Y and Z

| **Formulation** | **Maximum Flexure load (kN)** | **Flexure stress at Maximum Flexure load (MPa)** | **Flexure extension at Maximum Flexure load (mm)** | **Maximum Flexure extension (mm)** | **Flexure strain at Maximum Flexure extension (%)** |
|---|---|---|---|---|---|
| A | 0.27467 | 181.59843 | 3.56669 | 6.09269 | 3.35098 |
| B | 0.26209 | 173.28062 | 1.80000 | 5.90831 | 3.24957 |
| C | 0.23243 | 185.94604 | 2.68337 | 8.41769 | 4.20384 |
| X | 0.21290 | 17.10835 | 2.50844 | 4.59244 | 12.24650 |
| Y | 0.22142 | 184.54655 | 2.65982 | 8.40568 | 4.20542 |
| Z | 0.17119 | 113.18204 | 1.76656 | 6.79131 | 3.73522 |

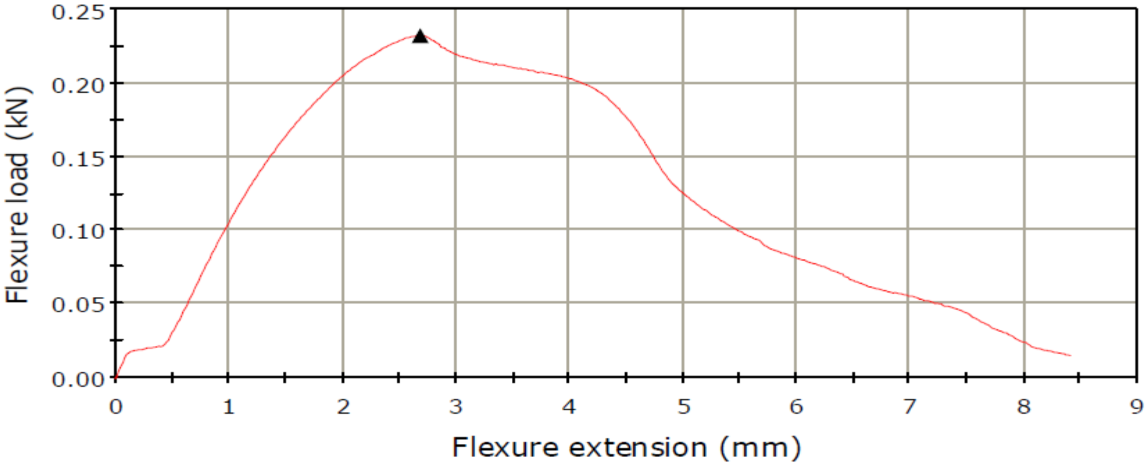


(a)



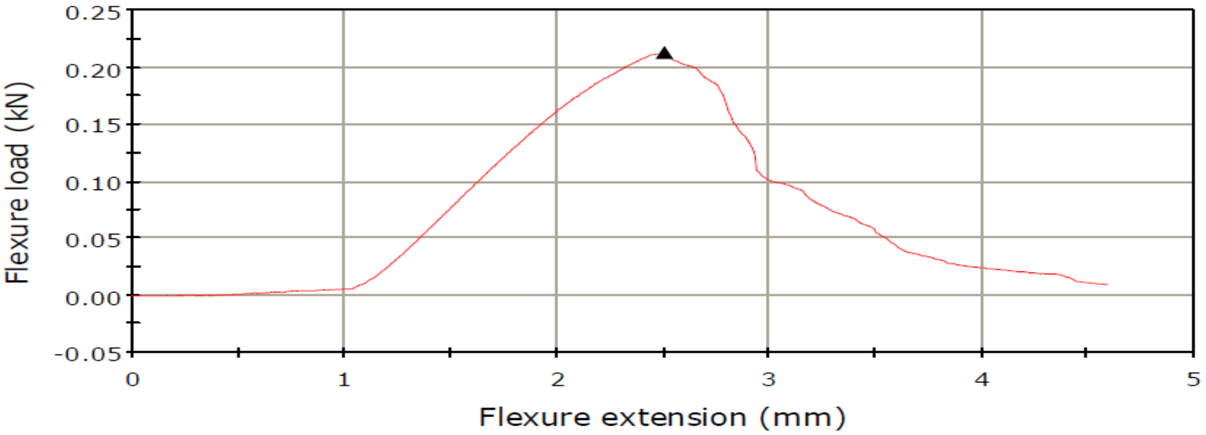
0.30
0.20
0.10
0.00
Flexure load (kN)
0
1
2
3
4
5
6
Flexure extension (mm)

(b)



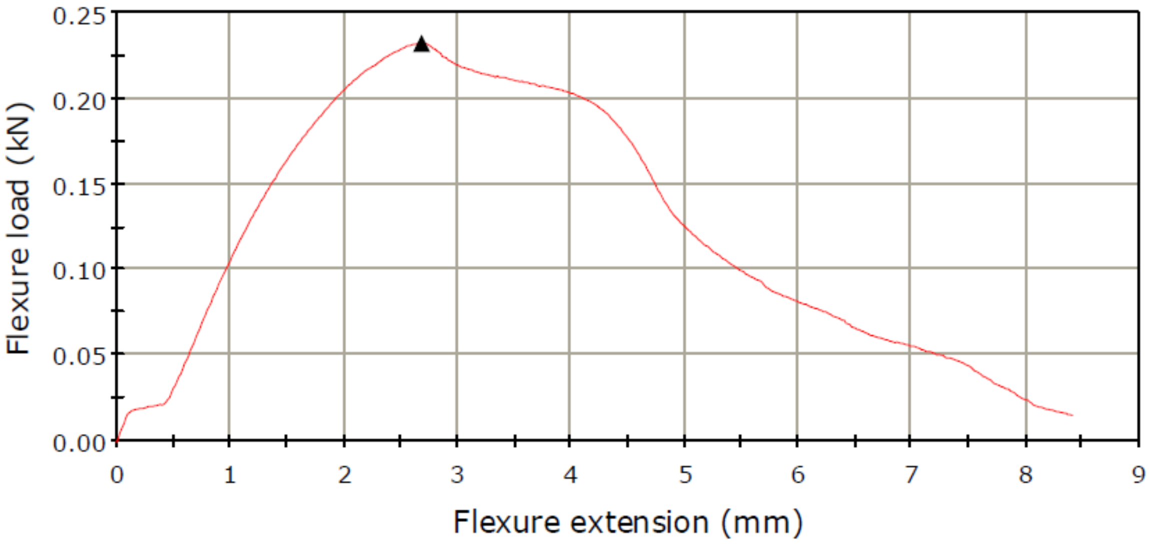
0.25
0.20
0.15
0.10
0.05
0.00
Flexure load (kN)
0
1
2
3
4
5
6
7
8
9
Flexure extension (mm)

(c)

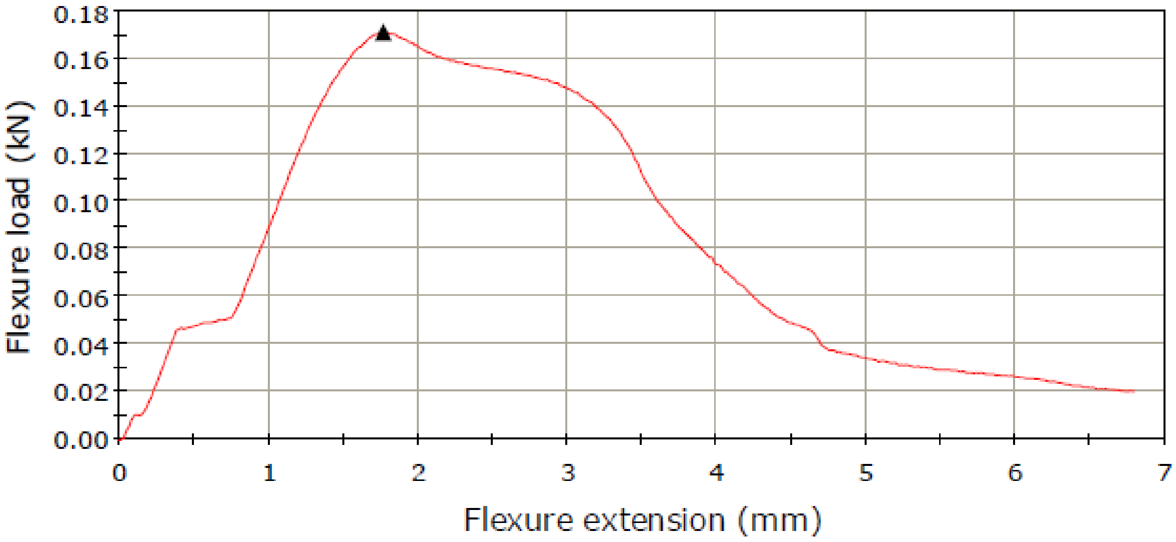


0.25
0.20
0.15
0.10
0.05
0.00
-0.05
Flexure load (kN)
0
1
2
3
4
5
Flexure extension (mm)

(d)



(e)



**(f)**

**Figure 4.20:** Flexural Strength for (a) formulation-A, (b) formulation-B, (c) formulation-C, (d) formulation-X, (e) formulation-Y and (f) formulation-Z

### 4.8.4 Hardness testing

Hardness is more important properties for application in construction, building industries and automotive industries. Shore D hardness test for the Castor Oil based Rigid Polyurethane with Different formulations of n-Pentane and Water was carried out. The hardness test carried out by Shore D hardness tester, indenter penetrates in the sample finding the results. Test results are reported in Table 4.4. It was found that with increase in concentration of blowing agent, there was decrease in hardness for both (formulation A to C) and (formulation X to Z). This may be due to increased pore size resulting decreases the hardness of the sample, when increases of the concentration of the blowing agents it was reported in SEM studies. The hardness values of water blown samples had been found less as compared to n-Pentane blown rigid polyurethane sample.

**Table 4.5:** Hardness of the Castor Oil based Rigid Polyurethane Foam

| **Sample** | **Hardness (Shore D)** |
|---|---|
| Formulation A | 91 |
| Formulation B | 87 |
| Formulation C | 88 |
| Formulation X | 86 |
| Formulation Y | 80 |
| Formulation Z | 81 |

## 4.9 Water Absorption in Foams

The water absorption testing of the n-Pentane and water blown Castor Oil based Polyurethane Foam had been carried out according to ASTM C 272 standards (Figure 4.20). After weighing, the specimen was immersed completely in water at room temperature. After immersion period, the specimen was removed, dried and weighed. Water absorption (%age) had been carried out using equation:

$$Water\ Absorbed\ (\%age\ of\ Water\ gained) = \frac{Weight\ gained}{Original\ Weight} \times 100$$

Test results for water absorption for n-Pentane and water blown Foams are as reported in Table 4.6. It was found that the increased concentration of blowing agent resulted in increased water absorption both for the cases of n-Pentane blown and water blown foams. The formulation A (10% water) was found to have absorbed least water among all other samples.

**Figure 4.21:** Water Absorption Test

**Table 4.6:** Percentage Water gained in Foams of Different Formulations.

| No. of Days | Water absorption in Percentage | | | | | |
|---|---|---|---|---|---|---|
| | Formulation A | Formulation B | Formulation C | Formulation X | Formulation Y | Formulation Z |
| 01 | 0.9684 | 1.2325 | 1.6246 | 1.4895 | 1.7562 | 1.6947 |
| 02 | 1.4528 | 1.4342 | 1.8695 | 2.1541 | 1.9895 | 2.6482 |
| 03 | 1.4589 | 1.9578 | 1.7782 | 1.9456 | 2.9576 | 2.8762 |
| 04 | 1.9875 | 2.2154 | 2.6578 | 2.6472 | 2.9112 | 3.7452 |
| 05 | 2.2354 | 2.2457 | 2.6987 | 3.1546 | 2.9987 | 3.9978 |
| 06 | 2.5846 | 2.4745 | 3.5418 | 3.5246 | 4.2975 | 4.1187 |
| 07 | 2.8975 | 3.2451 | 3.8974 | 3.9957 | 4.2586 | 4.5689 |
| 08 | 3.6845 | 3.7859 | 4.8975 | 5.6273 | 5.9875 | 6.8574 |
| 09 | 5.3578 | 5.2462 | 5.1895 | 5.7894 | 6.8874 | 7.1879 |
| 10 | 5.6482 | 6.1972 | 6.0854 | 8.4457 | 8.2475 | 9.6842 |

## 4.10 Density and Thermal Conductivity Measurement

Density of foam samples was measured according to ASTM procedure D 1622-03. Thermal conductivity of samples was determined after curing at room temperature (23ºC) for 24 h by a Fox 200 Heat Flow Meter (Laser Comp, Wakefield, MA)(Figure 4.21) as per the ASTM C 518-04. Sample was placed in the test section between the two plates which were maintained at different temperatures during the test. Upon achieving thermal equilibrium and establishing a uniform temperature gradient throughout the sample, the thermal conductivity of the PU rigid foam was measured. For density measurement, the foam was cut into specimen of size 30 × 30 × 30 mm. The densities of five specimens per sample were measured and averaged. The results for Density and Thermal Conductivity values for foams with different formulations are given in Table 4.7. It was observed that density of the foam decreases with the concentration of the blowing agent. For n-Pentane blown Castor Oil based Rigid Polyurethane foams, the density is highest for formulation A with 10% concentration of blowing agent, which further decreases for formulation B(15%n-Pentane) and Formulation C (20%n-Pentane).The high density value is sue to more closely packed structure of Formulation A. The thermal conductivity values also follow the same trend, but the difference is not much significant. The same type of behaviour was observed for water blown foams (formulation X, Y and Z), but difference in densities of both systems are significant.

**Figure 4.22:** Thermal Conductivity Meter

**Table 4.7:** Density and Thermal Conductivity of the Rigid Polyurethane Foam for Different For Formulations

| **Formulation** | **Density (kg/m$^3$)** | **Thermal conductivity (kcal/mh$^o$C)** |
|---|---|---|
| **Formulation** A | 80.9 | 0.0274 |
| **Formulation** B | 70.2 | 0.0259 |
| **Formulation** C | 62.3 | 0.0255 |
| **Formulation** X | 50.6 | 0.0249 |
| **Formulation** Y | 40.3 | 0.0233 |
| **Formulation** Z | 35.3 | 0.0213 |

## 4.11 Flammability Test

Flammability tests are typically used to determine flammability for transport purpose and do not reflect very well dangers at work place. The flammability test of Castor Oil based Rigid Polyurethane with different formulation had been carried out according to ASTM D 3014 standards. The test procedure for flammability test of rigid polyurethane foam in vertical and horizontal direction (Figure 4.23) was according to UL 94 V and UL 94 HB respectively. For vertical direction test procedure, the test specimen was mounted vertically on a vertical stand and was ignited with a Bunsen burner for 10 sec. A small 3/4th inch high blue flame is applied to the bottom of the specimen for 10 sec, withdrawn and then reapplied for an additional 10 sec. The duration of flaming and glowing is noted as soon as the specimen is extinguished. A layer of cotton is placed beneath specimen to determine whether dripping material will ignite it during the test period. For Horizontal direction test procedure, the burner was ignited to produce 1 inch high blue flame. A depth of ¼th inch flame was applied to specimen for 30 seconds without changing the position of the burner and is removed from the burner. If the specimen burns to the 1 inch mark before 30sec, the flame is withdrawn. If the specimen continues to burn after removal of the flame, the time for the flame front to travel from the mark 1 inch from the free end to the mark 4.0 inch from the free end is determined and rate of burning is calculated.

**Figure 4.23:** Flammability Test for Castor Oil based Rigid Polyurethane Foam

The results obtained in flammability test for Castor Oil based Rigid Polyurethane Foam with Different Formulations are as given in Table 4.8.  Low burning rates were observed for formulation-A (10% n-Pentane), which increased substantially for formulation B (15% n-Pentane) and Formulation C (20% n-Pentane). and more burning rates in formulation-Z.  This is due to more dense structure of Formulation A. The burning rates are generally less for materials with closed and compact pore size, as reported in formulation A. However, processes using pentane or pentane-containing polyurethane raw materials must take into account the potential hazard of explosive atmospheres being created. The explosion risk applies to the entire processing line, from the pentane storage area to the cured polyurethane foam. Water blown PU foams are normally less flammable. Water and Issocyanate reaction generally produces isocyanurate structures.  It is well known that a significant improvement on thermal stability and fire behaviour of polyurethane foams (PUR) may be achieved through the introduction in polyurethane matrix of isocyanurate structures, as these are generally more stable from a thermodynamic point of view than are urethane links[52,53]. The same behaviour is observed in formulation X (10% water). For formulation Y (15% water) and Formulation Z (20% water), due to less dense and less close packed structure, the observed burning rate is more. The burning rate can further be adjusted by designed addition of anti flammable agents, without affecting the foam properties.

**Table 4.8:** Burning rates (mm/sec) in vertical (V) and horizontal (H) position

| **Formulation** | **Burning Rates (mm/sec)** | |
|---|---|---|
| | **Vertical** | **Horizontal** |
| **Formulation** A | 1.12 | 0.49 |
| **Formulation** B | 1.34 | 0.69 |
| **Formulation** C | 1.46 | 0.60 |
| **Formulation** X | 1.38 | 0.54 |
| **Formulation** Y | 1.47 | 0.67 |
| **Formulation** Z | 1.39 | 0.66 |

## 4.12 Biodegradability Testing

The test for checking the Biodegradability of Castor Oil based Rigid Polyurethane Foam was carried out by Burial Test. The samples with different formulations were buried in soil for 90 days. The amount of weight loss was measured and there Structural properties were tested for any change. The results of weight loss on burial testing of different formulations are as reported in Table 4.9. The other changes in structure was monitored by the SEM analysis, that indicated clear and sharp changes in structure and pores of the buried samples The loss in mechanical properties were studied with the help of universal testing machine. Tensile strength measured after 90 day landfill was found decreased and is reported in Table 4.10.

The observed results showed a clear changes due to biological degradation, which can be further enhanced by addition of special ingredients or bio-fillers.

**Table 4.9:** Biodegradation of Castor Oil based Rigid Polyurethane Foam

| **Formulation** | **Initial Foam Weight (gm)** | **After 90 Days Foam Weight (gm)** | **After 90 Days Loss of Foam Weight (gm)** | **%ge Loss of** |
|---|---|---|---|---|
| Formulation A | 10.3293 | 10.2154 | 00.1139 | 1.1027 |
| Formulation B | 09.6548 | 09.5112 | 00.1436 | 1.4873 |
| Formulation C | 10.5471 | 10.4067 | 00.1404 | 1.3312 |
| Formulation X | 08.2791 | 08.1287 | 00.1504 | 1.8166 |
| Formulation Y | 11.6245 | 11.4968 | 00.1277 | 1.0985 |
| Formulation Z | 10.3254 | 10.1947 | 00.1307 | 1.2658 |

**Table 4.10:** Tensile strength after 90 days Landfill of Castor Oil based Rigid Polyurethane Foam

| Formulation | Tensile stress at Tensile Strength (MPa) | Tensile stress at Tensile Strength (MPa) after 90 Days |
|---|---|---|
| A | 32.68509 | 24.72641 |
| B | 31.34387 | 24.87922 |
| C | 20.51491 | 16.65487 |
| X | 18.43563 | 13.02548 |
| Y | 2.51574 | 1.97965 |
| Z | 1.98097 | 1.09855 |

# CHAPTER-5

# COCLUSION

The use of n-pentane as a physical blowing agent and water as a chemical blowing agent for Castor Oil based Rigid Polyuretnane Foams has been evaluated. The attempt was made to develop a material for commercial use that is more environments friendly. As Polyol and Polyissocyanite are the important constituents of Polyurethane formation. The Polyol had been prepared from the Castor oil, by modification. Both the blowing agents used have zero value for Oxygen Depletion Potential (ODP). So the rigid Polyurethane foam had been produced using eco-friendly raw material source. Different formulations of the blowing agents had been used to make studies. The effect of the different formulation of blowing agents n-Pentane and Water had been studied on the properties of the foam. These studies have clearly revealed that the Castor Oil can be successfully employed for the production of high density rigid foam. In the past, usually petroleum polyols were used for rigid polyurethane foam production, with the diminishing and non-renewable petroleum resource, vegetable oil based novel polyols found to have potential to replace these petroleum polyols. Because of lower costs, more environmental friendly and bio-renewable polyols derived from vegetable oils have a great prospective to partially replace the petroleum resource. Glycerol modification of castor oil results in more crosslinked and stiffer polymer structure. The tensile compressive, flexural strength and hardness of rigid polyurethane foams were found to be influenced by blowing agents. It has been found that the foam with formulation -A (10% n-Pentane) was found to be best among all other formulations in its properties and structure. SEM studies had also shown evidence for improved cell morphology and closed cell packing in low amount of n-pentane content (10%) as a blowing agents. The resulted castor oil based rigid polyurethane foams, due to their high strength and load bearing capacity are found suitable to replace petrochemical based Polyurethane Foam in commercial applications. The biodegradable characteristics of resulted foam are also found good and can be improved further.

# Appendix-1

## A1.1 Characterization of Raw Materials

### A1.1.1Determination of Specific Gravity

Cleaned and dried specific gravity bottle was first weighed and its weight Mc gm was noted down. Now the bottle filled with Sample was weighed to get weight Mo gm. The sample was then substituted with water of the same volume and reweighed to give weight equal to Mw gm. The specific gravity of the Sample was determined using the equation:

$$Specific\ gravity = \frac{M_{o-}M_{C}}{M_{W-}M_{C}}$$

**Calculations:**

**Specific Gravity of Castor Oil**

Weight of bottle (Mc) = 110.5 gm

Weight of castor oil and bottle (Mo) =205.5 gm

Weight of water and bottle (Mw) =210.5 gm

Specific gravity of castor oil = 205.5-110.5 / 210.5-110.5 **=0.95**

**Specific Gravity of Glycerol**

Weight of bottle (Mc) = 110.5 gm

Weight of glycerol and bottle (Mo) =235.5 gm

Weight of water and bottle (Mw) =210.5 gm

Specific gravity of glycerol = 235.5-110.5 / 210.5-110.5 **=1.25**

**Specific gravity of Modified Polyols**

Weight of bottle (Mc) = 110.5 gm

Weight of modified polyols and bottle (Mo) =208.5 gm

Weight of water and bottle (Mw) =210.5 gm

Specific gravity of modified polyols = 208.5-110.5 / 210.5-110.5 **=0.98**

**Specific gravity of MDI**

Weight of bottle (Mc) = 110.5 gm

Weight of modified polyols and bottle (Mo) =230.5 gm

Weight of water and bottle (Mw) =210.5

Specific gravity of modified polyols = 230.5-110.5 / 210.5-110.5 **= 1.2**

### A1.1.2 Determination of pH

The pH of polyols and 4, 4-diphenylmethane diisocyanate (MDI) was determined directly using pH meter (Model no. BL-501, Digital pH/ mv / $^0$C meter, Biolab).

**Figure A1.1:** Digital pH Meter (Model no. BL-501)

### A1.1.3 Determination of Acid Value

Approximately 2-3 gm of sample was dissolved in 100 ml of Methyl Ethyl Ketone with slightly heating. The mixture was then cooled at room temperature and was titrated against 0.1 N KOH solution, using phenolphthalein as indicator. The Acid Value (in mg KOH/gm) can be given by using the equation:

$$Acid\ Value = (S - B) \times \frac{N}{W} \times 56$$

Where, S is the volume (mL) of standard KOH solution consumed in sample titration, B is volume (mL) of standard KOH solution consumed in blank titration, W is weight of Sample(gm) and Nis the normality of KOH (equivalent concentration of standard KOH solution in mol/L.

**Calculations:**

**Preparation of 0.1 N KOH solutions**

Weight of KOH (W) = EVN/1000

Where, E = Equivalent weight = molecular weight/ functionality

E = 56.1 / 1 = 56.1

Weight of KOH (W) = 56.1 x 1000 x 0.1 / 1000 = **5.61** gm

Dissolve 0.08 gm of Amido Sulphonic acid ($H_3NO_3S$) (molecular weight-97.09 g/mol) in 100 ml water and titrate against KOH solution formed above using phenolphthalein as indicator.

Volume of KOH used = 7.81 ml

**Normality of KOH** =1000 x 0.08 gm (sulphonic acid) **/** 97.09 x Volume of KOH (in mL)

= 1000 x 0.08 **/** 97.09 x 7.81= **0.1055**

**Sample size for Acid Value**

2.3 gm and maximum 10 gm for very low acid value

**Acid value of Castor Oil**

Weight of castor oil sample (W) = 3.39 gm

Consumption of KOH in titration for sample (S) = 1.0 ml

Consumption of KOH in titration for blank (B) = 0.45 ml

Castor Oil Acid value (mg KOH/g) = (S - B) ×N (KOH) ×56.1 **/** W

= 1.0 – 0.45 x 0.1055 x 56.1 / 3.39 = **0.96**

**Acid Value of Glycerol**

Weight of glycerol sample (W) = 3.225 gm

Consumption of KOH in titration for sample (S) = 0.8 ml

Consumption of KOH in titration for blank (B) = 0.6 ml

Glycerol Acid Value (mg KOH/g) = (S - B) ×N (KOH) ×56.1 **/** W

= 0.8 – 0.6 x 0.1055 x 56.1 / 3.225 **= 0.37**

**Acid Value of Modified Polyols**

Weight of modified polyols sample (W) = 2.324 gm

Consumption of KOH in titration for sample (S) = 0.83 ml

Consumption of KOH in titration for blank (B) = 0.45 ml

Modified polyols Acid value (mg KOH/g) = (S - B) ×N (KOH) ×56.1 **/** W

= 0.83 – .45 x 0.1055 x 56.1 / 2.324 **= 0.96**

**Figure A1.2:** Arrangement for Titration

### A1.1.4 Determination of Hydroxyl Value

Weigh < 3 gm of sample in a conical flask and add 10 mL of acetylating solution (20 mL acetic anhydride in 80 mL of pyridine) into it. Stir the content by means of a magnetic stirrer under total reflux conditions for 30 minutes at $120^{o}$C. Cool down the contents at room by running water through condenser. Titrate the contents of the flask against 1 N NaOH solution using phenolphthalein as indicator. Similarly repeat the procedure for blank solution (without sample). The Hydroxyl Value (mg KOH/g) can be calculated using the equation:

$$Hydroxyl\ Value = (B - S) \times \frac{N}{W} \times 56.1$$

Where, B is Volume of standard 1N NaOH solution (mL) for blank solution, S is Volume of standard 1N NaOH solution (mL) for Sample titration, W is weight of the sample (gm) and N is equivalent concentration of NaOH standard solution, mol/L.

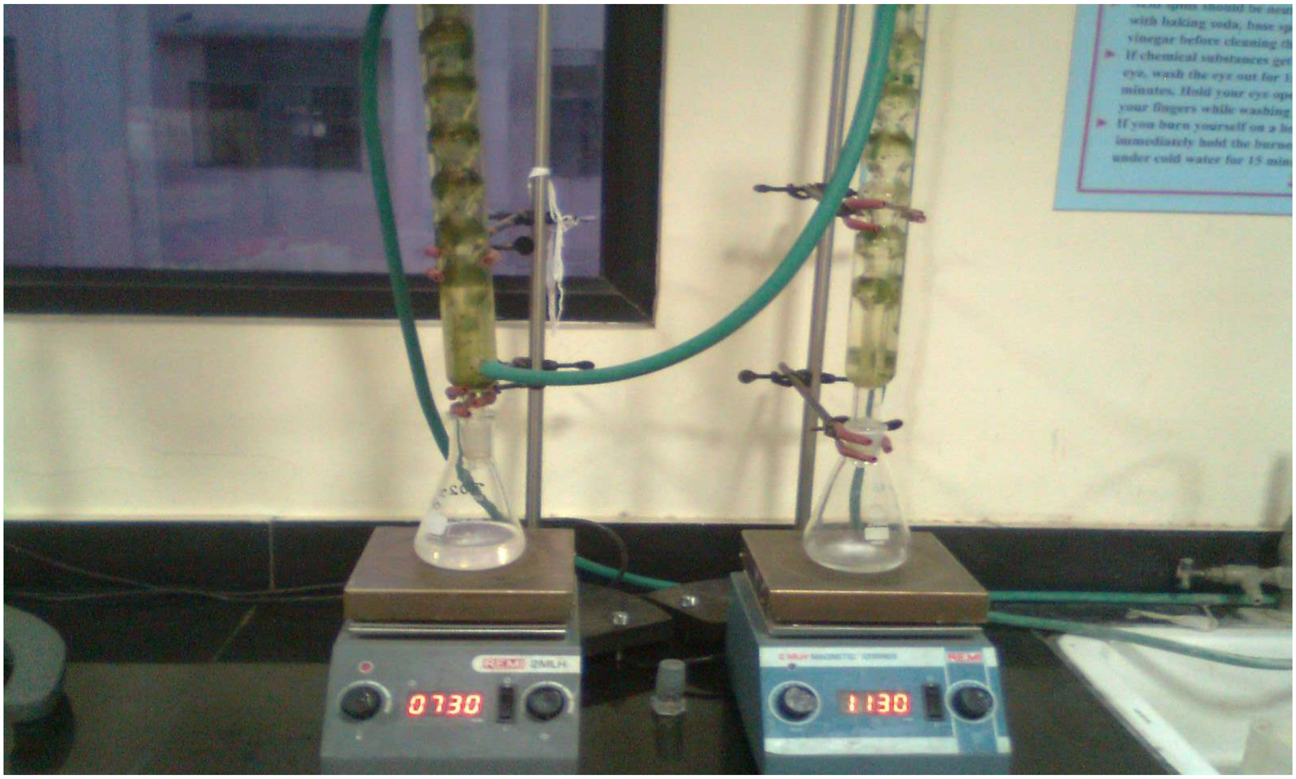


**Figure A1.3:** Magnetic Stirrer Heating Arrangement with Water Condenser

**Calculations:**

**Preparation of 1N NaOH Solutio**n

Weight of NaOH (W) = EVN/1000

Where, E = Equivalent weight = molecular weight/ functionality

E=40/1 =40

V= Volume = 1000 ml

N = Normality =1

W = 40 x 1000 x 1 / 1000 = 40 gm

Dissolve 40 gm NaOH in 960 ml of water and make solution.

**Standardization of NaOH solution**

Dissolve 0.8 gms of Amido Sulphonic acid ($H_3NO_3S$) (molecular weight=97.09 g/mol) in 100 mL water and titrate with NaOH solution formed above using phenolphthalein as indicator.

Volume of NaOH used = 8.72 mL

**Normality of NaOH** =1000 x 0.8 gm (sulfanic acid) / 97.09 x Volume of NaOH(ml)

= 1000 x 0.8 / 97.09 x 8.72 = **0.9449**

**Hydroxyl Value of Castor Oil**

Sample (1) Castor oil weight ($S_1$) = 1.86 gm

Sample (2) Castor oil weight ($S_2$) = 1.92 gm

Consumption of NaOH in titration for sample ($S_1$) = 41.75 ml

Consumption of NaOH in titration for sample ($S_2$) = 41.6 ml

Consumption of NaOH in titration for blank (B) = 47.45 ml

**Castor Oil Hydroxyl value (mg KOH/g)** = (B - S) ×N ×56.1 / W

$OHV_1$= 47.45-41.75 x 0.9449 x 56.1 / 1.86 = 162.45

$OHV_2$= 47.45-41.6 x 0.9449 x 56.1 / 1.92 = 161.51

OHV = OHV1+ OHV2 = 162.45+161.5 =**161.98**

**Hydroxyl Value of Glycerol**

Sample (1) Glycerol weight ($S_1$) = 1.35 gm

Sample (2) Glycerol weight ($S_2$) = 1.331gm

Consumption of NaOH in titration for sample ($S_1$) = 2.1 ml

Consumption of NaOH in titration for sample ($S_2$) = 1.99 ml

Consumption of NaOH in titration for blank (B) = 47.45 ml

**Glycerol Hydroxyl value (mg KOH/g)** = (B - S) ×N ×56.1 / W

$OHV_1$= 47.45- 2.1 x 0.9449 x 56.1 / 1.35 = 1780.7

$OHV_2$= 47.45-1.99 x 0.9449 x 56.1 / 1.331 = 1810.51

OHV = OHV1+ OHV2 = 1780.7+1810.51 =**1795.61**

**Hydroxyl Value of Modified Polyols**

Sample (1) modified polyols weight ($S_1$) = 1.985 gm

Sample (2) modified polyols weight ($S_2$) = 2.114 gm

Consumption of NaOH in titration for sample ($S_1$) = 28.0 ml

Consumption of NaOH in titration for sample ($S_2$) = 2.114 ml

Consumption of NaOH in titration for blank (B) = 42.35 ml

**Modified Polyols Hydroxyl value (mg KOH/g)** = (B - S) ×N ×56.1 / W

$OHV_1$= 42.35- 28.0 x 0.9449 x 56.1 / 0.985 = 383.31

$OHV_2$= 42.35-26.78 x 0.9449 x 56.1 / 2.114 = 390.42

OHV = OHV1+ OHV2 = 383.31+390.42 =**386.87**

### A1.1.5 Determination of Water Content

The water content of polyols is a very important parameter in the formulation of Polyutethane foams, as water present if any reacts with isocyanate groups and produces carbon dioxide, which act as blowing agent and thus affect the actual blowing process for foam formation. The water content of the samples were determined using Schott Titroline automatic Karl Fisher titration.

**Figure A1.4:** Karl Fisher Titration

### A1.1.6 Determination of Viscosity

The viscosity of the sample was measured by using Brookfield viscometer (ASTM D6821 -12). For this, sample was taken in a beaker. The temperature was maintained at $25^0$C and set rpm at 20. The results are obtained directly on the digital screen.

**Figure A1:5:** Brookfield Viscometer

### A1.1.7 Determination of % of NCO content

Take1 to 1.25 gm of MDI sample in round neck flask and dissolve it into 20 mL of Dibutyl amine solution. Heat the content by means of water bath under total reflux conditions using air condenser for 30-40 minutes. Cool the contents to room temperature and mix 50 mL of Methanol. Titrate it against 0.5 N HCl solution using bromo-phenol blue as an indicator. % NCO Content can be calculated using the equation:

$$Percentage\ of\ NCO(\%) = (B - S) \times \frac{N}{W} \times 4.2$$

Where, B is volume of the standard HCl solution consumed in blank titration (in mL), S is volume of standard HCl solution consumed in sample titration(in ML), W is weight of the sample (in gm) and N is the Normality of standard HCl solution (in mol/L).

**Figure A1.6:** Water bath with Air Condenser

**Calculations:**

**Preparation of 0.5 N HCl solutions**

Weight of HCl (W) = EVN/1000

Where, E = Equivalent weight = molecular weight / functionality

E = 36.5 / 1 = 36.5

Weight of HCl (W) = 36.5 x 1000 x 0.5 / 1000 = **18.25** gm

18.25 gm for 100%

For 36.5 % = 100/35.6= 2.8

So required quantity of HCl = 2.8 x 18.25 = **51.1** gm

Consumption of NaOH solution in titration of HCl = 16.6 ml

**Normality of HCl**

$N_1V_1 = N_2V_2$

$N_1$ x 16.6 = 0.9449 x 10

N HCl = **0.5692**

**% of NCO content of MDI**

% of NCO = (B - S) ×N (HCl) ×4.2/W

Weight of MDI sample-1 ($W_1$) = 1.115 gm

Weight of MDI sample-2 ($W_2$) = 1.094 gm

Consumption of HCl in titration for sample-1 ($S_1$) = 14.01 ml

Consumption of HCl in titration for sample-2 ($S_2$) = 14.19 ml

Consumption of HCl in titration for blank (B) = 29.4 ml

% of NCO contents sample-1 = 29.4- 14.01 x 0.5692 x 4.2 / 1.115 =32.99

% of NCO contents sample-2 = 29.4- 14.19 x 0.5692 x 4.2 / 1.094 =33.24

MDI % of NCO= % of NCO contents sample-1+% of NCO contents sample-2 / 2

MDI % of NCO = 32.99 + 33.24 / 2 =**33.12**

## A1.1.8 Determination of Percentage of Solid Contents

**Calculations:**

**Percentage of Solid Contents in Modified Polyols (S)**

S=Weight of sample after heating in oven at120$^{O}$C (D) x 100/ Initial weight of Sample (W)

Initial weight of sample-1 ($W_1$) = 3.470 gm

Weight of sample-1 after heating in oven at120$^{O}$C ($D_1$) = 3.43 gm

Initial weight of sample-2 ($W_2$) = 3.465 gm

Weight of sample-2 after heating in oven at120$^{O}$C ($D_2$) = 3.415 gm

Initial weight of sample-3 ($W_3$) = 3.210 gm

Weight of sample-3 after heating in oven at120$^{O}$C ($D_3$) = 3.165 gm

$S_1 = D_1 \times 100 / W_1$

$= 3.43 \times 100 / 3.465 = 98.85$

$S_2 = D_2 \times 100 / W_2$

$= 3.415 \times 100 / 3.470 = 98.56$

$S_3 = D_3 \times 100 / W_3$

$= 3.165 \times 100 / 3.210 = 98.60$

**Percentage of Solid contents (S) in Modified Polyols** = $S_1 + S_2 + S_3 / 3$

= 98.85 + 98.56 + 98.6 / 3 = **98.67**

**Percentage of Solid Contents in MDI**

S= Weight of sample after heating in oven at120$^{O}$C (D) x 100/ Initial weight of Sample (W)

Initial weight of MDI sample-1 ($W_1$) = 3.227 gm

Weight of sample-1 after heating in oven at120$^{O}$C ($D_1$) = 3.207 gm

Initial weight of MDI sample-2 ($W_2$) = 3.314 gm

Weight of sample-2 after heating in oven at120$^{O}$C ($D_2$) = 3.269 gm

Initial weight of MDI sample-3 ($W_3$) = 3.124 gm

Weight of sample-3 after heating in oven at120$^{O}$C ($D_3$) = 3.089 gm

$S_1 = D_1 \times 100 / W_1$

= 3.207 x100 /3.227 = 99.38

$S_2 = D_2 \times 100 / W_2$

= 3.269 x100 /3.314 = 98.64

$S_3 = D_3 \times 100 / W_3$

= 3.089 x100 /3.124 = 98.88

**MDI Percentage of Solid contents (S)** = $S_1 + S_2 + S_3 / 3$

= 99.38 + 98.64 + 98.88 / 3 = **98.97**

# Appendix-2

## A2.1 Calculations of the Formulation for Polyurethane Foam Formation

Polyurethanes are formed by the reaction of polyols and polyisocyanates resulting in a urethane linkage. .A urethane linkage is produced by reacting as isocyanate group, -N=C=O with a hydroxyl (alcohol) group, -OH. For complete reaction, it is needed to ensure that an NCO group of the polyisocyanate is available for each OH group of the polyol. For this purpose, the raw material system is needed to be formulated based upon the presence hydroxyl group (-OH) present in the system. This formulation of raw materials is based upon the NCO Index.

### NCO Index (KZ)

The NCO index is defined as the number of moles of NCO per mol of OH multiplied by100.

$$KZ = \frac{\propto_{NCO}}{\propto_{OH}} \times 100$$

When the index is 100, the above condition is met. An index > 100 means an excess of NCO. With polyurethane formulations, an index > 100 ensures the complete reaction of the OH group. Formulations for producing rigid polyurethane foam normally have an index is between 105 and 125, and those for rigid polyisocyanurate-polyurethane foams an index is between 180 and 350. Excess NCO groups react, for example, while forming allophanate structures. For the foam systems using water as blowing agent, NCO Index should be >100. Moreover the system is influenced by the presence of moisture in the base polyol, Thus, for the calculation of a foam formulation hydroxyl number (OH value), water content and isocyanate content (NCO) have to be ascertained.

As $\alpha_{NCO}$ and $\alpha_{OH}$ cannot be directly determined, they are calculated with the aid of NCO content and the OH values.

**Calculation of the OH value and of $\alpha_{OH}$:**

To determine the hydroxyl value (OH value), 1 gram of the polyol is reacted (esterified) with the anhydride of a dicarboxylic acid and the released hydroxyl- equivalent acid is titrated with potassium hydroxide (KOH). The hydroxyl value is defined as the necessary quantity of KOH in mg per g of polyol. If the quantity $M_{polyol}$ is used instead of 1 g of polyol, the definition of the OH value is as follows:

$$OHZ = \frac{M_{KOH}}{M_{polyol}}$$

If this equation is not related to mg of KOH but to mMol of KOH, both sides of the equation must be divided by 56.1 (molecular weight of KOH):

$$\frac{OHZ}{56.1} = \frac{M_{KOH}}{M_{polyol} \times 56.1} = \frac{\alpha_{KOH}}{M_{polyol}}$$

$\alpha_{KOH}$ = Mole KOH

Since it follows from determining the hydroxyl value that one mol of OH corresponds to each mol of KOH, $\alpha_{KOH}$ and $\alpha_{OH}$ can be equated:

**Calculation of α $_{NCO}$:**

The quantity of NCO in the polyisocyanate is normally given in % by weight of NCO, being:

$$\boxed{\% \text{ NCO} = \frac{M_{NCO}}{M_{polyisocyanate}} \times 100}$$

If the connection between quantities and molarity is taken into consideration in accordance with

$$\boxed{\alpha_{NCO} = \frac{M_{NCO}}{42}}$$

Where, 42 = molecular weight of NCO

and mol is converted simultaneously to mMol, then one obtains

$$\boxed{\% \text{ NCO} = \frac{\alpha_{NCO} \times 42}{1000 \times M_{polyisocyanate}}}$$

Hence, α $_{NCO}$ can be calculated from the transformation

$$\boxed{\alpha_{NCO} = \frac{\% \text{ NCO} \times M_{polyisocyanate}}{4.2} \qquad \text{Equitation 3}}$$

**Calculation of the Polyisocyanate content of a Formulation**

If equations 2 and 3 are inserted into equation 1, the amount of polyisocyanate necessary for a specific quantity of polyol at a predetermined characteristic value can be calculated:

$$KZ = \frac{\%\ NCO \times M_{polyisocyanate} \times 56.1}{4.2 \times OHZ \times M_{polyol}}$$

$$= \frac{\%\ NCO \times M_{polyisocyanate} \times 1336}{OHZ \times M_{polyol}}$$

Transformation gives

$$M_{Polyisocyanat} = \frac{OHZ \times M_{polyol}}{1336 \times \%\ NCO} \times KZ \qquad \text{Equitation 4}$$

This formula makes it possible to calculate the quantity of polyisocyanate necessary at a specific index for a given quantity of polyol given the OH value and the NCO content of the polyisocyanate.

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