CHAPTER - 3
POLYURETHANE FOAMS
FROM BIO-BASED POLYOL
Height

The major potential for application of agricultural waste in polymers is for polyols for polyurethanes. Polyurethanes are the most resourceful polymer.

The principal application of polyurethane is in the area of flexible and rigid foams. In the present part of the thesis polyurethane rigid foams are prepared from *Nicotina tabacum stem* and different non-traditional oil based polyol.
3. Introduction

Polyurethane (PU) is one of the most versatile polymer that have been used in a wide both industry and everyday life, and commercially available first in 1940. Polymer foams were first made in the 1930's and -40's, with foamed polystyrene being the first polymer foam in 1931. Polyurethane was invented by Dr. Otto Bayer at the start of the second World War. It was first used as a replacement for rubber and also used as a coating to protect other common materials at the time such as metals and wood. A few years after the war, the flexible polyurethane foam was invented and it was first, then that it started being used for cushioning in furniture and automotive industry. The two decades following made polymer foams more widely used as new technologies developed, introducing methods such as injection molding, twin screw for foam and several extrusion techniques. The use of blowing agents that contributed to the ozone layer depletion raised concerns in later years and has lead to a focus on finding blowing agents that will not have a negative environmental impact. Polyurethane rigid foams are among the most important class of polyurethanes commonly used as two predominant applications along with coatings, sealants, elastomers, and adhesives as being other, and foams have low density, low thermal conductivity, and good mechanical properties, hence these are generally used on large scale for insulation purposes and exploitation endure to develop at a rapid rate all over the world [1-15]. As these are highly energy-efficient materials of polyurethane product and are having good physical, mechanical and chemical properties in all temperature conditions [16-19]. PUs is produced by gas bubbles formed during the polyurethane polymerization process, that is the rearrangement reaction between compounds having active hydroxyl groups, such as polyols, with
organic isocyanates. The foremost polyisocyanates employed are toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI) and the polyols for PU foams are liquid oligomers or polymeric compounds with at least two hydroxyl groups. Such polyols comprise polyether polyols, polyester polyols and hydroxyl-containing vegetable oils. As the accessible choices of poly-functional isocyanates are rather limited, significant research effort has been given to produce biobased polyols for the formulation of polyurethane with the requisite properties [20].

3.1 Types of polymer foam [21 22]

Polyurethane

Polyurethanes are any type of polymer containing a urethane linkage. The urethane linkage is -NH-CO-O-. The way to form polyurethanes is done by reacting isocyanates with compounds that have an active hydrogen, such as diols, that contain hydroxyl-groups, in the presence of a catalyst. Since there are many compounds containing active hydrogens and many different diisocyanates, the number of polyurethanes that can be synthesized is also large. The specific properties of the polyurethane can be tailored to a specific need by combining the appropriate compounds.

Polyurethanes can exist as both rigid and flexible foams, and as a coating or adhesive material. Since polyurethanes come in so many forms and can have a wide variety of properties, it is also used in many different applications. Rigid polyurethanes are used as insulation and flotation, while flexible ones are used for cushioning and packaging. In addition, they are used as adhesives in
construction and transportation. Rhinoskin is an example of a polyurethane used for coating and protection. It is sprayed onto a surface and then sets to protect the underlying layer. Polyurethanes are mostly thermosets, which means they are hard to melt and reprocess and can therefore have the disadvantage of being non-recyclable.

**Biodegradable foams**

Biodegradable polymer foams are investigated not only because of the increasing waste and environmental problems for traditional polymer foams, but also because of the increasing price of petroleum products that are used in manufacturing the polymer foams. Biodegradable foams are water soluble and sensitive to humidity, while traditional petroleum-based foams are more inert to water. Biodegradable foams are also limited in making foams that have microcellular structure, which means they will be hard to make into thin sheets. However, they are important in reducing the amount of CO$_2$ emission. There is also a wide range of different candidates of biomaterials that can be used for biodegradable foams, including ethylene vinyl alcohol, polyvinyl alcohol, polycaprolactone, polylactic acid and starch.

**Starch**

Starch foam was made already in 1989 as biodegradable packaging, and is an alternative material to the traditional polystyrene foams. Starch is a polysaccharide made up of glucose units linked by glycoside linkages, and its length is generally between 500-2000 repeat units. Starch is made up of amylose and amylopectin. Amylose is more linear and gives the foam flexibility and keeps
the density low, while amylopectin is highly branched and makes the product more foamable. Starch can be extracted from, for example, corn or potatoes. Starch foams are produced by extrusion where the starch is melted and mixed with a blowing agent. The blowing agent for starch is often water or methanol, which is turned into steam when the system is heated and forms air bubbles within the starch matrix. The extrusion process is a continuous, low-cost method that is easy to use. It is still hard to make the foam smooth and have a high number of closed cells. The use of thermoplastic polymer additives can help even out the surfaces, but can also decrease the degradability of the foam by incorporating slowly degrading or non-degradable polymers.

3.2 Polyurethane foam synthesis

As stated earlier polyurethanes are made by the addition reaction of polyisocyanates and polyols.

Two basic reactions used to produce polyurethane forms are as follows:

Isocyanate + Polyol $\rightarrow$ Urethane

Isocyanate + Water $\rightarrow$ CO$_2$ for foaming

When there are two functional groups it's termed a diisocyanate and diol as seen below.

![Functional groups of diisocyanate](image)

*Figure 1. functional groups of diisocyanate*
The oxygen's electronegativity on the hydrogen at the end of the diol attracts the nucleophile, which wants to bind to a nucleus (nucleophile=nucleus loving). Then oxygen reacts with a carbon on an isocyanate group. This leaves the nitrogen on the isocyanate group to be negative, which is highly unfavourable. The nitrogen will give off its negative charge to the hydrogen atom on the alcohol group, finally forming a urethane bond between the two monomer units, resulting in a urethane dimer.

The dimer will have one end group that is isocyanate, while the other is an alcohol group. Each end can now react with other monomers and oligomers until polyurethane is formed. This is called a step-growth reaction. Step-growth reactions are characterized by longer chains being able to react and add to a growing chain just like monomers can, unlike chain-growth polymerization where only monomers can add to the growing chain. It is also a rearrangement reaction since no small compounds are given off during the reaction.

![Figure 2. step-growth reaction of isocyanate](image-url)
The difference between making polyurethane and polyurethane foam is that a gas has to be incorporated in the final product. To achieve this the isocyanate group reacts with water forming an amine and CO$_2$ gas. Because the isocyanate group turns into an amine, the reaction with other diisocyanates will result in some urea-linkages in the polyurethane foam, but this doesn’t affect the properties of the polymer foam much, and is necessary to get the gas to be produced and expand the polymer into a foam. [23]

3.3 Blowing agents [24]

A blowing agent is a substance which is capable of producing a cellular structure via a foaming process in a variety of materials that undergo hardening or phase transition, such as polymers, plastics, and metals. They are typically applied when the blown material is in a liquid stage. The cellular structure in a matrix reduces density, increasing thermal and acoustic insulation, while increasing relative stiffness of the original polymer. As we know, water was used as a blowing agent to produce CO$_2$. Because the water needed to be part of a reaction, it’s a chemical blowing agent. Physical blowing agents don’t take part in a chemical reaction, but are the volatile liquids that evaporate and make the foam expand. First generation physical blowing agents are mostly outruled because of their negative environmental impact on the ozone layer. This is especially the case for chlorofluorocarbons. CFC’s and HCFC’s CFC’s are ideal blowing agents besides the tremendous environmental concerns associated with them. They are not flammable, have fitting boiling points and are non-toxic. They also have good thermal insulation properties. This is why it has been hard to find a replacement for these blowing agents that has equivalent properties. Hydro-chloro-
fluorocarbons (HCFC) and hydrofluorocarbons (HFC) are blowing agents with a lot smaller impact on the ozone layer and with similar properties. HCFC's are being phased out since they still have ozone depletion problems. Although HFC's have no impact on the ozone depletion, it has high global warming potential. However, they have a lower shelf life and can sometimes be flammable, which creates concern because this decreases the safety of polyurethane foams.

### 3.3.1 CO$_2$

Liquid CO$_2$ is used as a blowing agent because it does not have the same environmental issues as CFC's and HCFC's. It has a low global warming potential and is inexpensive. It is also easier to obtain low density foams using CO$_2$.

### 3.3.2 Physical Blowing Agents [26 27 28]

#### 3.3.2.1 Inert Gases:

These gases specially carbon dioxide and nitrogen are two of the most widely used blowing agents. The specialty of nitrogen is that it is cheap, abundant and more environmentally friendly as it is obtained from the atmosphere itself. A material is in a supercritical fluid state when it is maintained at a temperature and pressure exceeding its critical temperature and pressure.

#### 3.3.2.2 Halogenated hydrocarbons:

Trichloro-fluoromethane (CFC11), chlorofluorocarbon-12 (CFC-12) and 1, 1-dichloro, 1,2,2,2-tetrafluoroethane (CFC-114).
3.3.2.3 Hydrochloro-fluorocarbons (HCFC):

These have at least one hydrogen bonded carbon in the molecule and are chemically less stable than CFC and tend to breakdown in the lower atmosphere into simple inorganic species. The ability of HCFC to migrate to the atmosphere and to decompose into ozone-depleting chlorine is much lower than CFCs. Some examples of HCFCs are HCFC-141b (CH3CCl2F), HCFC-141b (CH3CClF2) and HCFC-22 (CHClF2).

3.3.2.4 Hydrofluorocarbons (HFC):

These are compounds with no chlorine in them. Most widely used are HFC-245fa (CH3CH3CF2), HFC-365mfc (CF3CH2CF2CH3), HFC-134a (CH2FCF2) and HFC-152a (CHF2CH3).

3.3.2.5 Hydrocarbons (HC):

Some low-boiling aliphatic hydrocarbons have the desirable characteristics like, low cost, halogen free, compatibility with polymer etc. that can be used as blowing agent. However, hydrocarbons are classified as VOC and are subjected to emission control in many countries. Pentanes are dominant blowing agents for PU foams and PS foams. Butanes and propane are the used for making foams from polyolifins.

3.4 Chemical Blowing Agents [25]

These compounds liberate gases during the processing of foam, either due to decomposition or chemical reactions. List of common chemicals blowing agents show in below: Sodium bicarbonate, Azodicarbonamide (ADC), 4,4-Oxybis
Almost all chemical blowing agents are finely divided solids and no special storage or handling equipment is generally needed to utilize them in processing. They are either blended with the plastics before processing or fed directly into a hopper during the process. Some of the factors must be considered when selecting a chemical blowing agent. The gas release temperature should closely match the processing temperature of the polymer. If the decomposition temperature of chemical blowing agent is significantly above the polymer process temperature, little or no foaming will occur. On the other hand, if it is significantly below the polymer process temperature, overblown or rupturing of cell structure results. Chemical blowing agent should be chosen so that it releases the gas at a controlled rate, failure of which also changes the formation of cell structure inside the foam.

3.5 As discuss above a simple mixing process for foam production can be seen as follows:

Step 1 - Mixing of the raw materials

During production, the raw materials (Suitable isocyanate, polyalcohol, blowing agents and additives) are mixed from their own storage tank to a common mixing chamber. Adequate dispersion can be achieved by the stirring of a high speed mixer.

Step 2 - Foam forming and settling
The foam gradually solidifies when traveling up the settling chamber by the action of paper conveyor. It is then cut into desired size of blocks by cutter after the foam is hardened.

Step 3 - Curing

The newly formed foam blocks are still very hot when transported to the storage area. They must be cured at room temperature for at least 18 hours before further processing. The schematic diagram showing the reaction for producing PU foam using TDI is shown figure00.

During the process, the blowing agent used to create bubbles is released during the reaction or which could be a part of ingredient, forms pores in the mass of polymer.

Due to above condensation reaction the rigid polyurethane foam would be produced when reaction carried out without blowing agents. There are mainly tow blowing agent in practice first is carbon dioxide, and the second is methylene chloride, which is produced in the reaction mixture as the water reacts with isocyanate group.

In the late 80's, traditionally CFC (chlorinated fluorocarbons) based solvents were used as blowing agents. But the ozone layer depletion effect of CFC based chemical was established, then the use of CFC was gradually banned. Methylene chloride, which is inert to ozone, is used as a substitute for CFC.
3.6 General mechanism of polyurethane Foam

The polyurethane foam production is a difficult process. The physical process of foam formation and the chemical processes of polymerization and gas formation occur instantaneously and are accompanied by a significant temperature rise and a complicated rheological profile. The initial polyol and isocyanate mixture is a low molecular weight, low viscosity fluid, which is reflected in the low strength of the bubble wall formed during foaming. This wall of such a bubble breaks easily and gas escapes. Therefore, it is necessary to increase the strength of the bubble wall (gel strength), which is achieved by increasing the molecular weight of the polymer.

The theory of bubble formation in foams is similar to bubble formation in water. The first stage of bubble formation is called nucleation. The number of bubbles will depend on the number of nuclei present in the system. The beginning of foam formation is characterized by the formation of a large number of nuclei. Their creation causes refraction of light on the walls of nuclei, which is demonstrated as whitening of the mass (cream formation) without a significant volume increase. The next stage is bubble growth from the nucleus due to the incoming evolved gas, and the volume increase of the foaming mixture. This stage is observed as the foam rise. The stability of a growing bubble depends on the surface tension. If the surface tension is too large and there is no nucleation, a small number of large bubbles will grow, and the shape should be elongated in the direction of rise. Such foams are usually not desirable since they show anisotropy in their mechanical properties.
Regulation of bubble growth is achieved by the addition of surfactants (usually silicone based materials). They lower the surface tension and enable bubble division into smaller, more regular shaped bubbles. This process is helped by vigorous mixing. Foam rise (due to gas diffusion into the bubbles) is completed when the polymerization has passed the gel point, and the infinite network of the polymer, spanning from one to the other end of the sample, is formed. [29 30 31]

### 3.7 Applications of Polyurethane foam

**Rigid polyurethane foams**

Foams are mostly used in thermal insulation applications such as refrigerators, freezers, insulated buildings, insulated trucks carrying produce, water heaters, thermoses etc. Hence, rigid polyurethanes contribute a lot to energy saving appliances. Polyurethane foams with a high closed-cell structure are moisture resistant and can be used as buoyancy in boats. The advantage is that the foam will not deflate upon a puncture, but retains its buoyancy even after many load-unload cycles.

**Flexible**

Most of the flexible polyurethane foam produced is made for cushioning. This includes furniture, packaging and transportation. Furnishings use polyurethane foam for carpet underlay, bedding, home furniture. The transportation industry uses it in seating cushions for the airlines, trains and bicycles and cars. It is also used in a wide range of other applications for cars such as sound insulation and vibration dampening. Other applications include clothing, toys, electronics and other applications for the protection or cushioning issues.
**Polystyrene foam**

Polystyrene foam's most known applications are the white polystyrene cups which are ideal for hot beverages because of the foam's good thermal insulation properties. Polystyrene foam is also used for packaging purposes, mostly food containers and disposable dishes and egg cartons. High-impact polystyrene can also be used in structural appliances instead of rigid materials like wood and metal.

**3.8 EXPERIMENTAL**

**3.8.1 Materials**

The prepared polyols from castor oil, tobacco seeds oil and karnja oil were used as polyhydroxy compounds. Double distilled water, prepared in the laboratory itself was used as blowing agent. Silicon oil was used as a surfactant (Kindly supplied by Berger Paints, V. U. Nagar, Gujarat, India). Toluene diisocyanate (TDI) adduct, containing 13.3 (60.4) % free ANCO, was supplied by Gads Fine Chem. Ltd., Ahmedabad, Gujarat, India.

**3.8.2 Preparation of polyurethane foams (PUFs)**

Polyurethane foam samples were prepared using a “one-shot method” [32]. For preparing the foams the prepared polyols from castor oil, tobacco seeds oil and karnja oil, TDI adduct, double distilled water, catalyst and surfactant were used. All chemicals were put into a plastic container and mixed for 2 min., with a glass stirrer, as shown below figure.
Figure 3. Foam production demonstration

During the mixing process the rpm of the stirrer was set at 2000. Subsequent to blending, the blend was then moved into an open Teflon shape, already lubed with a silicon form discharge specialist. The form was kept up at 55 °C for 50 s, and accordingly arranged froth was post-cured at room temperature for 1 week. Three replicas were prepared for all the foams. Amount of chemical ingredients was varied to obtain different foam samples. The parameter used for different ingredients is given in the table.

Table 1. Parameters used for foam preparation

<table>
<thead>
<tr>
<th>Code</th>
<th>Polyol</th>
<th>TDI (phpp)</th>
<th>Surfactant (phpp)</th>
<th>Catalyst (phpp)</th>
<th>Blowing Agent (phpp)</th>
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<tbody>
<tr>
<td>CAS</td>
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<td>150-255</td>
<td>5-15</td>
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<td>5-15</td>
<td>1-3</td>
<td>0.2-20</td>
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<td>KA</td>
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<td>150-255</td>
<td>5-15</td>
<td>1-3</td>
<td>0.2-20</td>
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<td>TS</td>
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<td>150-255</td>
<td>5-15</td>
<td>1-3</td>
<td>0.2-20</td>
</tr>
</tbody>
</table>
3.9 Testing

*Fourier Transforms-Infrared Spectroscopy (FT-IR).*

The liquefied product as well as prepared polyol were characterized by FT-IR analysis of tablets prepared from 1 mg of sample with 100 mg of KBr, using a Perkin Elmer Spectrum GXFT-IR spectrophotometer. The infrared spectrum was recorded in the 4000 to 500 cm\(^{-1}\) range by accumulating 32 scans with the resolution of 4 cm\(^{-1}\).

*Universal Testing Machine:*

Compressive strength of the prepared PUF samples were measured according to ASTM D 1521 under ambient conditions with a Universal Testing Machine (UTM), LR 30 K Plus, Lloyd Instruments Ltd., Hampshire, U K, at pulling rate of 5.0 mm/min. The crosshead speed was 3.00 mm/min. The strength of three specimens per sample were measured and averaged.

*Thermal Conductivity.*

Thermal conductivity of prepared foam was measured by divided base method. In this method a thin sample plate is sandwiched between two metal roads. The cross-section of sample is the same as the shape of metal roads. Heat is provided from one end of the block. Temperature are measured at given point and its allow us to determine the thermal conductivity.

*Thermo-gravimetric Analysis (TGA).*

TGA was carried out using Mettler Toledo thermo-gravimetric analyzer (TGA) model (TGA/STDA 851 e). The weight loss of samples during temperature
ranging from 50°C to 61°C was measured under nitrogen flow 10 mL min⁻¹ with a heating rate of 10°C min⁻¹.

**Dynamic Mechanical Analysis:**

(DMA) was carried out on Tritech 200 DMA, Triton Technology, equipped with a liquid nitrogen cooling apparatus, in a single cantilever clamp mode with constant heating rate of 2°C/min. Rectangular samples were taken of the dimension of 18 mm x 13 mm x 4 mm. DMA analysis was done at a fixed frequency of 1 Hz and a fixed oscillation displacement of 0.05 mm.

**Scanning Electron Microscope (SEM).**

A study of morphological properties by SEM images of the samples were obtained in a Theophylline Microspheres (FEG-SEM) operating at 5 kV. The samples were placed on a plastic support.

Density Measurements: Density of prepared PUFs was measured according to ASTM D1622. The specimen was cut into dimension of 30 x 30 x 30 mm. The density of three specimens were measured and averaged.

### 3.10 RESULTS AND DISCUSSIONS

#### 3.10.1 Processing Parameters

For the effect of different additives and catalyst etc. are important for on the foaming characteristic of foam. The processing parameter are the Cream time, rising time, and gel time was measured with error of 1.5 s, the NCO/OH ratio for each form sample was 1.5 for prepared foams. Cream time was determined by time required for obtained proper thick paste. Rise time was determined by
means of time required for complete foaming after pouring the paste to the mould. Gel time was the time required for the foam completely stable at the normal condition without any tacky feel. Density of prepared foam was measured according to ASTM D1662. The specimen was cut into dimension of 30 × 30 × 30 mm. The density of three specimens was measured and averaged. The density of foams is greatly affected by the blowing agent.

The four different sample of PUFs prepared castor, soy, karanja and tobacco seeds oil based polyols having hydroxyl value 200 and 300 and processing parameters were noted which are shown in below table.

**Table 2. Processing parameters for castor oil-based PUFs-1**

CAS 201 to CAS 204: The PUF derived from polyol based on communis oil were found having hydroxyl value of 200.

#Sample was unstable and foam collapsed

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Processing Parameter</th>
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<tbody>
<tr>
<td></td>
<td>Cream time(sec)</td>
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<tr>
<td>CAS 200</td>
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<td>CAS 202</td>
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<td>CAS 204</td>
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<td>CAS 206</td>
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<tr>
<td>CAS 207#</td>
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Table 3. Processing parameter for cummunis oil (castor oil)-based PUFs-2

CAF 301 to CAF 305: were found to have hydroxyl value 300 with varying percentage of polyester

<table>
<thead>
<tr>
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<th>Cream time (sec)</th>
<th>Rise time (sec)</th>
<th>Gel time (min)</th>
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<td>CAS 307</td>
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Table 4. Processing parameter for soy oil-based PUFs-3

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**Table 5. Processing parameter for soy oil-based PUFs**

<table>
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<td>SY 306</td>
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**Table 6. Processing parameter for tobacco seed oil-based PUFs**

<table>
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<td>TSP 206</td>
<td>105</td>
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Table 7. Processing parameter for tobacco seed oil-based PUFs-6

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<td>TSP 306</td>
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Table 8. Processing parameter for blend of karanja oil-based PUFs-7

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Table 9. Processing parameter for karanja oil-based PUFs-8

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<tr>
<td>KOP 306</td>
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From above results it shows that the PUFs prepared from polyols having hydroxyl value 300 which increased the strength of cell walls of the foam in less time. And TSP, KAP, and CAS based PUFs required less time to process and to get optimum level of strength than Soy based PUFs. Its indicate the more reactivity of former with isocyanate.

3.10.2 Density of prepared polyurethane foams

The density of foams is colossally affected by the blowing agent. Water is use as blowing agent for get ready PUFs. Increasing the measure of water in the formulation of 1 to 10 parts per hundred parts of polyol, the density of foam decreased from 241 to 140 kg/m³ (Figure 4). The viewed diminish in density of the foam with expanding the measure of blowing administrator is particularly related to the pore size of the readied foam. As the water content was expanded the substance response amongst water and TDI deliver more measure of carbon dioxide, which is trailed by more air pocket improvement.
Figure 4. Density of the foams (pphp parts per hundred parts of polyol).

These air pockets coagulate bringing about greater cell measure because of which mass per unit volume diminishes. which diminishes the weight per unit volume of the foam bringing about lessening in density of foam.

The strength was measured by Universal Testing Machine and diminished from 2.0 to 0.3 MPa as the water content in the formulation increased from 1 to 10 pphp, as show in (figure 5) the size of cells increases, because of the force applied by the surfactant to limit the cells in regular shape which results in thinning of cell walls which eventually diminishes compressive strength.
Figure 5. Compressive strength of the foams (pphp parts per hundred parts of polyol)

A general known fact is that mechanical properties of a cellular material like foam mainly depend on its density. A rule can be used to depict the relationship between density and compressive strength [43] which is as follows: 

\[ \text{Strength of material} = A \times (\text{Density})^B \]

Where A is a constant and B is related to the deformation mechanics of cellular materials.
3.11 FTIR Characterization

Figure 6. FTIR spectra of PUF obtained from castor oil-based polyol

Figure 7. FTIR spectra of PUF obtained from tobacco seed oil-based polyol
Figure 8. FTIR spectra of PUF obtained from karanja oil-based polyol

Figure 9. FTIR spectra of PUF obtained from soy oil-based polyol
Figures show FT-IR spectroscopy, in which Spectrum shows the characteristic functionalities of castor oil based PFs, Soy oil based PUFs, Tobacco seeds oil based PUFs, and Karnaja oil based PUFs, respectively and it also indicate some bonds additional present as compared to the band revealed in the polyol spectrum. The hydroxyl and amine stretching frequencies were found to be in the region of 3300 cm\(^{-1}\) to 3900 cm\(^{-1}\), characterise the amine group formed during polyurethane formation. The peak appearance at 1330 cm\(^{-1}\) to 1600 cm\(^{-1}\) which is attributed to the development of PU bonds. The bands observed between 1680 cm\(^{-1}\) to 1730 cm\(^{-1}\) is for carbonyl urethane linkages, whereas bands at between 1225 to 1245 cm\(^{-1}\) is due to C – N stretching of polyester chain present in polyurethane. The splitting of C = O indicates the H bond and non H bonded C = O in which marginally more intensity for CAS and SY its indicates more H-bonding. Herein, the peak of splitted non H-bonded C=O is at lower wavenumber then the other H-bonded C = O. PUs are efficient in forming hydrogen bonds due to the presence of an electron rich donor N-H group and an electron deficient C=O acceptor group in the urethane linkage. The peak at 2274 cm\(^{-1}\) is attributed to the –NCO group, which shows in figure due to presences of unreacted isocyanate in PUFs.

3.12 Thermal Conductivity Study

Thermal conductivity is the important thermal property that manages insulation applications for rigid PU foams, and it is closely related to the foam density and cell morphology. Low thermal conductivity values for CAS and TSP foams results from a small aver- age cell size and high contents of closed cell. For better insulation performance rigid PU foams shall have closed cell contents as high as
possible. The thermal conductivities for all prepared foam samples were measured and comparatively given in Table 9. In this work thermal conductivities of a bio-polyols have the lowest thermal conductivity, 0.029 W/mK, which is toward the higher thermal conductivity limits of common PU construction foams (0.020 to 0.030 W/mK for densities ranging from 30 to 100 kg/m³) [15]. The obtained thermal conductivity results are similarly in a respectable agreement with the reported results of thermal conductivity (0.0257–0.0329 W/mK) of rigid PU foams prepared from various types of lignins (Alcell, Indulin, Curan and Sarkanda) at different ratios [16].

**Table 10. Thermal Conductivity Study**

<table>
<thead>
<tr>
<th>PUFs Samples</th>
<th>Thermal conductivity (Kcal/mh °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAS</td>
<td>0.018</td>
</tr>
<tr>
<td>SY</td>
<td>0.022</td>
</tr>
<tr>
<td>TSP</td>
<td>0.019</td>
</tr>
<tr>
<td>KOP</td>
<td>0.025</td>
</tr>
</tbody>
</table>

### 3.13 Thermo-gravimetric Analysis (TGA)

The thermal stability of the rigid polyurethane foams was evaluated using TGA. Typically, the thermal stability of PUFs various on the quantity of aromatics molecules and urethane linkages present in the geometry, as they can withstand a considerable limit of heat. The thermal constancy of polyurethane foams CAS and TSP relies upon the functionality of polyols.
Figure 10. TGA of PUF obtained from tobacco seed oil-based polyol

The TGA spoke in figure of the CAS and TSP based foam tests demonstrated three stage bends. Initially decay of urethane bond breaking at 200 to 250 °C and the come about degradation is seen in to 2 – 20% weight reduction, in light of the substitution pattern of the isocyanate and polyol backbone. Secondary decay brings about 40-50% weight loss was observed between the temp. range of 300 to 350 °C. Decay happens in light of the fact that the breakdown of part contributed by polyol. The decay of hydrocarbon chain appears in the scope of 400 to 450 °C and brought about 61 – 81% weight reduction is final step of decay. Were the overall thermal stabilities of PU rigid foams possess higher
thermal stability.

![TGA of PUF obtained from castor oil-based polyol](image)

**Figure 11. TGA of PUF obtained from castor oil-based polyol**

### 3.14 Scanning Electron Microscopy (SEM)

SEM is use for the morphological study of prepared foam. Its provide details about, mechanical and thermal properties upto certain limits. SEM performed to determine the morphology of pores, cell attachment on the polymer surface. Figure 12, 13, 14 and 15 show SEM of PUF prepared from castor oil-based polyols, Soy oil-based, tobacco seeds oil-based and karanja oil-based polyols.

The shape of the pores was found to be spherical or oval and the size was ranging from about 0.1 – 1.0 mm. The PUF prepared from soy oil and karnja oil based
polyol was larger compared to castor oil-based and tobacco seeds oil based polyols. The morphological study concludes that the pore size and cell structure of the prepared foams samples from castor and tobacco seeds oil-based polyol were more even than the other. However, all of the foam samples shows good characteristics for their use in insulation purpose as more cell obtained were closed type, which increases the due to this gas retention inside the cell resulting in increased thermal insulation.

It is also demonstrated by the thermal conductivity analysis for prepared foam samples from castor oil and tobacco seeds oil based PUFs have initial thermal conduction less than the PUFs prepared from Soy oil and karanja oil due to the more compact and closed structure of castor oil and tobacco seeds oil based foams.
Figure 12. SEM of the prepared foam Castor oil-based polyol.
Figure 13. SEM of the prepared foam tobacco seed oil-based polyol.
Figure 14. SEM of the prepared foam soy oil-based polyol.
Figure 15. SEM of the prepared foam tobacco seed oil-based polyol.
3.15 Conclusion

The energetic dynamism in arrears the efforts was the urge for the conservation of depleted feedstock as well as growing consciousness of environment. The obtained polyol based on agricultural waste was further utilized as precursor in synthesis of polyurethane foam was successfully prepared by synthesized polyol reacting with different isocyanate adducts. A respectable equilibrium among mechanical and chemical properties was observed in the polyurethane foam systems.

Processing parameters for prepared PUFs were studied. These were analysed by FTIR investigation and inspected for the effect of blowing agent concentration and surfactant concentration on density and compressive strength. Density and compressive strength of PUFs decreased with increasing amount of blowing agent and then became constant; compressive strength increased and became constant afterwards.

From SEM analysis, as more of the cell structure obtained was closed cell, thermal insulating properties were observed. The thermal conductivity of PUFs obtained from castor oil-based and tobacco seeds oil-based polyols in the range of 0.011 to 0.018 and 0.011 to 0.019 kCal/mhoC whereas for PUFs prepared from soy oil-based polyols, it was in the range of 0.014 to 0.022 kCal/mhoC.

From the morphological investigation using SEM, it was detected that the cell structure of PUFs obtained from castor oil-based polyol as well as tobacco seeds oil-based polyol was more symmetrical and regular due to which they performed slight better in thermal insulation than PUFs obtained from soy oil-based and karanja oil-based polyols.
3.16 REFERENCE


