

STUDIES ON THE EFFECT OF ADDITION OF IRON DUST/ IRON NANOPARTICLES ON THE PROPERTIES OF CASTOR OIL BASED RIGID POLYURETHANE FOAM

A Major Project report submitted towards the partial fulfillment of the requirement for the award of the degree of

MASTER OF TECHNOLOGY IN POLYMER TECHNOLOGY

Submitted by
Aditi Gupta (2K14/PTE/13)

Under the guidance of
Dr. Raminder Kaur

DELHI TECHNOLOGICAL UNIVERSITY



DEPARTMENT OF APPLIED CHEMISTRY AND POLYMER TECHNOLOGY
DELHI TECHNOLOGICAL UNIVERSITY
DELHI-110042, INDIA



CERTIFICATE

This is to certify that the project titled **STUDIES ON THE EFFECT OF ADDITION OF IRON DUST/ IRON NANOPARTICLES ON THE PROPERTIES OF CASTOR OIL BASED RIGID POLYURETHANE FOAM** is a record of the bonafide work done by **ADITI GUPTA** (*Reg. No: 2K14/PTE/13*) submitted in partial fulfilment of the requirements for the award of the Master of Technology (M.Tech) in Polymer Technology of Delhi Technological University, Delhi during the academic year 2015-16.

Dr. Raminder Kaur ,
(Project Supervisor)
Department of Applied Chemistry
and Polymer Technology

Prof. R.C Sharma,
Prof. and HOD,
Department of Applied Chemistry
and Polymer Technology

ACKNOWLEDGEMENT

I am pleased to acknowledge, **Prof. R.C. Sharma**, HOD, Department of Applied Chemistry and Polymer Technology for providing an opportunity to carry out this project work. I am very thankful to him for his support and guidance whenever required.

I am heartily thankful to my project supervisor, **Dr. Raminder Kaur**, Assistant Professor, Department of Polymer Science and Chemical Technology, for taking out her valuable time and patiently familiarizing me with the fundamentals, for teaching with complete enthusiasm and vigor and helping me through-and-through.

I am also grateful to **Ms. Anuja Agrawal, Mr. Mukesh Kumar and Mr. Manjit Malik**, Research Scholars, Department of Applied Chemistry and Polymer Technology who helped me clear doubts whenever they arose and helped me substantially for my project and without whose lion contribution this project would not have been possible.

Finally, I would like to thank the Technical and Non-technical Staff of the department for providing us with an environment where I was able to contribute and accomplish tasks equal to my interest and knowledge. I solemnly acknowledge the fact that this report would have been incomplete without the invaluable suggestions, comments and co-operation of the staff at the department.

Finally, my appreciation goes to my family for their unconditional support, love and encouragement. I solemnly acknowledge the fact that this report would have been incomplete without the invaluable suggestions, comments and co-operation of everyone who supported me while working on this work.

ADITI GUPTA

(ROLL NO: 2K14/PTE/13)

Contents		
		Page No
List of Tables		6
List of Figures		6
Abstract		8
Chapter 1	INTRODUCTION	9
1.1	Background	10
1.2	Chemistry	12
1.3	Chemicals involved in PU synthesis	14
1.3.1	Isocyanates	14
1.3.2	Polyols	16
1.3.3	Blowing Agents	21
1.3.4	Cataysts	22
1.3.5	Surfactants	24
1.3.6	Chain Extenders & Cross Linkers	24
1.4	Polyols from Bio-based Materials	26
1.4.1	Methods to produce polyol from vegetable oil	28
1.5	Objective of Research Work	38
Chapter 2	LITERATURE REVIEW	39
2.1	Introduction of Castor Oil	40
2.2	Castor Seed Yield	43
2.3	Uses of castor oil	44
2.4	Interpenetrating polymer network based on castor-oil PU	47
2.5	Use of castor oil in development of polyurethane nanoparticles	47
Chapter 3	CASTOR OIL BASED POLYURETHANE FOAM	48
3.1	Background	49
3.2	Materials used	49
3.3	Experimental Setup	50

	3.3.1	Procedure Involved	50
	3.3.2	Preparation of Castor Oil Rigid PU Foams with Fillers	51
	3.4	Hydroxyl Value and Calculation	52
	3.5	Characterization of PU Foam	53
	3.5.1	Scanning Electron Microscope (SEM) Analysis	53
	3.5.2	Fourier Transform Infrared Spectroscopy	54
	3.5.3	X-Ray Diffraction	54
	3.5.4	Thermogravimetric Analysis	55
	3.5.5	Differential Scanning Calorimetry	55
Chapter 4 RESULT AND ANALYSIS			
	4.1	Effect of filler content on appearance of PU foam	58
	4.2	SEM results of pure and castor oil based PU Foam	60
	4.3	FTIR results of pure and castor oil based PU Foam	61
	4.4	Mechanical properties of samples	64
	4.5	XRD of PU foam samples	69
	4.6	TGA of PU foam samples	71
	4.7	Preparation of PU foam using Iron Nanoparticles	72
	4.7.1	Synthesis of Iron Nanoparticles by Co-precipitation method	72
	4.7.2	Characterization of Iron Nanoparticles	72
	4.8	Effect of fillers on PU Foam	74
	4.9	Characterization of Fe NP reinforced PU foam	75
Chapter 5 CONCLUSION AND FUTURE SCOPE			
	5.1	Conclusion	78
	5.2	Future scope of work	78
REFERENCES			79

LIST OF TABLES

Table No	Table Title	Page No
1.1	General Properties of Polyurethane	11
1.3.2	Commonly used initiators	14
1.3.6	Commonly used chain extenders	24
1.3.6.1	Functionalities of some catalysts, cross linkers and extenders	25
1.4	Fatty acid profiles of various vegetable oils	28
3.3.2	PU Foams with Iron Dust as Filler	51

LIST OF FIGURES

Figure No	Figure Title	Page No
1.1	Segments of a polyurethane structure	10
1.1.2	Various applications of polyurethane	12
1.2	Synthesis of polyurethane	13
1.3.1	Chemical structures of TDI	14
1.3.1.1	Structure of pure and polymeric MDI	15
1.3.2	Synthesis of polyols	17
1.3.2.1	Variation of polyol reactivity with increasing primary hydroxyl	21
1.3.4	Structure of tertiary amine	22
1.4	Triglyceride structure of vegetable oils	27
1.4.1	Chemical structures of major fatty acids found in vegetable oils	27
1.4.A	Synthesis of polyols by transesterification	29
1.4.B	Synthesis of polyols by hydroformylation	32
1.4.C	Synthesis of polyols by ozonolysis	33
1.4.C.1	Synthesis of polyester polyols by ozonolysis using ethylene glycol	34
1.4.D	Synthesis of vegetable oil-based polyols by thiol-ene coupling	35
1.4.E	Synthesis of polyols by transesterification reaction	36
1.4.E.1	Synthesis of polyols by amidation reaction	37

2.1	Triglycerides of ricinoleic acid	40
2.1.1	Production of castor oil based polyol via ethoxylation reaction	42
2.2	Growth of Castor seed in different months	43
2.2.1	Castor Seed Yield in India	43
2.3	Castor Seed Value Chain	44
2.3.3	Conversion of vegetable oil to biodiesel	46
3.3.1	Stages involved in the formation of polyurethane foam	50
3.5.2	Simple interferometer with a beam-splitter and compensator plate	54
4.1	Effect of filler content on appearance of PU Foam	58
4.2.1	SEM of pure PU	61
4.2.2	SEM of castor oil based PU	61
4.3.1	FTIR result of castor oil PU Foam	62
4.3.2	FTIR result of iron dust filler	63
4.3.3	FTIR result of castor oil PU foam with iron dust filler	63
4.4	Flexural and compressive strength of samples	64
4.5	XRD analysis of PU foam samples	69
4.6	TGA analysis of PU foam samples	71
4.8	Effect of fillers on the appearance of PU foam	74
4.9	characterization of Fe NP reinforced PU foam	75

ABSTRACT

Polyurethane foams constitute an important class of materials and are used in a wide range of applications, both commercial and daily life such as furniture, carpets and mats, packaging, thermal insulation, etc. owing to their unique properties. Traditionally, polyurethane foams were synthesized by the reaction between isocyanates and polyols derived from petroleum resources. However, due to the non-renewable nature of these fossil resources, the focus has now shifted on the use of bio-based materials with polyols being derived from natural and renewable resources such as vegetable oil (possessing good functionality) offering excellent alternative and great potential for use in industrial applications.

The present study focuses on the use of castor oil to produce polyurethane foams because apart from being low cost oil, it has a high degree of unsaturation and low $-OH$ functionality. Iron dust was incorporated as the filler in the foam. The prepared PU foams were characterized using techniques such as SEM, FTIR, XRD, TGA and DSC. In addition, the mechanical properties such as flexural and compressive strength of the iron dust reinforced RPUF were also studied. It was observed that with an increase in the content of iron dust in the foam, the foam's capability to withstand compressive force and flexural strength also increased. This is attributed to the fact that the iron dust fills the void space within the foam and hence helps it to withstand external breaking force.

CHAPTER 1

INTRODUCTION

1.1 Background

Polyurethane is defined as a polymer that contains the group NHCOO in its backbone chain and is one of the most important examples of specialty polymer [1]. The polymer is characterized by the presence of a urethane linkage (formed due to the reaction between hydroxyl groups and isocyanate group). The development of polyurethane dates back to 1937 when German scientist Dr. Otto Bayer synthesized it successfully in his lab [2].

This polymer offered some benefits over other plastics that were synthesized by polymerization of olefins or by polycondensation reaction. Gradually, in 1954, the first flexible polyurethane foam was developed using isocyanate and polyester polyol [2]. Soon, in the 1980s, a new class of foams called water-blown microcellular flexible foams were developed and used in gaskets molding for automotive panels and air filter seals, thereby providing a replacement for PVC plastisol used in automotive applications [3]. Polyurethane foams have now found use used in oil filter applications involving high-temperature. Polyurethane foam is made using a small amount of blowing agents to give less dense foam, better cushioning effect, energy absorption or thermal insulation.

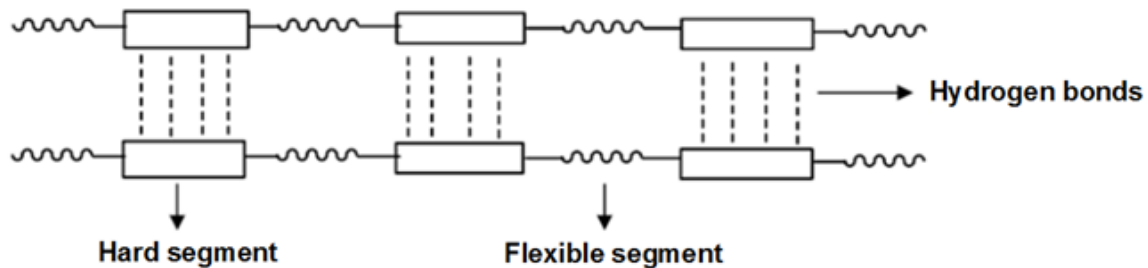


Fig1.1 Segments of a polyurethane structure

Polyurethanes fall in the category of compounds called reaction polymers, and include epoxies, phenolics and unsaturated polyesters. Polyurethanes are produced by the reaction of an isocyanate having two or more isocyanate groups per molecule with a polyol having two or more hydroxyl groups per molecule in the presence of a catalyst or by activation with ultraviolet light [5]. The main advantages of using polyurethane is that it has high impact strength even at reduced temperatures, resistant to abrasion, oxidation, tear, humidity, aliphatic hydrocarbons, dilute bases and dilute acids although it is degraded by chemicals such as ketones, esters, strong bases, strong acids and steam. Polyurethane is not suitable for

applications involving high temperature as the highest temperature thermoplastic polyurethane can withstand has been reported to be approximately 104⁰C.

	American Engineering	SI
Processing temperature	385–450°F	196–232°C
Linear mold shrinkage	0.004–0.014 in/in	0.004–0.014 cm/cm
Melting point	400–450°F	204–232°C
Density	69.9–77.4 lb/ft ³	1.12–1.24 g/cm ³
Tensile strength, yield	4.9–35.0 lb/in ² × 10 ³	3.4–24.6 kg/cm ³ × 10 ³
Tensile strength, break	4.9–35.0 lb/in ² × 10 ⁵	3.4–24.6 kg/cm ³ × 10 ²
Elongation, break	100.0–500.0%	100.0–500.0%
Tensile modulus	0.6–45.0 lb/in ² × 10 ⁵	0.4–31.6 kg/cm ³ × 10 ⁴
Flexural strength, yield	6.0–60.0 lb/in ² × 10 ³	4.2–42.2 kg/cm ³ × 10 ²
Flexural modulus	0.1–0.4 lb/in ² × 10 ⁵	0.0–0.2 kg/cm ³ × 10 ⁴
Compressive strength	1.2–29.5 lb/in ² × 10 ³	0.8–20.7 kg/cm ² × 10 ²
Izod notched, R.T.	1.5 ft-lb/in-no break	8.1 kg/cm/cm
Hardness	A55-A95 Rockwell	A55-A95 Rockwell
Thermal conductivity	1.7–2.3 BTU-in/h-ft ² -°F	0.25–0.33 W/m ^o -K

Table 1.1 General properties of polyurethane [4]

Polyurethane foam is widely used in both daily life and industry applications. For example, polyurethanes are used in the manufacture of rigid foam insulation panels; foam seals and gaskets; durable elastomeric wheels and tires used in roller coaster, escalator, shopping cart, elevator, and skateboard wheels; shoes; furniture; vehicles; packing material, refrigerator, electrical compounds; high performance adhesives; surface coatings and surface sealants; synthetic fibers; building materials; carpet underlay; water vessels; new iPad Smart Covers; and hoses. Most polyurethane are thermosetting polymers, that is do not melt when heated, however thermoplastic polyurethanes are also available in market [6]. The following figure represents the applications of polyurethane and has been divided into seven major groups:

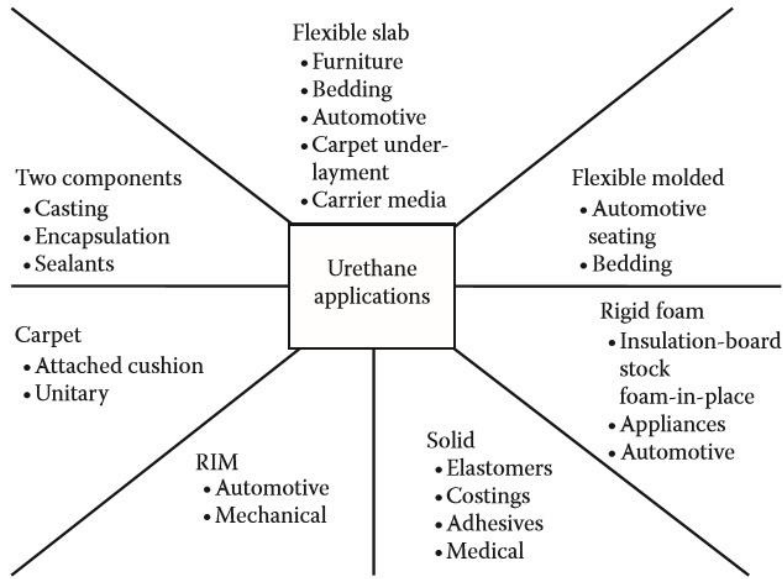
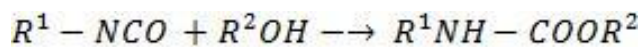


Fig. 1.1.2 Various applications of polyurethane [4]

1.2 Chemistry

The conventional method for synthesis of polyurethane polymers involves the reaction between di- or polyisocyanate and a polyol. Both the reagents used contain two or more functional groups per molecule on average. In 1956 DuPont introduced polyether polyols, especially poly(tetramethylene ether) glycol. The advantage of polyether polyols was that they were cheaper, convenient in handling and more water-resistant as compared to polyester polyols, and thus became more popular [6]. A generalized urethane reaction between an isocyanate group with a hydroxyl group is shown below:



Where;

$R^1 = C_1$ to C_{36} , aliphatic, aromatic or cycloaliphatic

$R^2 = C_1$ to C_{36} , aliphatic, aromatic, cycloaliphatic or polymeric

The properties of polyurethane are greatly influenced by the type of isocyanates and polyols used in the reaction to synthesize it. Long and flexible segments, contributed by the polyol, yield a soft and elastic polymer[7]. Whereas, on the other hand, high amounts of crosslinking result in tough or rigid polymers. Similarly, long chains and low crosslinking result in a polymer that is very stretchy in nature whereas

short chains with numerous crosslinks leads to a hard polymer. Long chains and intermediate crosslinking result in a polyurethane polymer that is helpful in making foam. The crosslinking in polyurethanes signifies that the polymer consists of a three-dimensional network and molecular weight of it is very high. Consequentially, typical polyurethanes are thermosetting in nature, i.e. do not melt or soften when heated at high temperature, although thermoplastic polyurethanes are also available commercially now [8]. The wide options available for the isocyanates and polyols, apart from a range of additives and processing conditions, helps in the production of polyurethanes with different properties and this makes them one of the most widely used polymers.

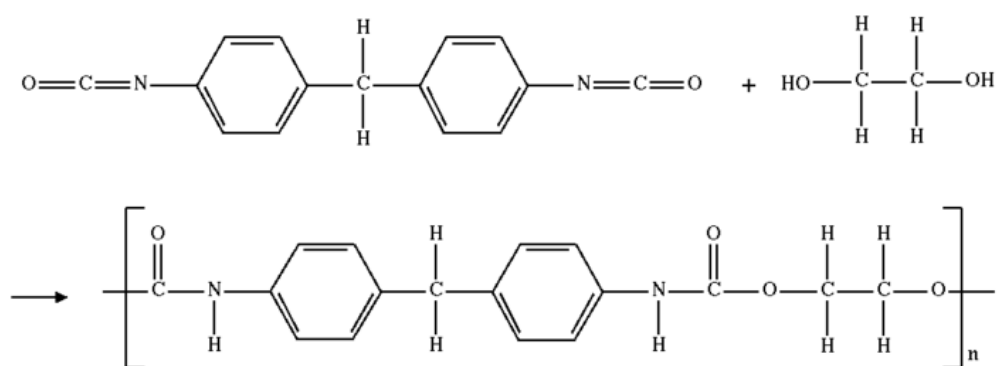


Fig. 1.2 Synthesis of polyurethane

Isocyanates are considered to be extremely reactive materials. Though this makes them useful in making polymers but at the same time, they also require a great precaution and care in handling and use. The aromatic isocyanates including diphenylmethane diisocyanate (MDI) or toluene diisocyanate (TDI) are more reactive than aliphatic isocyanates like hexamethylene diisocyanate (HDI) or isophorone diisocyanate (IPDI) [9].

Polyether polyols, the other component involved in polyurethane synthesis, are mainly made by copolymerization reaction between ethylene oxide and propylene oxide and a suitable polyol precursor. The polyols used in the manufacture of polyurethanes are not "pure" compounds as they are often mixtures of similar molecules with different molecular weights and different numbers of hydroxyl groups, which is why the "average functionality" is often mentioned [10]. The final properties of the synthesized polymer depend upon the length of the polyol chain and its functionality. Rigid polyurethanes are made by polyols that have molecular weight in the hundreds while flexible

polyurethanes are derived from polyols having molecular weights up to several thousand or more. When making foams, water is intentionally added in the reaction mixture, and this reacts with the isocyanate to form a urea linkage and releases carbon dioxide gas (a brief introduction of the blowing agents used is given in the chapter below) and the resulting polymer thus contains both urethane and urea linkages. This reaction is called blowing reaction and generally occurs in the presence of catalysts like tertiary amines (bis-(2-dimethylaminoethyl)ether).

1.3 Chemicals

Isocyanates and polyols are the two main chemical components used in the synthesis of polyurethane foams [11]. Other chemicals such as blowing agents, catalysts and surfactant are also needed to change the properties of the final polymer.

1.3.1 Isocyanates

Isocyanates are referred to as organic compounds with an isocyanate group, that is containing functional group with the formula $R-N=C=O$. Di-isocyanates are isocyanates with two isocyanate groups. These along with polyols are used in the production of polyurethanes [11]. The two most important types of isocyanates used in polyurethane production are methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI).

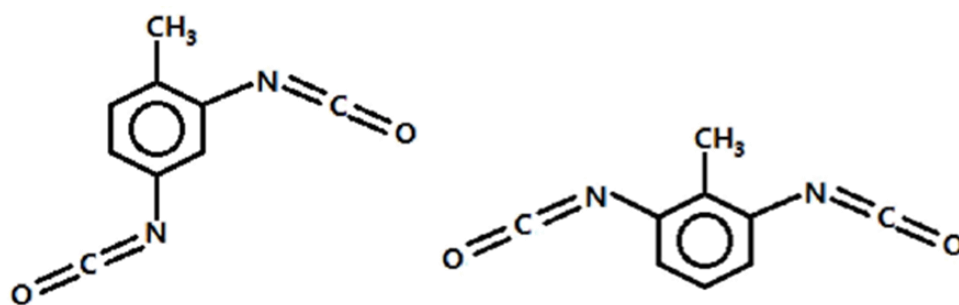
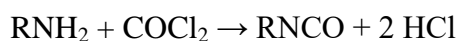


Figure 1.3.1 Chemical structures of TDI. (Left: 2,4-TDI; Right: 2,6-TDI)

The production of isocyanates involves the reaction between amines and phosgene. The following reaction occurs:



However, due to the hazardous nature of phosgene, the production and handling of isocyanates requires special care and precaution. The global market for diisocyanates was 4.4 million tons in the year 2000. The breakdown includes 61.3% for methylene diphenyl diisocyanate (MDI), 34.1% for toluene diisocyanate (TDI), 3.4% for hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI), and 1.2% was the total for various others [12].

The starting material for MDI is aniline. Before the amino groups are converted into isocyanate, aniline is first reacted with formaldehyde to produce diphenylmethane diamine. The diphenylmethane diamine thus formed is transformed into diisocyanate. Because of the structures of diamines, pure MDI mixture consists of three major isomers: 4,4'-MDI, 2,4'-MDI, and 2,2'-MDI [12]. Another isocyanate known as polymeric MDI can also be formed as a type of polyisocyanate during the distillation of the MDI. Because this polymeric MDI mixture has lower vapor pressure and is also less hazardous compared to TDI, it is more commonly used in the polyurethane industry.

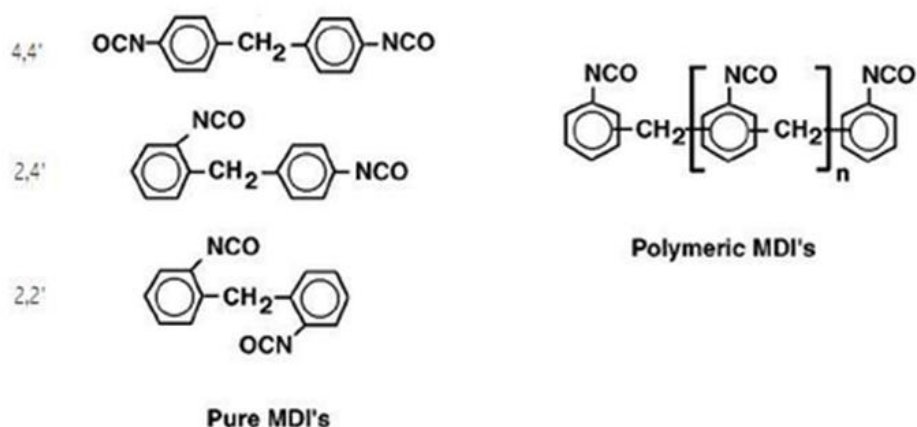


Fig. 1.3.1.1 Structure of pure and polymeric MDI

Since isocyanates are chemically very reactive, they are extremely hazardous in nature. Isocyanates are proven to be potentially dangerous to the eyes and respiratory tract causing irritation. One hazardous calamity of isocyanates includes Methyl isocyanate that was released in the Bhopal disaster resulting in the death of nearly 4000 people.

ISOCYANATE INDEX: It is defined as the the ratio of the actual amount of isocyanate used to the theoretical amount of isocyanate required times 100. It is a significant parameter that directly has an impact on the properties of polyurethane foams [13].

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

Generally, higher value of isocyanate index leads to more hardness. For rigid polyurethane foams, the isocyanate index is usually over 100. Variation of the isocyanate index in a foam has a significant effect on the hardness of the final foam. This increase in hardness has been attributed to the increased covalent cross-linking because of complete consumption of isocyanate reactive sites due to the presence of excess isocyanate groups [13]. The isocyanate index normally ranges from 105 to 115 in the case of production of flexible slabstock foams. Within this range, the foam's hardness can be safely and readily controlled. In general, as the index increases, the foam becomes harder. However, there occurs a point beyond which hardness does not increase and only other physical properties begin to suffer.

Additionally, the ability of excess isocyanate groups to react depends on the ambient humidity conditions during curing of foam [14]. When humidity is higher, a phenomenon called 'summer softening' occurs which leads to softer foam. By varying the isocyanate index, the hardness of the foams can be adjusted. Most common isocyanate indexes lie in the range of 85 to 110.

1.3.2 Polyols

Polyols are generally defined as compounds consisting of multiple hydroxyl groups. They can be classified into polyether polyols and polyester polyols. Polyether polyols are synthesized by the reaction of epoxides with active hydrogen containing compounds [6]. Polyester polyols are made by the polycondensation reaction between multifunctional carboxylic acids and polyhydroxyl compounds. Conventional polyester polyols make use of virgin raw materials and are made by the direct polyesterification reaction involving high-purity diacids (like adipic acid) and glycols (1,4-butanediol). These polyols are usually more expensive and viscous than polyether polyols, but they make polyurethanes with better properties like improved solvent, abrasion, and cut resistance.

Polyols can also be classified based on their end use. Polyols having higher molecular weight (2,000 to 10,000) are used in making more flexible polyurethanes while polyols having lower molecular weight are used to make more rigid products [9]. Some polyols like specialty polyols are polycarbonate polyols, polycaprolactone polyols, polybutadiene polyols, and polysulfide polyols. These are used in applications like elastomer, sealant, and adhesive that require superior weatherability, and have good resistance to chemical and environmental attack.

Another type of polyols includes fluorinated (FEVE) polyols made by the co-polymerization of chlorotrifluoroethylene or tetrafluoroethylene with vinyl ethers containing hydroxyalkyl vinyl ether. Fluorinated polyurethanes exhibit superior resistance to UV, acids, alkali, salts, chemicals, solvents, weathering, corrosion, fungi and microbial attack due to the fact that they contain a high percentage of fluorine-carbon bonds, that are the strongest bonds among all chemical bonds. These polyols find application in high performance coatings and paints [10]. Another class of phosphorus-containing polyols that are chemically bonded to the polyurethane matrix finds use as flame retardants. The covalent bonding in them prevents migration and leaching of the organophosphorus compound.

MANUFACTURING OF POLYOLS

A polyether polyol is formed by the polymeric reaction product of an organic oxide with an initiator compound containing two or more active hydrogen atoms. In the presence of a base catalyst, the active hydrogen compound leads to ring opening and oxide addition, which is continued until the desired molecular weight is obtained [15]. A diol results if the initiator has two active hydrogens.

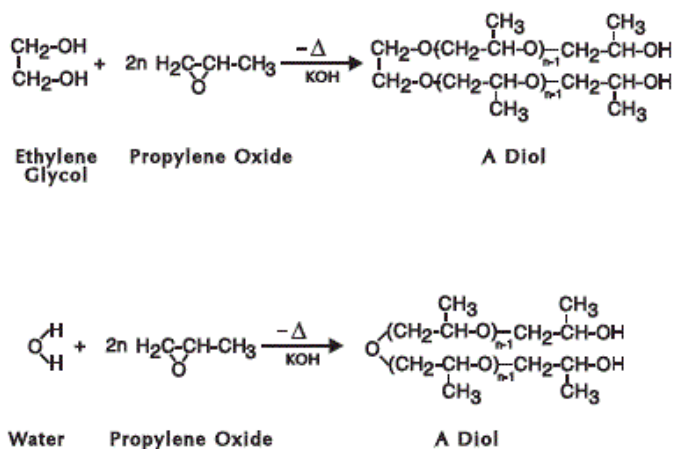
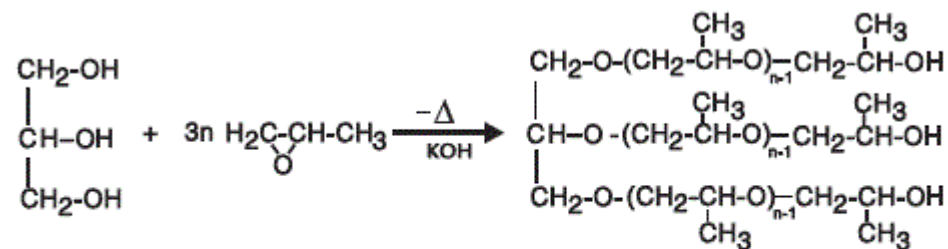


Fig. 1.3.2 Synthesis of polyols

Oxide addition produces chain growth in three directions, and a triol results if a trifunctional initiator such as glycerine is used.



Glycerine

Propylene Oxide

A Triol

Some of the commonly used initiators used are mentioned in Table 1.3.2 below:

Desired Functionality	Example Initiator	Initiator Structure
2	Water	$\text{H} \begin{array}{c} \diagup \\ \text{O} \\ \diagdown \end{array} \text{H}$
2	Ethylene glycol	$\begin{array}{c} \text{CH}_2\text{-OH} \\ \\ \text{CH}_2\text{-OH} \end{array}$
2	1,2-Propylene glycol	$\begin{array}{c} \text{CH}_3\text{-CH-OH} \\ \\ \text{CH}_2\text{OH} \end{array}$
3	Glycerine	$\begin{array}{c} \text{CH}_2\text{-OH} \\ \\ \text{CH-OH} \\ \\ \text{CH}_2\text{-OH} \end{array}$
3	Trimethylolpropane	$\begin{array}{c} \text{CH}_2\text{-OH} \\ \\ \text{CH}_3\text{-CH}_2\text{-C-CH}_2\text{-OH} \\ \\ \text{CH}_2\text{-OH} \end{array}$
4	Ethylene diamine (1,2-diaminoethane)	$\text{H}_2\text{N-CH}_2\text{-CH}_2\text{-NH}_2$
4	Pentaerythritol	$\begin{array}{c} \text{CH}_2\text{-OH} \\ \\ \text{HOCH}_2\text{-C-CH}_2\text{OH} \\ \\ \text{CH}_2\text{-OH} \end{array}$
5	Diethylene triamine	$\text{HN} \begin{array}{l} \diagup \text{CH}_2\text{-CH}_2\text{-NH}_2 \\ \diagdown \text{CH}_2\text{-CH}_2\text{-NH}_2 \end{array}$

HOW ARE POLYOLS CHARACTERIZED?

It is very important to have adequate criteria for characterizing a polyol. Some of the most commonly used criteria for characterizing polyol is [16]:

1.) Functionality – This criterion arises from the choice of initiator or blend of initiators used. It is defined as the average number of reactive sites of isocyanate per molecule. It can also be given by the definition of the number of reactive hydroxyl groups on a single polyol molecule [10]. Two important variables that must be considered while calculating functionality are: level of monol and level of diol.

2.) Hydroxyl Number – It is a measure of the amount of reactive hydroxyl groups that are available for polyurethane reaction. This value is reported as the number of milligrams of potassium hydroxide equivalent to the hydroxyl groups found in one gram of the sample [12]. It is calculated by: wet chemical methods and infrared method. The most commonly used methods for hydroxyl value determination are available in ASTM D 4274-88.2.83

$$\text{Hydroxyl value (mg KOG/gm)} = \frac{56100}{\text{Equivalent Weight}}$$

Apart from the hydroxyl amount of a polyol, there are other three types of hydroxyl groups that are also very important. These can be classified as primary, secondary and tertiary hydroxyl groups. Primary hydroxyl groups are extremely reactive in the polyurethane synthesis and approximately 3.3 times faster as compared to secondary hydroxyl groups in polyurethane reaction rate, while the tertiary hydroxyl groups can hardly react with isocyanate. Polyester polyols and polyether polyols, that are petroleum-based polyols, contain primary hydroxyl groups. However, most of the biobased polyols have secondary hydroxyl groups [3].

3.) Equivalent Weight – It is simply defined as the molecular weight of a polyol divided by the functionality. Functionality of a polyol is intricate due to the presence of monols from isomerization of propylene oxide and diols (derived from water). In practice, the equivalent weight is calculated from the hydroxyl (OH) number. This criterion is necessary for calculation of isocyanate requirement and is given by the following expression [16]:

$$\text{Equivalent Weight} = \frac{\text{Molecular Weight}}{\text{Functionality}}$$

$$\text{Equivalent Weight} = \frac{56.1 \times 1000}{\text{OH Number}}$$

4.) Primary Hydroxyl Content - The reactivity of a polyol with isocyanates is directly affected by the distribution of primary and secondary hydroxyl groups. Generally, as the primary hydroxyl content increases, the polyol reactivity also increases. The differences in solution based reaction rates was the earliest measurements used in the calculation of primary and secondary hydroxyl contents [16]. Nowadays, Nuclear magnetic resonance (NMR) is the most preferred analytical method. Using the NMR method, the primary and secondary hydroxyl end groups can be distinguished from one another and from the propylene oxide and ethylene oxide units in the polyol chain. Another method known as polarographic method has also been reported in the calculation of primary hydroxyl content.

5.) Cloud Point – It is defined as the temperature ($^{\circ}\text{C}$), at which a polyol solution in a water or water-alcohol mixture becomes turbid upon the application of heat. Cloud point is directly dependent on the polyol molecular weight and content of ethylene oxide in the polyol [17]. As polyol molecular weight increases, the cloud point decreases and it increases with the addition of ethylene oxide to the polyol. The analysis of cloud point is taken to be a measure of the water solubility, surfactant properties and reactivity of the polyol used.

6.) CPR – Stands for controlled polymerization rate. This value defines the weakly basic materials present in a polyol quantitatively. These materials are determined as the total weak acid salts of the strong bases and are not defined qualitatively. During the reaction between polyols and isocyanates, these salts may act as catalysts [4].

7.) Reactivity – It is defined as a measure of the rate at which a polyol undergoes reaction to synthesize a polyurethane. In recent years, a refined test known as Brookfield Viscosity Test (BVT) has proved to be helpful for reactivity quantification of ethylene-oxide-capped polyols. Additionally, the BVT test is also useful in detecting polyol contamination [18]. Apparent polyol reactivity in the BVT model reaction is also strongly influenced by the terminating effects of monol (unsat) in the polymer-chain. Besides this test, other viscosity-based reactivity tests have also been used.

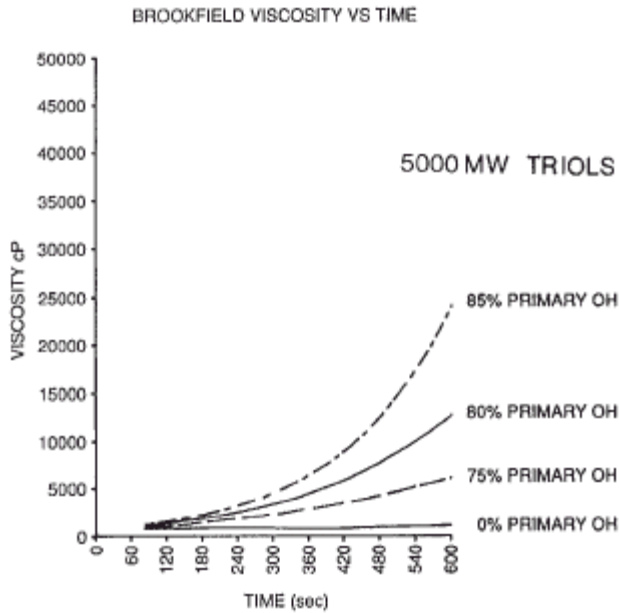


Fig 1.3.2.1: Variation of polyol reactivity with increasing primary hydroxyl content

1.3.3 Blowing agents

A blowing agent is defined as a substance that is capable of producing a cellular structure due to the foaming process in a variety of materials that undergo hardening or phase transition process, like in polymers, plastics, and metals [18]. The cellular structure in a matrix reduces density, while increasing relative stiffness of the original polymer and also causing an increase in thermal and acoustic insulation. Blowing agents are also known as 'pneumatogens' and are related to the mechanisms of creating holes in a matrix producing cellular materials. Blowing agents are an important part in the synthesis of polyurethane foam. They can be classified into physical, chemical and mixed physical/chemical blowing agents as follows:

- 1.) Physical blowing agents- These include CFCs (ozone depletants), HCFCs (replaced CFCs, but are still ozone depletants), hydrocarbons (e.g. pentane, isopentane, cyclopentane), liquid CO₂. The foamation process using them is irreversible and endothermic in nature, i.e. requiring heat [19]. However, on cooling the physical blowing agent will condense, i.e. result in a reversible process.
- 2.) Chemical blowing agents- In the synthesis of polyurethane foam, isocyanate and water are most widely used [20]. The advantages of using water as a blowing agent include its cheaper cost

environmental friendly nature. Also, the CO₂ produced from the reaction is nontoxic and can lead to the improvement of many other properties like density and thermal conductivity [21]. Other examples of chemical blowing agents are azo-, hydrazine and other nitrogen-based materials used in thermoplastic and elastomeric foams, and sodium bicarbonate i.e. baking soda used in thermoplastic foams. Additional exothermic heat is also released due to the blowing reaction that forms low molecular weight compounds acting as the blowing gas. However, the reaction involved is irreversible in nature i.e. the low molecular weight compounds once formed will never get back to the original blowing agent(s).

3.) Mixed physical/chemical blowing agents- Such agents are used to produce flexible PU foams with very low densities. In such blowing agents, both chemical and physical blowing agents are used at the same time, to balance each other out in terms of the thermal energy released/absorbed and also to reduce temperature rise [17]. This is necessary as thermal degradation of the developing thermoset or polyurethane material can occur due to the excessive exothermic heat evolved. For example, in the production of very low density flexible PU foams for mattresses, liquid carbon dioxide (which boils to give gaseous form) is used with isocyanate and water (which react to form carbon dioxide) in polyurethane synthesis.

1.3.4 Catalysts

Catalysts used in polyurethane formation can be classified into two broad categories, amine compounds and metal complexes. Most commonly used amine catalysts that have been used are tertiary amines like triethylenediamine (TEDA), 1,4-diazabicyclooctane or DABCO, dimethylcyclohexylamine (DMCHA), and dimethylethanolamine (DMEA).

Tertiary amines are the most commonly used catalysts in flexible polyurethane foam production. Generally considered as blowing catalysts, most amines also help in the gelling reaction. The presence of a free electron pair on the nitrogen atom renders to the catalytic activity of amines [22]. This is illustrated by the figure given below:



Fig. 1.3.4 Structure of tertiary amine

Tertiary amine catalysts are selected based on whether they drive the urethane (polyol+isocyanate, or gel) reaction, the urea (water+isocyanate, or blow) reaction, or the isocyanate trimerization reaction (e.g., using potassium acetate, to form isocyanurate ring structure). Catalysts that contain a hydroxyl group or secondary amine, which react into the polymer matrix, can replace traditional catalysts thereby reducing the amount of amine that can come out of the polymer [23].

Metal complex catalysts used in polyurethane formation are based on mercury, lead, tin, bismuth, and zinc. One such example is of mercury carboxylates that are particularly effective catalysts for polyurethane elastomer and coating applications as they are very highly selective towards the reaction between polyol and isocyanate, but they offer a major disadvantage of being toxic. Bismuth and zinc carboxylates have been used in place of it [22]. Other examples include alkyl tin carboxylates, oxides and mercaptides oxides that are used in almost all types of polyurethane applications.

The main factors influencing the relative catalytic activity of various amines are steric hindrance about the nitrogen atom and the electronic effects of substituent groups. In some foam formulations, various amines of varying compositions are combined in order to balance both the gelling and blowing reactions so that the foaming process can be properly controlled.

In order to satisfy process requirements such as cream times, rise profiles, gel times and even cure of the outer surface skin, various types and concentration of amine catalyst(s) can be chosen. Some amines impart a different residual odor to the foam, thus limiting their use in applications such as in making beds and furniture [21]. However, usage of volatile amines may reduce odor in the final product but this can also help reduce cure due to rapid loss of the content of catalyst. In general, flowing are the characteristics needed for good catalytic activity:

- The catalyst should be a strong nucleophile and should be capable of attacking the carbon in the isocyanate group;
- The catalyst should be capable of forming an active hydrogen amine complex readily
- The catalyst should be soluble in water and be able to form stable hydrogen bonds in it.

1.3.5 Surfactants

Surfactants are an important component that are used to alter the properties of both foam and non-foam polyurethane polymers. Examples include: silicone oils, nonylphenol ethoxylates, and other organic compounds [14]. These play the role of air release and antifoaming agents (e.g. wetting agents) in non-foam applications to abolish surface defects such as pin holes and sink marks, etc. Additionally, surfactants play important functions like mixing raw chemicals uniformly and controlling the size of gas bubbles in the foam. In the case of rigid foams, the surfactant is selected so as to provide strength to the cell walls and protect them from breaking, which in turn results in a low thermal conductivity. For flexible foams, the surfactant works in a completely opposite manner i.e. it is needed to break the cell wall.

1.3.6 Chain extenders and cross linkers

Chain extenders having functionality of 2 and cross linkers having functionality greater than or equal to 3 are defined as compounds that play an important role in the polymer morphology of polyurethane fibers, adhesives, and foams etc. and are characterized by amine terminated and low molecular weight hydroxyl compounds. The phase separation of the hard and soft copolymer segments of the polymer renders these materials elastomeric properties. Since the nonpolar (especially), low melting soft segments are not compatible with the polar, high melting hard segments, the phase separation occurs [13]. The main difference between soft and hard segments is that soft segments are formed from high molecular weight polyols and tend to be mobile in nature whereas hard segments are formed from isocyanate and chain extenders and tend to be stiff and immobile. Elastomeric resiliency is created when the plastic flow nature of the polymer chains is inhibited as the hard segments are covalently bonded to the soft segments. The type of the chain extender used in the polymer synthesis also affects various properties like flexural, heat and chemical resistance. Some of the common chain extenders are:

Table 1.3.6 Commonly used chain extenders

Material	Mol. wt	Density (g/cm³)	m.p. (°C)	b.p. (°C)
Ethylene glycol	62.1	1.110	-13.4	197.4
Diethylene glycol	106.1	1.111	-8.7	245.5

Triethylene glycol	150.2	1.120	-7.2	287.8
Propylene glycol	76.1	1.032	Supercools	187.4
1,3-Propanediol	76.1	1.060	-28	210
1,3-Butanediol	92.1	1.005	—	207.5
Neopentyl glycol	104.2	—	130	206
1,6-Hexanediol	118.2	1.017	43	250
Ethanolamine	61.1	1.018	10.3	170

Table 1.3.6.1 Functionalities of some catalysts, cross linkers and extenders

Material	Functionality	Hydroxyl Number	Equivalent Weight
Chain Extenders			
ethylene glycol	2	1807.9	31.0
Diethylene glycol	2	1057.4	53.0
Triethylene glycol	2	747.0	75.1
Tetraethylene glycol	2	577.7	97.1
Propylene glycol	2	1474.6	38.0
Dipropylene glycol	2	836.3	67.1
Tripropylene glycol	2	583.5	96.1
1,4 butane diol	2	1244	45.1

Cross-Linkers:			
glycerine	3	1827.6	30.7
diethanol amine	3	1601.0	35.0
triethanol amine	3	1128.2	49.7
VORANOL 360	4.5	360.0	155.8
Catalysts:			
DABCO [†] 33-LV	--	560.3	100.1
Isocyanates:			
toluene diisocyanate	2	--	87.1
PAPI 4901	2.3	--	132
PAPI 4027	2.7	--	134

1.4 Polyols from Biobased Materials

Owing to the concern over environment and green and sustainable nature, polyols derived from vegetable oils have garnered a lot of interest. Vegetable oils (also referred to as triglycerides or triacylglycerols) are triesters of various fatty acids and glycerol. The fatty acid side chains consist of carbon numbers (in the range 8 to 24) and carbon-carbon double bond numbers (ranging from 0 to 5). These polyols include oils modified using soybean, cotton seed, palm, rapeseed, canola, peanut, sunflower and castor. These oils offer an excellent option for the current petroleum-based polyols [10]. These natural oil polyols also referred to as NOPs or biopolyols are abstracted using various techniques/methods. The main use of them is in the manufacture of polyurethane.

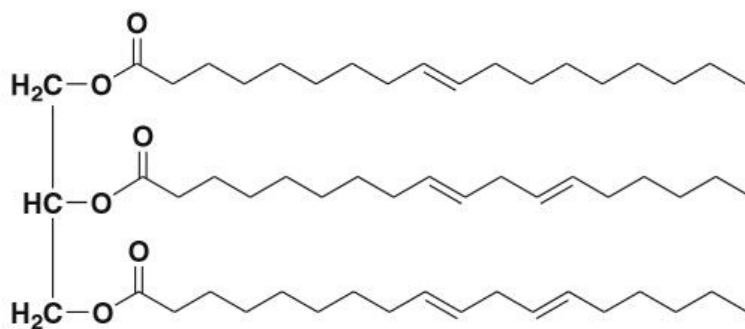


Fig. 1.4: triglyceride structure of vegetable oils

The general properties of these are generally same: they are all clear liquids with the color range from colorless to slight yellow. The viscosity also varies from oil to oil and generally depends on the molecular weight and hydroxyl content i.e. oils with high molecular weight and hydroxyl content are more viscous [11]. Odor is another significant property that varies from one polyol to another. Odor is generally not desirable in the polyols themselves, but essentially in the materials made from them. There are a limited number of naturally occurring vegetable oils (triglycerides) which contain the unreacted hydroxyl groups that account for both the name and important reactivity of these polyols. Apart from castor oil, that is the only natural oil polyol, available commercially, that is produced directly from the plant, all other polyols need some form of chemical modification. Majority of the vegetable oils consist of five major fatty acids: palmitic acid, stearic acid, oleic acid, linoleic acid, and linolenic acid [12]. The general structure of these acids is given below:

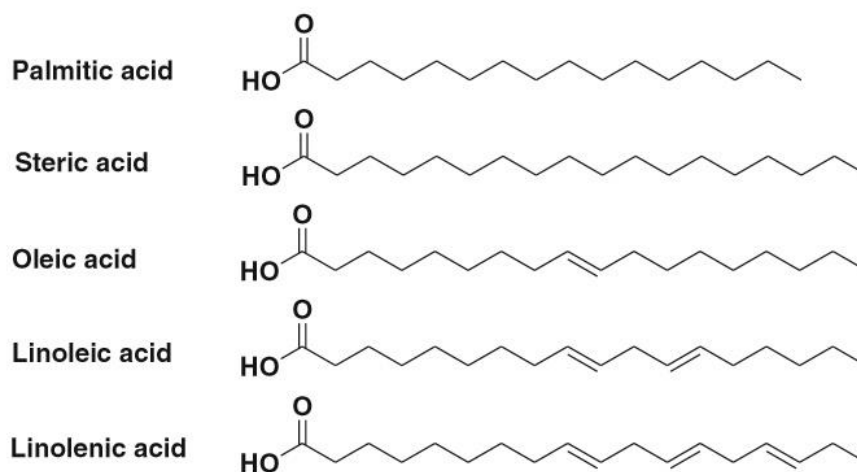


Fig. 1.4.1 Chemical structures of five major fatty acids found in vegetable oils

The three different derivatives of vegetable oils include: Fatty acids, fatty acid esters, and glycerol. Out of them, fatty acids are produced by the hydrolysis of vegetable oil with water and fatty acid esters by the trans-esterification of vegetable oil with alcohol. The below table shows the fatty acid profiles of different vegetable oils:

Vegetable oils	Fatty acid profiles (wt%)				
	C16:0	C18:0	C18:1	C18:2	C18:3
Palm oil	44.0	4.5	39.2	10.1	0.4
Soybean oil	11.3	3.4	23.1	55.8	6.4
Rapeseed oil	4.0	2.0	56.0	26.0	10.0
Sunflowerseed oil	5.9 (3.8)	4.4 (4.1)	19 (78.4)	67.5 (11.3)	2.9 (trace)

Table 1.4 Fatty acid profiles of various vegetable oils

Apart from castor and lesquerella oil, natural vegetable oils do not contain hydroxyl groups. The two major functional parts present in structures of vegetable oils are carbon-carbon double bonds and ester bonding [5]. Nearly all the synthetic routes for the NOP production (like: epoxidation, hydroformylation, ozonolysis, thiol-ene coupling, transesterification, and amidation) begin from either ester linkage or carbon-carbon double bond. Apart from these methods, methods such as dimerization of fatty acids and hydro-silylation of fatty acid esters have also been studied for the synthesis of polyols [7]. In the production of polyurethane for various applications, polyols are produced due to the presence of multiple reactive sites in glycerol that help in esterification and trans-esterification.

1.4.1 METHODS TO PRODUCE POLYOL FROM VEGETABLE OIL

There are five main different methods that are generally used to synthesize polyols from natural vegetable oils. These methods and the characteristics of these polyols are given below:

A.) Epoxidation and Oxirane Ring-Opening

This is one of the most commonly and widely used method for functionalizing double bonds of carbon [24]. Epoxidation of oils can be conducted either in bulk or in solution using either homogeneous or heterogeneous catalysts [25]. It is usually conducted for 10-20 hours at temperatures ranging between 30⁰C and 80⁰C, depending upon the type of reactants involved in the epoxidation reaction. Conversion

yields as high as 90% can be achieved under optimum conditions [25]. Side reactions can be largely reduced by conducting the reaction in a solution and using low temperature conditions. A wide range of compounds containing active hydrogen such as amines, water, alcohol, hydrogen, etc. can be used to produce polyols [26]. A schematic representation of polyols produced by this method is given below:

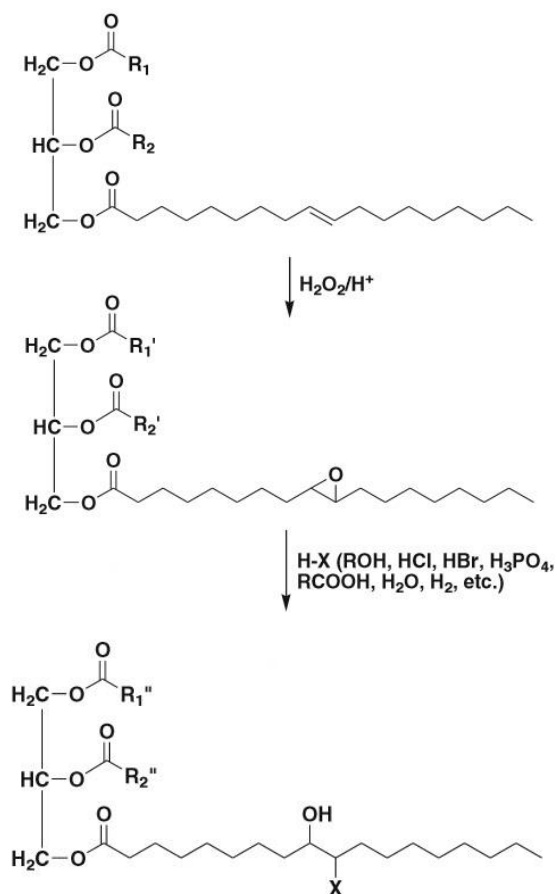


Fig. 1.4.A Synthesis of polyols by transesterification

Generally, two steps are needed to conduct epoxidation and ring opening reactions although a process comprising of a single step consisting of both the reactions has also been reported [27]. Polyols produced by this method have properties depending on various production variables like characteristics of feedstock and types of ring-opening agents used. Polyols with high -OH functional groups are produced from vegetable oils having a high degree of unsaturation, thus leading to the production of polyurethanes with high tensile strength and high cross-linking density [28]. Oxirane ring-opening agents can be classified into three important categories as follows:

I.) Alcohols: When monoalcohols are used as oxirane ring-opening agent, each epoxy group generates only one secondary –OH group, which is far less reactive than primary –OH groups [29]. The most commonly used monoalcohol is methanol because of: low molecular weight and boiling point and low cost [30]. Diols such as ethylene glycol and 1,2-propanediol are used as oxirane ring-opening agents in order to produce polyols having high functionalities and primary –OH groups [31]. However, the increase in hydroxyl numbers leads to polyols being more viscous in nature.

II.) Acids: Acids such as acetic acid and formic acid are used as ring-opening agents in the production of polyol and have proved to have applications such as anti-wear [32]. Other examples of acids used as oxirane ring-opening agents include inorganic acids like HCl, H₃PO₄ and HBr. However, while using inorganic acids, polar organic solvents such as acetone are generally added to avoid incompatibility between the epoxidized vegetable oils and inorganic acids and are thus added during the reaction to facilitate compatibility. Another major drawback of using such acids is that the polyols produced by them wax at room temperature [33] or contain a high amount of oligomers due to the oligomerization reactions that occur between the oxirane groups [34].

III.) Hydrogen: Polyols produced using hydrogen as an oxirane ring-opening agent using Raney Nickel catalyst grease at room temperature and this limits their use in the production of polyurethane [35]. Polyols derived from natural oils like rapeseed and soybean oil have been used to prepare rigid and flexible polyurethane foams. In comparison to petroleum-based polyols (that contain primary –OH groups mostly), such polyols have low reactivity and on reaction with isocyanates, need longer curing time, in the production of polyurethane foam. Epoxidized polyols modified by various methods like mixing with polyols derived from petroleum sources or addition of cross-linking agent or modification by alcoholysis have been used to produce rigid polyurethane foams. [36] Due to glycerol's high –OH number (1829 mgKOH/g) and a highly compact backbone, it is used as an excellent cross-linking agent and is thus helpful in increasing the rigidity of polyurethane foams derived from epoxidized polyols [37]. Rigid polyurethane foams produced by 10-25 wt% of soy polyol and glycerol addition showed satisfactory mechanical and thermal properties that were comparable to the foams produced from commercially available polyether polyols.

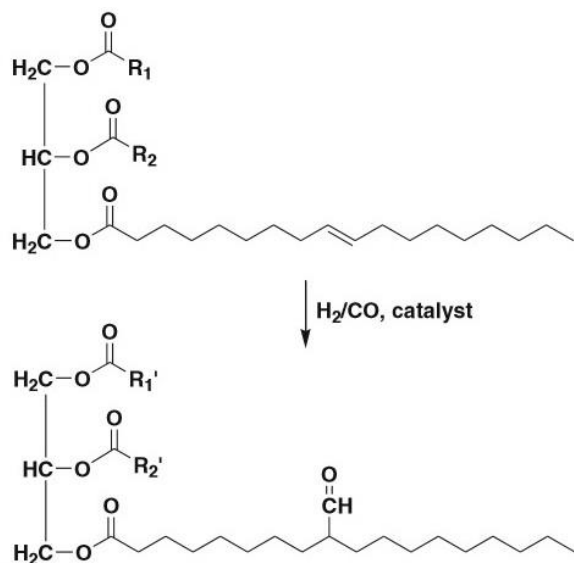
Epoxidized polyols have been partially used in place of commercial polyols derived from petroleum resources and have shown great potential in producing polyurethane foams with high rigidity [38].

However, such polyols suffer from one major drawback i.e. the ageing rate is high (high N₂ permeation causing an increase in thermal conductivity with time and this effect may be enhanced on the addition of a cross-linking agent such as glycerol). Blending method has been used to synthesize flexible polyurethane foams using epoxidized polyols. This method involving blending polyols derived from petroleum with epoxidized polyols (up to 50 wt%), [39] thereby causing an increase in mechanical properties like compressive strength and modulus. Many factors such as high glass transition phase in vegetable oils, high concentration of hard segments contribute to this phenomenon [40].

Methoxylated soybean oil polyols have been used to develop waterborne polyurethane (anionic, cationic and hybrid) dispersions [41]. The foams developed showed high transition temperature, tensile strength and cross-linking density with an increase in the polyol functionality and/or hard segment. A functionality range between 2.4 to 4 resulted in polyurethane films ranging from elastomers to rigid plastics to ductile plastics [42]. Emulsion polymerization has been used to develop urethane-acrylic and urethane-styrene-acrylic hybrid latexes based on soybean oil. These films offered the advantage of better thermal stability, tensile strength, as compared to other polyurethane films [43].

B.) Hydroformylation and Hydrogenation

This is yet another method for preparing polyols based on vegetable oils. In this method, double bonds in the vegetable oils undergo changes twice: they are first converted to aldehydes due to hydroformylation by syngas and then to –OH groups due to hydrogenation of aldehyde [44]. Most commonly used catalysts for hydroformylation are Rhodium and Cobalt-based.



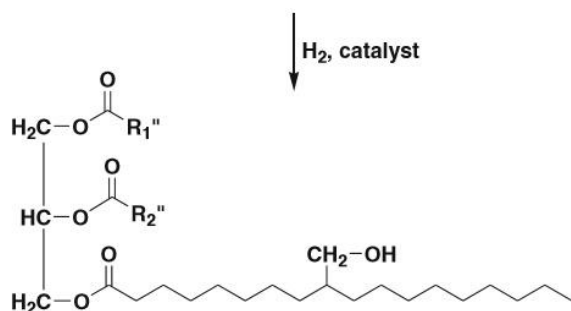


Fig. 1.4.B Synthesis of polyols by hydroformylation

The disadvantage of using rhodium catalysts is that besides being expensive, such catalysts when used as hydroformylation catalysts require the use of raney nickel catalyst additionally in the hydrogenation process [45]. On the other hand, cobalt based catalysts are less expensive compared to them but need harsh reaction conditions. Reports based on the use of both the catalysts show that polyols obtained using the former have higher hydroxyl numbers [46]. Consequently, polyurethanes produced from such polyols were rigid plastic-like in nature while those derived from cobalt-based catalysts were hard rubber-like in nature [45].

The main difference between this method and epoxidation and ring opening method is that the hydroformylation- hydrogenation technique leads to the formation of primary –OH groups whereas the latter leads to secondary –OH groups [47]. Thus, polyols produced by this method are more reactive in nature and only a small amount of catalyst is required for the reaction between polyol and isocyanates. Also, such polyols exhibited shorter gel time and better curing efficiency. When a crosslinking agent such as glycerol is added to such polyols, polyurethane foam with significant rigidity can be obtained [38].

C.) Ozonolysis

Ozonolysis is defined as a reaction where ozone is used to break the unsaturated bonds of alkenes, alkynes, or azo compounds. The production of polyol from vegetable oils using this technique involves two steps [49]:

1. Formation of ozonide at the unsaturation sites of vegetable oils and simultaneous decomposition of ozonide into aldehyde and carboxylic acid; and
2. Reduction of aldehyde into alcohols with a catalyst, such as Raney nickel.

Since all the double bonds are broken during ozonolysis, polyols having functionality of maximum three are obtained as one primary -OH group is introduced at each unsaturated fatty acid chain. Polyols derived using this method may contain a mixture of mono-, di-, and tri-ols and saturated triglycerides, depending on the composition of fatty acids of vegetable oils. During ozonolysis of oil, small molecules of alcohol like hexanol, 1,3-propanediol, etc. [50] may also be generated by the cleavage of double bonds during this method, which on separation and purification may be of significant value and serve as intermediates in chemical industries. However, for manufacturing polyurethane foams, such molecules are generally removed as they have adverse effects on polyurethane properties [50]. Polyols derived from this technique are characterized by primary -OH groups at terminal ends. Consequently, such polyols have faster curing rates with isocyanates.

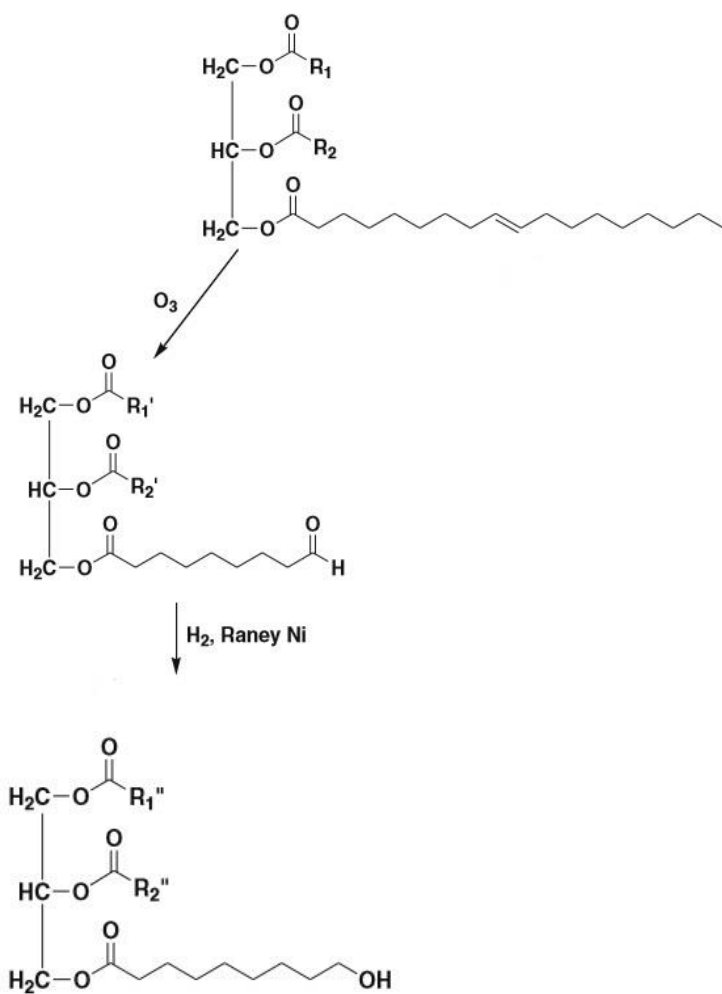


Fig. 1.4.C Synthesis of polyols by ozonolysis

Polyols based on natural vegetable oils have been produced by reactions consisting of only single step without hydrogenation. Generally, alcohols containing multiple –OH groups such as glycerol and ethylene glycol are mixed with a vegetable oil in the presence of a catalyst such as sulfuric acid or sodium hydroxide [51]. On reaction with ozone during ozonolysis, ester linkage is produced due to the reaction of alcohol with ozonide and polyols with –OH groups at terminal ends are produced. Because of its simplicity and low cost, this method is more advantageous in synthesizing polyols with a wide range of properties [52].

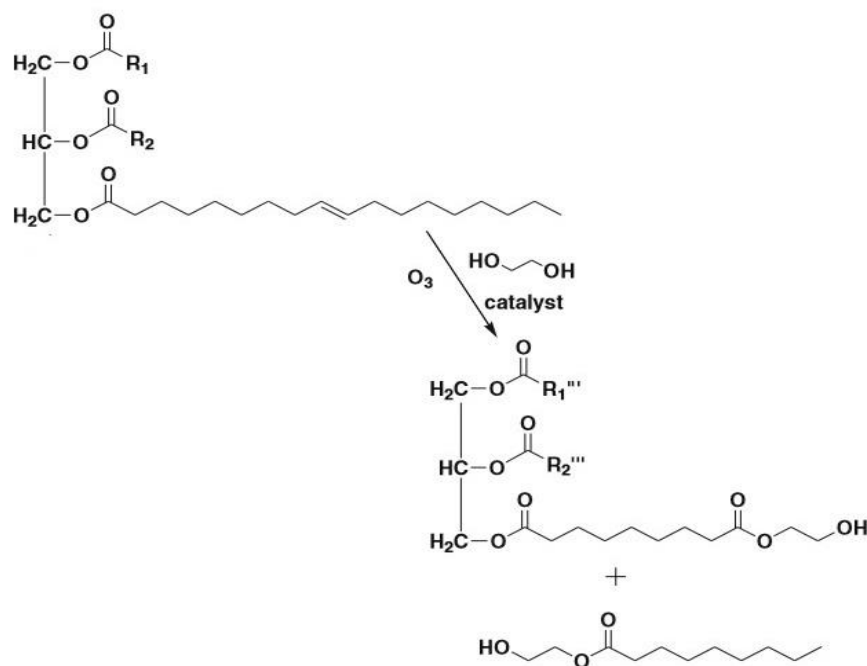


Fig 1.4.C.1: Production of polyester polyols by ozonolysis with the addition of ethylene glycol.

Polyurethane coatings containing zero or very low volatile organic content prepared by this method using soya oil based polyols were characterized by superior mechanical properties like hardness, gloss and good chemical resistance. Such coatings can be applicable to various applications like industrial and automotive [53]. Rigid polyurethane foams prepared using glycerol and soybean oil polyol also exhibited good mechanical and thermal properties, very similar to those obtained using a commercial polyol. The use of glycerol serves two purposes: it increases the –OH number in polyols and also acts as a cross linking agent at the same time, thereby increasing mechanical properties like strength of the foams. Also, complete bio-based polyurethanes based on canola oil and oleic acid-based isocyanates have been prepared [54]. Such polyurethanes are characterized by properties like higher elongation and lower Young's modulus.

D.) Thiol-ene Coupling Method

This process involves reactions of a free radical chain mechanism whereby thiols are grafted onto double bonds. Thiols are unsensitive to oxygen and thus this reaction can be done through a photoreaction in the absence of photoinitiators [55]. A thiol-ene coupling reaction initiated by UV radiation using 2-mercaptoethanol as thiol monomer is generally used for synthesizing polyols from vegetable oils due to two important factors: high conversion yield and fast reaction rate [56].

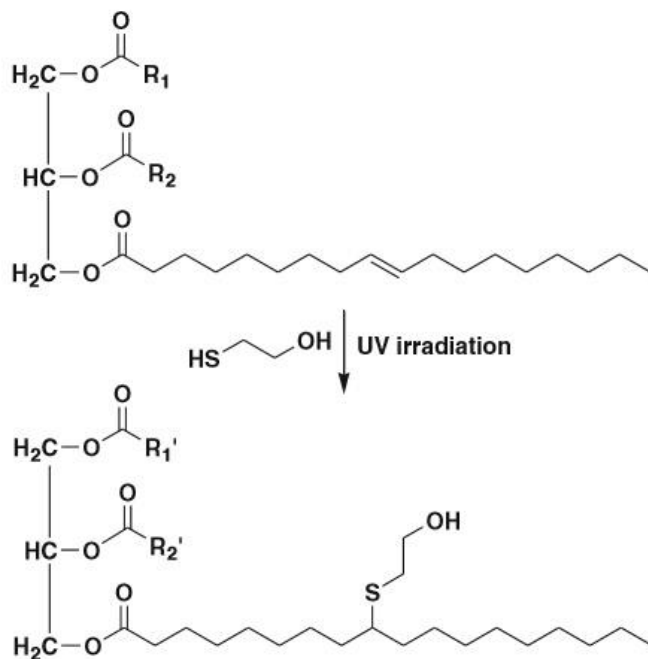


Fig 1.4.D: Production of vegetable oil-based polyols via UV-initiated thiol-ene coupling pathway using 2-mercaptoethanol as a thiol monomer

Where;

R₁ and R₂ signify fatty acid side chains of vegetable oil;

R₁' and R₂' signify modified fatty acid side chains of vegetable oil

For example: Polyols derived from rapeseed oil using this method with 2-mercaptoethanol gave an acid number of 2.5 mg KOH/g, -OH number of 223 mg KOH/g, and an average functionality of 3.6 while polyols based on soybean oil yielded an acid number of 2.5 mg KOH/g and a -OH number of 200 mg KOH/g [57]. It is seen that polyurethane produced from these two polyols had thermal and mechanical properties similar to that of a polyol available commercially. Heat-initiated thiol-ene coupling reactions are also used, like in the case of soybean oil-based polyols but the reaction time is longer as compared to

UV-initiated thiol-ene coupling. A thiol-ene coupling process of vegetable oils is characterized by many side reactions that occur including formation of disulfides, isomerization of double bond, etc. Even in these side reactions, the byproducts contain –OH functional groups and can also take part in polyurethane formation [57]. Polyols obtained by this method contain –OH groups located in the middle of fatty acid chains, just like polyols obtained from the method one and two mentioned above.

E.) Transesterification and Amidation Process

The methods discussed above for producing vegetable oil-based polyols take place at the part containing double bond. However, in the case of transesterification and amidation, reaction for producing polyols occurs at the ester part in the vegetable oil. Transesterification reaction makes use of alcohol with glycerol being the most widely used alcohol. Other examples include: triethanolamine [58] and pentaerythritol [59]. The below reaction depicts transesterification reaction with glycerol:

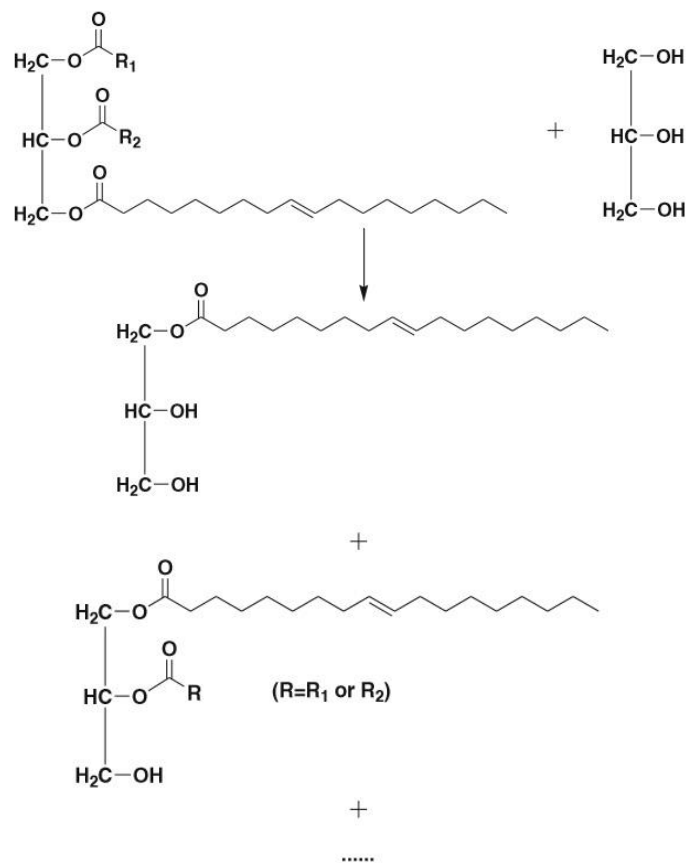
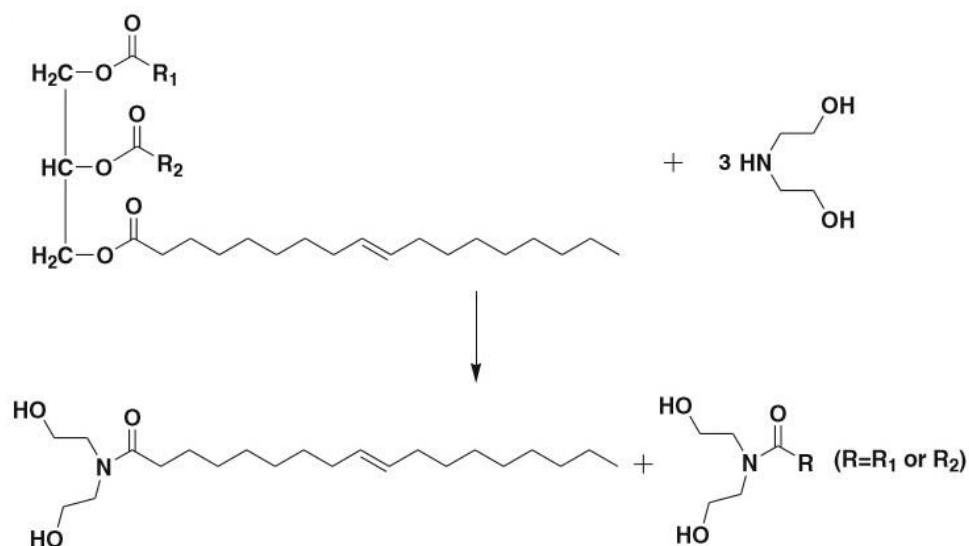


Fig. 1.4.E Synthesis of polyols by transesterification reaction

To improve the compatibility between glycerol and triglycerides, a small amount of soap is added during the transesterification reaction which acts as an emulsifier and also increases the production efficiency of monoglycerides [60]. Organic and inorganic bases such as sodium hydroxide, calcium hydroxide and metal oxides such as lead oxide and calcium oxide are mostly used as catalysts in transesterification reaction. Transesterification using glycerol gives a mixture of mono-, di-, and tri-glycerides and residual glycerol for polyols produced from vegetable oils [61]. Among this mixture, monoglycerides (containing two –OH groups per molecule) play a very important role in the synthesis of polyurethane. Petroleum based polyols can be partially or fully replaced by the polyols produced by transesterification method for the production of polyurethane coatings and foams and are proving to be an excellent alternative.

Similar to the transesterification process, PU foams can be produced by using diethanolamine to convert vegetable oils into diethanol fatty acids by a process called amidation with amines [62]. This process is carried out at a lower temperature (110⁰C) in contrast to the transesterification reaction that is done in the presence of glycerol at much higher temperatures (230-250⁰C). Commonly used oils such as soybean, rapeseed, coconut, sunflower, linseed and cottonseed have been used to derive polyols using this technique and have successfully been used in the production of polyurethane foam with comparable physical and mechanical properties such as hardness, adhesion and chemical resistance [63]. The reaction below shows the amidation reaction with diethanolamine:



1.4.E.1 Synthesis of polyols by amidation reaction

1.5 OBJECTIVE OF RESEARCH WORK

The present study emphasizes on the use of castor oil based polyurethane foam keeping in mind the non-renewable nature of polyols derived from petroleum based resources. Some of the major drawbacks that petrochemical based polyols include high technology processing system (thus using high amount of energy), expensive nature of petroleum resources, non-biodegradable nature on disposable (thus leading to degradation of environment) and an increased public desire of environment friendly green products.

The previous studies had shown that the mechanical properties of the rigid polyurethane foam increase with the addition of effective fillers. The final properties of the foam more or less depend on the type of the filler employed. Due to their unique physiochemical properties and potential in a wide range of applications such as catalysis, controlled drug release and magnetic resonance imaging, magnetic fillers (especially nanoparticles) have garnered a great interest in recent years. Additionally, the use of such nanoparticles helps in enhancing the thermal and mechanical properties of the foam which helps in synthesis of magnetic polyurethane foam that can be used extensively in the fields of magnetic and electromagnetic wave absorption.

Castor oil has been chosen as it offers advantages such as volume and price stability apart from having high hydroxyl functional groups naturally. The objectives of this work are summarized as:

1. Modification of castor oil to synthesize polyol.
2. Characterization of castor oil based polyol
3. Synthesis and characterization of iron nanoparticles.
4. Synthesis of castor oil based polyurethane foam containing different concentrations of iron filler.
5. Characterization of iron dust and iron nanoparticles filled castor oil polyurethane foam.

CHAPTER 2
LITERATURE REVIEW

2.1 Introduction of castor oil

Castor oil is a vegetable oil that is derived by refining or pressing castor oil plant's seeds. This plant is most widely found in tropical regions like Africa, South America and South Asia. An important source of castor oil is ricinoleic acid, which is a monounsaturated fatty acid consisting of 18 carbon atoms. This acid is quite different from other fatty acids as the 12th carbon atom [64] contains a –OH functional group. The presence of this functional group causes the acid and thus castor oil to be more polar. Also, the presence of an alcohol group in it allows for chemical derivatization, which is unlikely for other seed oils [65]. The existence of ricinoleic acid content makes castor oil a valuable chemical in industries and is thus priced at higher rates than other seed oils.

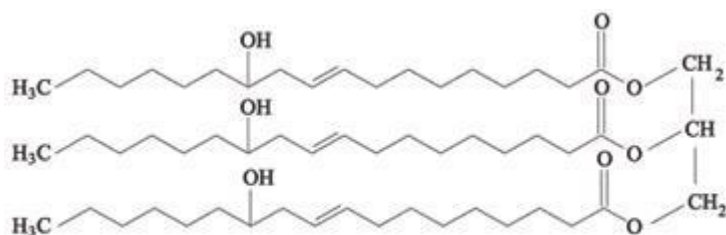


Fig. 2.1 Triglycerides of ricinoleic acid

Castor oil appears to be a colorless to pale yellow liquid with a unique smell. It has a boiling point of 313⁰C and density of 961 kg/m³. The majority of fatty acid chains (approximately 90%) are ricinoleate. Oleate and linoleates make up for the remaining 10%. It grows mostly in tropical and sub-tropical countries in large quantities. It is cheap in cost and the plant can tolerate variable weather conditions quite appreciably [66]. However, due to its toxic nature, it is not used for ornamental purposes. Since the seed is poisonous, it is also not suitable for animal feed stock. Owing to the toxicity of the seed, the farmers in US do not grow the plant extensively. Extraction of castor oil is done by the process of mechanical pressing or solvent extraction or a combination of both. In the first method, seeds are crushed and warmed in a steam-jacketed vessel to get low moisture content. After this, they are crushed and sent to hydraulic presses where they are pressed by mechanical means to obtain oil. The oil thus extracted has a light color and low content of FFA (free fatty acids) [67]. However, mechanical pressing removes only approximately 45% of the oil present in the seeds and the remaining oil in the cake can be recovered by the process of solvent extraction. In the solvent extraction method, the crushed seeds are extracted in a Soxhlet extractor or commercial extractor using solvents such as hexane, heptane and petroleum ethers.

Refining: Just like other vegetable oils, refining is a crucial step to refine the oil obtained by mechanical pressing or solvent extraction. The main purpose of refining is for the removal of impurities such as colloidal matter, free fatty acid, coloring matter and other undesirable components, hence rendering the oil more resistant to degradation during storage [68]. Refining includes: (1) removal of solid and colloidal matter by techniques like settling and filtration, (2) neutralization of the free fatty acid by some alkali, (3) removal of colored matter by bleaching method, and (4) deodorization of solution by treating with steam at high temperature and low pressure. The general method used for refining edible oils is also applicable to castor oil.

Structural analysis of castor oil shows that it has an average –OH functionality of 2.7 due to the presence of triols (70%) and diols (30%) and absence of monoalcohols. Polyurethanes based on castor oil with semi-rigid and semi-flexible properties have been developed due to its low functionality and low reactivity because of the presence of secondary –OH groups in the fatty acid chains [69]. In order to improve the properties and hence the applications of polyurethanes produced from castor oil for wider use, two major methods have been developed. The first method involves the transesterification-amidation reaction making use of the ester linkages while the other method, alkoxylation, uses the –OH groups. Transesterification reaction using alcohols such as glycerol, pentaerythritol and amidation reaction using diethanolamine help in increasing the functionality and –OH number of polyols based on castor oil [70]. This helps in obtaining polyurethanes with better rigidity. Studies report that using the aforementioned methods have led to hydroxyl numbers ranging from 291 to 512 mg KOH/g. As a result, polyurethane coatings derived from them showed an increase in tensile strengths from 14.1 MPa to 19.8-57.4 MPa.

Alkoxylation is defined as a polymerization process used to produce polyols by the incorporation of the epoxide monomers such as ethylene oxide and propylene oxide into an alcohol. Using ethylene oxide for ethoxylation or propylene oxide for propoxylation, polyols based on castor oil with higher molecular weights and low –OH numbers can be obtained [71]. The figure below shows the production of castor oil based polyol via ethoxylation reaction.

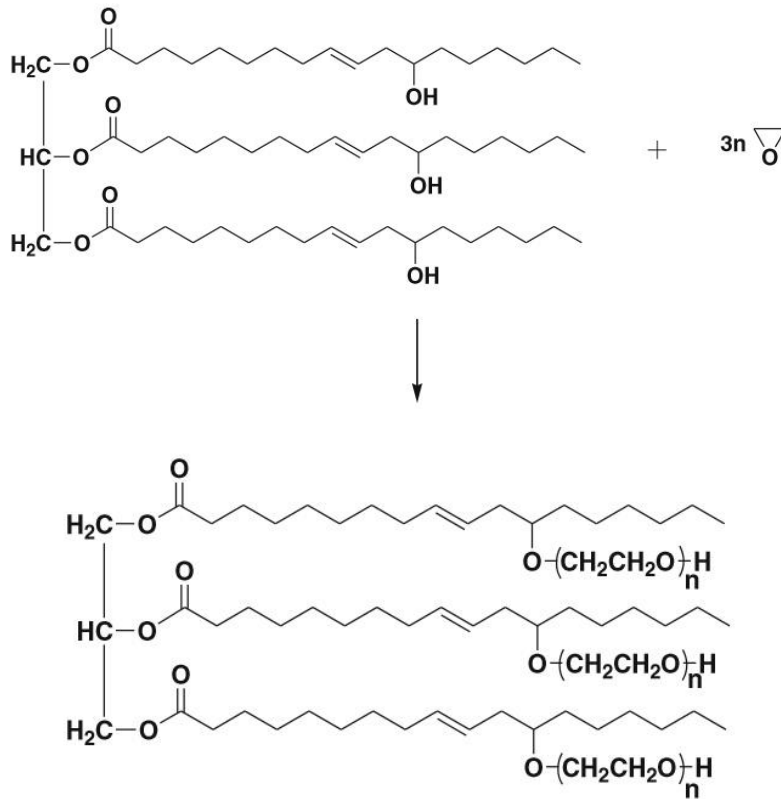


Fig. 2.1.1 Production of castor oil based polyol via ethoxylation reaction.

Apart from these two methods, modification by mixing petroleum-based polyol with castor oil based polyol and reacting with isocyanates results in fast reaction rates and helps in improving the properties of polyurethane. Addition of triisopropanolamine has shown to increase the compressive strength of the rigid foams derived from castor oil [72]. Varying polyurethane formulations such as polyol and chain extender content has shown to increase physical and mechanical properties of polyurethane elastomers based on castor oil and polypropylene glycol. Such elastomers showed an improvement in tensile strength, resilience, slightly reduced abrasion resistance as compared to polyols derived from petroleum sources. It is also observed that with an increase in the cross-linking density, polyurethane coatings with improved tensile strength and insulating properties are obtained [73].

However, castor oil offers its own pros and cons while using it the production of polyurethane. The benefits of using it include resistance to water and good flexibility whereas low reactivity and low functionality due to the presence of secondary $-\text{OH}$ groups are the major drawbacks [74]. These

disadvantages, however, can be avoided by reacting polyols like glycerol with castor oil, thus yielding higher –OH number [75].

2.2 Castor Seed Yield

Castor plant has a tendency to grow in arid and semi-arid areas. It is a kharif crop in India with the sowing occurring in the months of July-August and harvesting from December to March. Castor oil plant sustains itself in a wide range of soils and requires a heavy rainfall of 500-600 mm throughout its cultivation [76]. The major Indian states involved in its production are Gujarat, Andhra Pradesh and Rajasthan, out of which Gujarat contributes the maximum of 86% production.

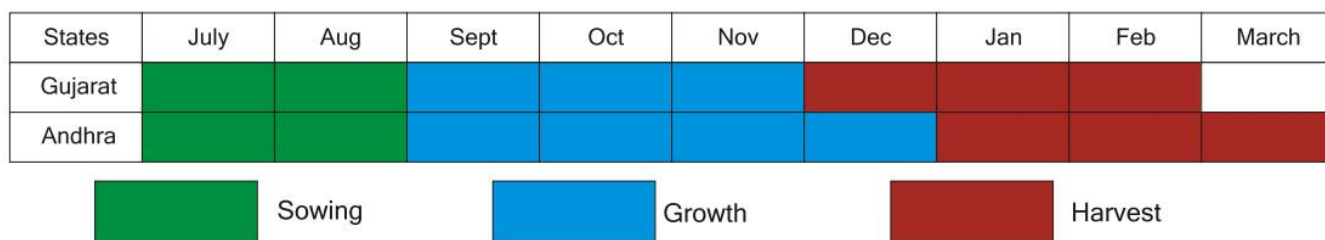


Fig. 2.2 Growth of Castor seed in different months

The production of castor seed in India is around 9-10 metric tons. Castor oil and derivatives of it have been used in a wide range of applications from manufacture of soaps, lubricants, perfumes, eaxes, dyes, inks, polishes, paints, lubricants to pharmaceuticals. India is the largest exporter of castor oil in the international market contributing about 70% followed by China and Brazil.

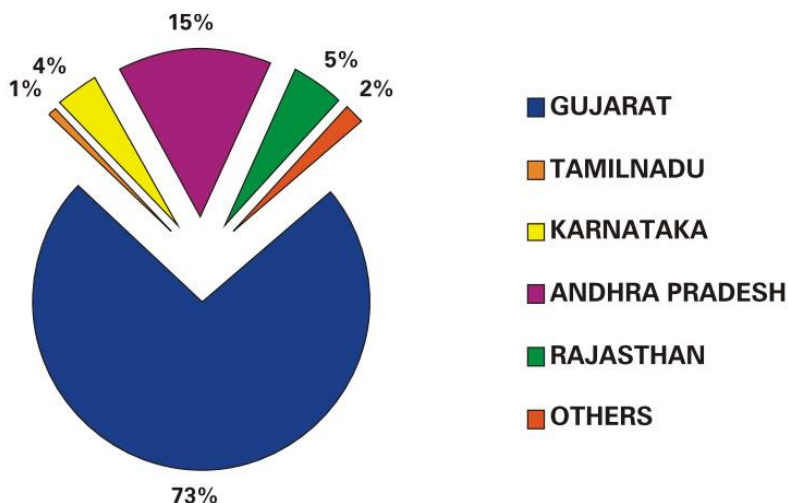


Fig. 2.2.1 Castor Seed Yield in India

2.3 Uses of castor oil

Castor oil derived polyol is the only polyol that is naturally occurring i.e. it does not require any modification. Other natural vegetable oils need modifications to incorporate isocyanate-reactive groups, thereby leading to an increase in viscosity and hence rendering them less useful in turning them into polymer polyols [77]. One such example is that when styrene and acrylonitrile are copolymerized with castor oil using a chain transfer agent and an unsaturated macromere polyol. The macromere polyol usually preferred is an EO/PO polyol (with a molecular weight of about 6000) which is then reacted with an unsaturated aliphatic isocyanate. This polyol helps in stabilizing styrene-acrylonitrile particles, thereby allowing a high amount of solid content. Polymer polyols are importantly helpful in producing flexible foams.

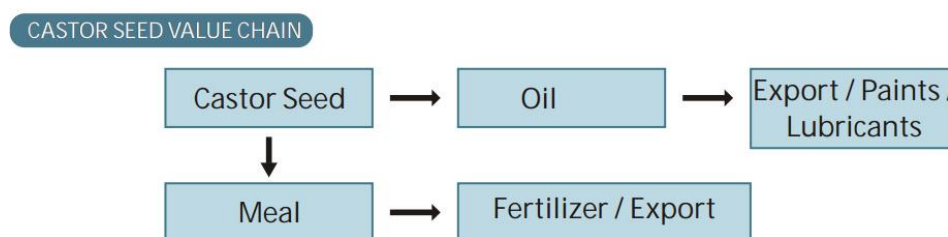


Fig. 2.3 Castor Seed Value Chain

2.3.1 Castor Oil in Food Industry

Castor oil seed contains toxic ricin protein, however, methods are available to detoxify its seed and make it useful for food purposes. Since half-life of this protein at 80°C is 9 minutes, heating or steaming is a very effective method to detoxify it [78]. An important application of castor oil used in food industry is its usage as food additive and flavoring agent. In South Asia, in order to prevent rotting of grains such as wheat, rice, etc. castor oil is usually coated on them.

2.3.2 Castor oil in Medicine

Castor oil is widely used in India and all over the world to help treat various medical ailments namely: bowel disorder, asthma, gastrointestinal infections, etc. It is also used as an analgesic and acts as an antimicrobial agent. Topical application of castor oil has proved to be useful for skin diseases like acne, ringworms, warts, keratosis, dermatosis, wound healing, etc. [79]. The presence of ricinoleic acid in it helps in enhanced absorption of agents in the skin.

For increasing immunity: Castor oils helps increase white blood cells and thus strengthens the immune system and helps in fighting infections. It increases the count of T-11 cells, a type of white blood cells and production of lymphocytes. Lymphocytes are disease-fighting cells and are mainly stored in the lymphatic tissue¹⁷. This helps the body to kill infections like viral, fungi, bacterial, etc. by producing more antibodies.

Treating constipation: When taken orally, castor oil acts as a laxative as ricinoleic acid is released in the intestine. Ingestion of castor oil creates heat that helps in the process of digestion and cleanses the digestive system, thereby improving bowel movement.

Treating joint pains: One of the most widely used application of castor oil is for treating arthritis due to the anti-inflammatory properties that makes it suitable for relieving nerve inflammation and joint pains. Continuous use of it has shown to give better results.

2.3.3 Castor Oil as Biodiesel

The process involving the conversion of natural vegetable oil into biodiesel is known as transesterification. If the oil contains a high amount of free fatty acid (>1%) and soap is formed on reaction with an alkaline catalyst, the conversion is said to be completed.

Esterification: Transesterification reaction in the presence of base catalysts is the most common method for converting most of the oils into biodiesel esters. However, this process cannot be used for certain oils such as olive, cotton seed and jatropha oil because the free fatty acid content in them is high. In order to determine if the oil can be transesterified or not, the acid value of the oil should be known [80]. For the production of biodiesel, the oil first goes through esterification reaction and then transesterification reaction. During the esterification reaction, reaction of the free acid content occurs. Trans-esterification reaction occurs for the remaining acid. This method is thus helpful for oils containing free fatty acid.

Transesterification: Also referred to as alcoholysis, this method uses an alcohol to displace another alcohol from an ester moiety. Some of the commonly used alcohols include: ethanol, methanol, butanol, propanol and amyl alcohol. Out of them, ethanol and methanol are used more often than the others. This method is mainly used for reducing the viscosity of triglycerides, which helps in improving the physical

and chemical properties of biofuel and thereby enhances the performance of engine [81]. Therefore, trans-esterification technique is used to produce biodiesel (i.e fatty acid methyl ester).

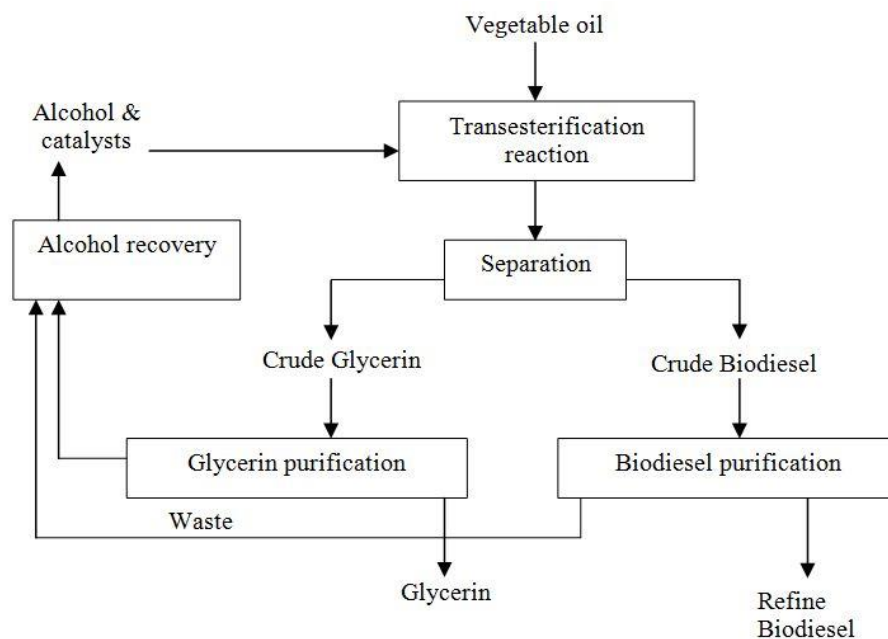


Fig. 2.3.3 Conversion of vegetable oil to biodiesel

2.3.4. Castor oil in cosmetic industry

Castor oil is the most important component in cosmetics as it is non-comedogenic in nature. It acts as a great bubble booster during the manufacture of soaps. It also acts as a humectant in shampoos, gels, hair wax due to the unique $-OH$ group on the ricinoleic acid [77]. Turkey red oil is one of the most important products of castor oil. It is prepared using castor oil and concentrated sulfuric acid and is thus a sulfated castor oil. Sodium hydroxide solution is used to neutralize the product. Turkey red oil is widely used in coloring hair as it acts as a good moistening agent and is helpful to pigments and dyes.

2.3.5 Lubrication using castor oil

Apart from having a high lubrication temperature, castor oil also offers a superior cold flow temperature. The viscosity of castor oil at $10^{\circ}C$ is 2420 Centipoise. Castor oil is increasingly used as a lucrative alternative in car engines. Another advantage that castor oil offers other oils is that it does not dissolve natural rubbers. Hence, it is considered as a superior lubricant for bicycles.

2.3.6 Castor oil in inks, paints, and adhesives

Castor oil has a unique pigment-wetting property due to the fact that it is a fatty alcohol and is a vital component in inks and printing. For application in paint and adhesive industry, viscosity is adjusted by using castor oil and ricinoleate. In the case of non-polar solvents, thixotropic structure is formed when long carbon chains present in castor oil wind each other. This results in an increase in viscosity and this helps prevent the precipitation of dyes [82]. On application of shear force, the viscosity is reduced as thixotropic structures unwound each other and this helps in the uniform dispersion of dyes.

Castor oil is also a non-drying liquid although dehydrated form of castor oil has found applications in semi-dried or dried paint and adhesive industry. Dehydrated castor oil consisting of conjugated double bond is obtained when the $-OH$ group on the ricinoleic acid is removed. This is how drying oil is obtained from dehydrated castor oil.

2.4 Interpenetrating polymer network based on castor-oil polyurethane

The first interpenetrating polymer produced from polyurethane derived from castor oil was first developed by Yenwo [83]. Tougher elastomers and plastics were further developed by Devia. Such elastomers could be extended to up to 125%. Gradually, polyurethanes derived from castor oil were found to have an improvement in tensile strength and cross-linking density and this was observed by Kumar V. Apart from this, polymers such as polymethacrylate, acrylonitrile and polyethyl-methacrylate have also been used to produce interpenetrating polymer network.

2.5. Use of castor oil in development of polyurethane nanoparticles

Polyurethane nanoparticles have garnered a lot of attention and interest in recent years due to their excellent mechanical properties, high stability and biocompatibility. Therefore, these nanoparticles find application in drug coating and drug delivery [75]. One such material that is used to produce polyurethane nanoparticles is cremophor i.e. hydrogenated form of castor oil and is most commonly used in the field of medicine. Some of the earlier works and research suggest that risk of severe hypersensitivity reactions can be reduced and biocompatibility of drugs can be enhanced by the use of polyurethane network. Castor-oil based polyurethanes are also used in tissue engineering without having any strong inflammatory reaction.

CHAPTER 3

EXPERIMENTATION

AND

CHARACTERIZATION

3.1. Castor Oil based Rigid Polyurethane Foam

Castor oil is one of the most widely used and studied polyol for the production of polyurethane as it is a natural vegetable oil that contains natural –OH groups and does not need any chemical modification. Various studies conducted have shown that foams made from castor oil have the highest compressive strength as compared to foams made with other oils such as canola or soybean or sunflower oil [84]. Castor oil is a triglyceride containing fatty acids out of which ricinoleic acids make up for 90% of them, which has a hydroxyl group on the 12th carbon atom. Hence, castor oil is an excellent option for developing polyurethane foams. Castor oil, due to the presence of active –OH group, can easily react with isocyanate and evolve carbon dioxide gas in the reaction.

The purpose of this project report was to characterize the polyurethane foam incorporated with iron dust filler using sophisticated techniques such as SEM, FTIR, XRD, TGA, etc. and investigate the effect of metallic filler on the mechanical properties i.e. flexural and compressive strength on the foam.

3.2 Materials Used

Raw materials used in the synthesis of polyurethane foams are divided into two groups: A-side (isocyanate) and B-side (polyol). In the present study, MDI was used as the isocyanate i.e. the A-side component. Castor oil was the vegetable oil that was obtained from Thomas Baker (Chemicals) Pvt. Ltd., Mumbai and is modified by transesterification reaction to convert into the desired polyol. Glycerol was obtained from Merck Specialities Private Limited, Mumbai. Pentane from Central Drug House, New Delhi, was used as the blowing agent. Silicone Oil was chosen as the surfactant in this study.

3.3 Experimental Setup

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 mantle. 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.

3.3.1 Experimental Procedure:

The reaction kettle was charged with natural vegetable castor oil. Glycerol was added drop-wise to the oil over a span of 10 minutes. Castor oil and glycerol are taken in ratio of 3:1 (%w/w). The reacting contents were heated to a temperature of $220 \pm 100^\circ\text{C}$. The stirring speed is kept constant at 1000 rpm. The progress of condensation reaction and its stability were confirmed by checking its properties. 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 this reaction was nearly 4 hrs. The resulted polyol was stored in dark bottles and kept away from direct sunlight.

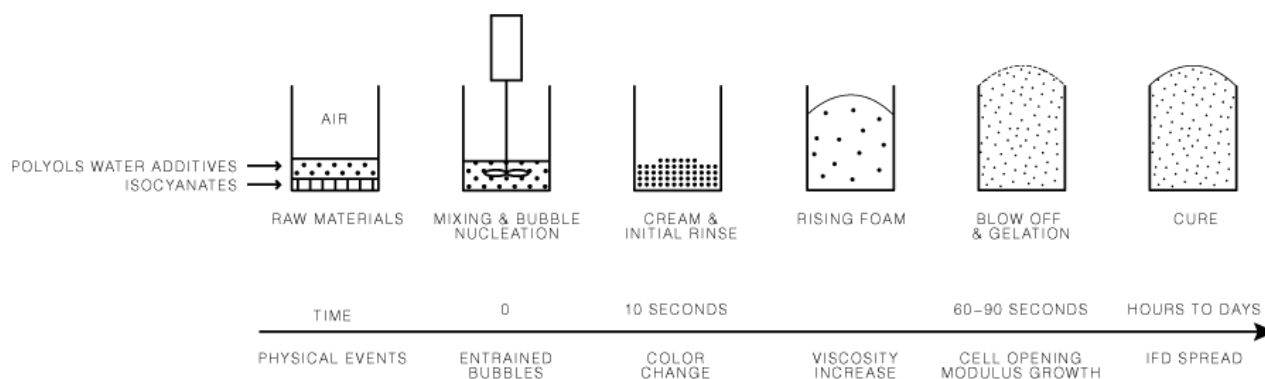


Fig. 3.3.1 Schematic representation of the stages involved in the formation of polyurethane foam

3.3.2 Preparation of Castor Oil Based Rigid Polyurethane Foams with Iron Dust Filler

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 (already carried out). Then in the subsequent step, the formed castor oil based rigid polyurethane foam is incorporated with varying amount of fillers i.e. iron dust. The procedure is as follows:

Calculated amount of modified polyol is mixed with other ingredients as such as catalyst: Stannous Octate, Surfactant: Silicon Oil, Blowing Agent: Pentane, in a beaker and thoroughly mixed under controlled temperature conditions at $35 \pm 20^\circ\text{C}$ to form a polyol-premix. The predetermined quantity of the filler is added to the contents of the beaker. The fillers were dehydrated in a vacuum oven at 600°C for 4 h before addition. The heating and mixing is continued for next 5-10 minutes. A calculated amount of

MDI is then added to the contents of the beaker. The contents of the beaker are then stirred by means of a high speed mechanical stirrer operating at 1000 rpm. Heating the contents can also result into the fastening of the reaction. After the heating and stirring of approximately two minutes, the viscosity of the reaction mixture increases and a cream like formation takes place with a color change from orange-yellow to pale yellow. The resultant reaction mixture was poured into a metal mold, coated with releasing agent i.e. silicon oil. The mold was thus closed and kept under a load of about 10 kN. To ensure complete curing, the molds were left to stand for 24 hours. After demolding, the resulted filled castor oil based rigid polyurethane foam was cut into desired dimensions and tested for its visual color, tensile strength, compression strength, flexural strength and morphology structure. Different concentrations of the filler i.e. iron dust is added to the foam.

Table 3.3.2: Formulations of PU Foams with Iron Dust as Filler

Sample→ Ingredient ↓	Foam 1	Foam 2	Foam 3	Foam 4	Foam 5	Foam 6	Foam 7	Foam 8
Polyol	25ml	25ml	25ml	25ml	25ml	25ml	25ml	25ml
MDI	28ml	28ml	28ml	28ml	28ml	28ml	28ml	28ml
Pentane	15%	15%	15%	15%	15%	15%	15%	15%
Catalyst TEA	3%	3%	3%	3%	3%	3%	3%	3%
Silicone Oil	3%	3%	3%	3%	3%	3%	3%	3%
Filler	-	0.2 gm	0.3 gm	0.4 gm	0.5 gm	1.0 gm	1.5. gm	2.0

3.4 HYDROXYL VALUE CALCULATION

Hydroxyl value is calculated using a solution of pyridine containing acetic anhydride, which is first acetylated, where excess acetylated reagent is hydrolyzed with water and acetic acid thus generated is titrated against potassium hydroxide till the endpoint is reached. The inflexion point on the titration curve determines the endpoint. Titration volume is used to calculate the hydroxyl value of polyether polyol.

Reagents Used:

Titrant: 0.5mol/L Potassium hydroxide Ethanol solution

Reagent: Pure water, Pyridine, Acetic ether, Perchloric acid (78%), Acetic anhydride

PROCEDURE:

A.) Pretreatment

- 1) Add 4.0g (2.35mL) perchloric acid to 400mL acetic ether.
- 2) Add 8mL acetic anhydride, and leave at room temperature for 30 minutes.
- 3) Cool it to 5°C, and add 42mL chilled acetic anhydride. Leave at 5°C for one hour.
- 4) The solution warmed at room temperature is the acetic anhydride solution.
- 5) Add 100mL water to 300mL pyridine to make pyridine + water (3+1)

B.) Measurement

- 1) Sample 3g in a 100mL beaker.
- 2) Add 10.0mL acetic anhydride, and stir for 15 minutes.
- 3) Add 2mL water and 10.0mL pyridine + water (3+1), and stir for 5 minutes.
- 4) Add 10.0mL pyridine.
- 5) Titrate with 0.5mol/L potassium hydroxide ethanol to obtain hydroxyl value.
- 6) Perform blank test likewise.

HYDROXYL VALUE CALCULATION

$$\text{Hydroxyl value (mg/g)} = \frac{(\text{BLI} - \text{EPI}) \times \text{TF} \times \text{Cl} \times \text{K1}}{\text{SIZE}}$$

Where;

EPI : Titration volume (mL)

BLI : Blank level (56.1542ml)

TF : Factor of titrant (1.00)

Cl : Concentration conversion coefficient (28.05mg/mL) (Formula mass of potassium hydroxide:
 $56.11 \times 1/2$)

K1 : Unit conversion coefficient (1)

SIZE : Sample size (gm)

Precautions to be taken:

- 1) If excessive water is contained in the sample, normal acetylation may not be obtained.
- 2) Pyridine and acetic anhydride are harmful and inflammable in nature. Acetic anhydride is highly corrosive. Caution must be taken while handling these chemicals.

3.5 CHARACTERIZATION OF POLYURETHANE FOAM SAMPLES

3.5.1.) Scanning Electron Microscope Analysis

The SEM analysis makes use of a focused beam of high-energy electrons that helps in the generation of a variety of signals at the surface of solid sample. These signals result due to the interaction between sample and electrons and yield information about the sample such as its morphology, crystalline structure, chemical composition, etc. These signals consist of secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light (cathodoluminescence—CL), and heat.

Most commonly used electrons for imaging samples are secondary electrons and backscattered electrons: secondary electrons are extremely helpful to find out the morphology and topography of samples while backscattered electrons are used to illustrate contrasts in composition in multiphase samples. Inelastic collisions between the incident electrons and electrons in atom shells in the sample result in the generation of X-rays. When the excited electrons get back to their lower energy states, X-rays of fixed wavelength are generated. As the generated X-rays caused by the electron interactions do not cause any volume loss of the sample, SEM analysis is said to be ‘non-destructive’ and thus it is possible to repeatedly analyze the same materials. One of the greatest strengths that SEM offers is the ease of operation. Additionally, samples require very minimum preparation. For several applications, data acquisition is quite fast i.e. less than 5 minutes/image during the analysis of SEI, BSE, spot EDS, etc. Most of the modern SEM analysis now generates data in digital format, which is highly portable.

3.5.2.) Fourier transform infrared spectroscopy

Also referred to as FTIR Analysis or FTIR Spectroscopy, it is defined as an analytical technique that uses infrared light to scan test specimens that include organic, polymeric, and in some cases, inorganic materials and studies their chemical properties. FTIR is also used to assess purity of the samples, base

polymer composition, presence of additives, organic contaminants, etc. It is used for both quantitative and qualitative analysis of the samples. FTIR produces an infrared absorption spectrum that helps in the identification of chemical bonds in the sample. FTIR is an effective analytical instrument that is helpful for the detection of functional groups and for characterizing covalent bonding information.

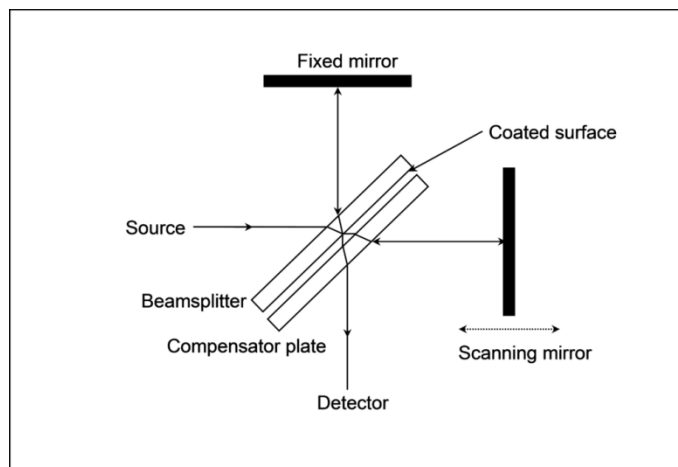


Fig 3.5.2: Simple interferometer with a beam-splitter and compensator plate

3.5.3.) X-Ray Diffraction

It can be defined as a phenomenon in which the atomic planes of a crystal cause an incident beam of X-rays to interfere with one another when they leave the crystal. It is a rapid analytical technique that is used for phase identification of crystalline material and provides information on unit cell dimensions.

XRD is helpful to determine the following:

- Measure the average space between layers of atoms
- Determination of the orientation of a single crystal
- Finding the crystal structure of an unknown material
- Measurement of the size and shape of small crystalline regions

Structural Analysis: X-ray diffraction provides most definitive structural information, Interatomic distances and bond angles

X-rays: To provide information about structures we need to probe atomic distances - for this, a probe wavelength of $1 \times 10^{-10} \text{ m}$ ~Angstroms is required

3.5.4.) Thermogravimetric analysis

TGA measures the amount of weight change of a material, either as a function of increasing temperature, or isothermally as a function of time, in an atmosphere of nitrogen, helium, air, other gas, or in vacuum.

It provides information on the determination of endotherms, exotherms, weight loss on heating, cooling, etc. Materials that can be analyzed by TGA are polymers, plastics, food, composites, coatings, rubber, laminates, ceramics, glasses, adhesives, pharmaceuticals, metals, organic materials, petroleum, chemicals, explosives and biological samples, inorganic samples, etc. TGA analysis makes use of heat to force reactions and induce physical changes in materials. It provides quantitative measurement of mass change in materials due to transitions and thermal degradation. TGA records change in mass from reactions such as dehydration, decomposition, and oxidation of a sample with time and temperature.

TGA is used for a lot of applications, with the common ones being:

1. Characterization of materials by analyzing characteristic decomposition patterns
2. Helps in the study of reaction kinetics and decomposition mechanisms
3. Organic content determination in a sample
4. Determination of inorganic (like ash) content in a sample, which may be helpful for chemical analysis
5. Determination of water content or residual solvent in the sample
6. Analyzing reaction with air, oxygen or other reactive gases
7. Determination of purity of organic or inorganic sample

3.5.5.) Differential scanning calorimetry

DSC is a thermal analytical technique that measures the amount of energy absorbed or released by a sample when it is heated or cooled and thus provides quantitative and qualitative data on endothermic (heat absorption) and exothermic (heat evolution) processes. Both the sample and reference are maintained at almost the same temperature throughout the analysis. It is used in the measurement of melting temperature, latent heat of melting, heat of fusion, glass transition temperature, precipitation temperature, crystalline phase transition temperature, specific heat or heat capacity. DSC can be classified into two types:

1. Power compensated DSC- which keeps the power supply constant
2. Heat flux DSC- which keeps the heat flux constant

The technique is used as both, a routine quality test as well as a research tool, in a wide range of applications. The DSC equipment is relatively easy to calibrate and is a reliable method for thermal analysis. This technique is used in polymers, liquid crystals, drug analysis, safety screening and general chemical analysis.

Example:

1. Use of DSC in polymer industry- DSC is used widely for determining thermal transitions in polymeric materials. The transitions may not identify composition uniquely but the observed thermal transitions can be utilized to compare materials. Complementary techniques such as IR spectroscopy may be used to determine the composition of unknown materials. Thermal degradation of polymers can also be studied using DSC by making use of a method known as Oxidative Onset Temperature/Time (OOT), however, this method poses a major drawback of the user contaminating the DSC cell, which can further leads to problems. Determination of decomposition behavior of samples can also be done with the help of thermogravimetric analysis method. Impurities contained in polymers can also be determined by examining thermograms for anomalous peaks, and plasticisers can be detected at their boiling points.

2. Liquid crystals- DSC is also used in the study of liquid crystals. Like some forms of matter undergo a transition from solid to liquid phase, there are some that go through a third stage i.e. a stage that displays the properties of both the phases. This anisotropic liquid is known as a liquid crystalline or mesomorphous state. Using DSC, small energy changes that occur when there is a transition in matter (from solid to liquid crystal and from liquid crystal to an isotropic liquid) can be observed.

CHAPTER 4
RESULTS AND DISCUSSION

Rigid PU foams are extremely energy-efficient materials and possess superior mechanical properties. One of the most important applications of this foam is in the industry of thermal insulating materials. Rigid polyurethane foams are synthesized from highly functional base materials; as a result they are highly cross-linked in nature and have high strength. Additionally, the choice of fillers added during the production of polyurethane foam further has an impact on its mechanical properties. Among inorganic fillers, it is well-known that incorporation of nanoparticles in polyurethane nanocomposites helps enhance its mechanical, thermal, and magnetic properties [85]. The present work focuses on the use of iron dust particles, a much cheaper source in place of nanoparticles, and study their impact on the chemical and mechanical properties of the synthesized castor oil based polyurethane foam.

4.1. Effect of Filler Content on the appearance of polyurethane foam

Varying amounts of filler content was added to the castor oil derived polyurethane foam samples and a slight variation in color and appearance of the foam was observed with each addition. The effect of addition of varying quantities of iron dust in RPUF is as shown in figure 1 to 9. It has been observed that as the filler content in the foam increased, the color of the foam changed drastically from yellow to pale yellow to gray. The yellow color present initially is due to the yellow color of the natural castor oil itself.

1. Neat PU Foam



2. PU foam containing 0.2 gm Fe dust



3. PU foam containing 0.3 gm Fe dust



4. PU foam containing 0.4 gm Fe dust



5. PU foam containing 0.5 gm Fe dust



6. PU Foam containing 1.0 gm Fe dust



7. PU foam containing 1.5 gm Fe dust



8. PU foam containing 2.0 gm Fe dust



9. PU foam containing 2.5 gm Fe dust



4.2 SEM RESULTS

The SEM analysis was carried out in the lab using machine HITACHI, model no. S-3700N with EDS-X. In pure polyurethane formation, isocyanate reacts with polyols during the polymerization reaction that results in the formation of polyurethane cell wall. The SEM of this is shown in the figure below:

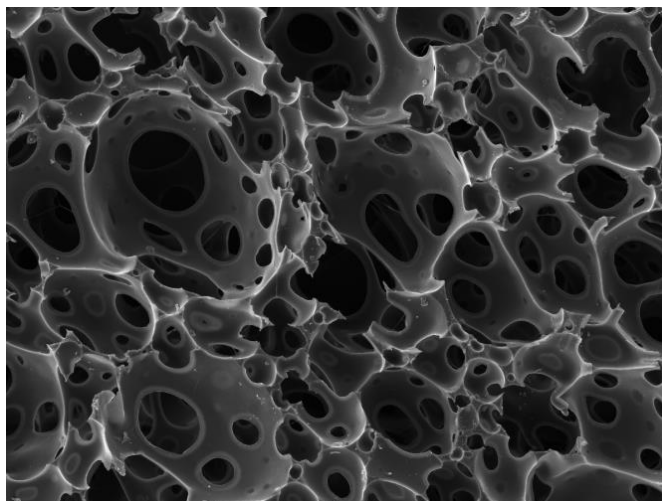


Fig. 4.2.1 SEM of pure PU foam

On mixing castor oil with glycerol to form polyol premix, the PU cell wall formation is slower and it consists of large cells owing to the low reactivity of castor oil. This is depicted by the SEM image as given below. Microphase separation in PU occurs easily due to the incompatibility in the structure owing to the difference in the chemical structure of soft and hard segments. In order to make the cell wall stronger, glycerol is added so that the hard segment is extended and the size of the cell is reduced.

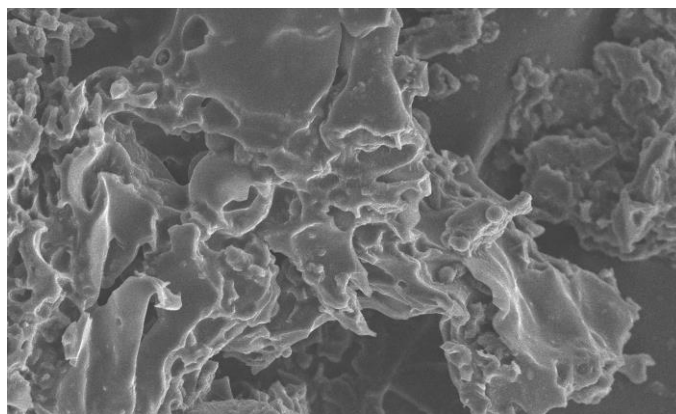


Fig. 4.2.2 SEM of castor oil based PU

4.3 FTIR RESULTS

4.3.1. Castor oil based PU foam

FTIR analysis was carried out in the lab using machine Thermoscientific Nicolet 380. The Fourier transform infrared spectrum of castor oil-based PU is shown in the figure below. The absence of the free

NCO group is confirmed by the absence of band in the range of 2260-2310 cm^{-1} which indicates that the urethane reaction has been completed. PU is characterized by some of the most important features such as the presence of bands at 1072 cm^{-1} (C–N stretching vibrations), 1123 cm^{-1} (C–O stretching vibrations), 1557–1580 cm^{-1} (C–N stretching and N–H bending), 1600 cm^{-1} (C–C stretching vibration), 1720–1730 cm^{-1} (C–O stretching vibrations from urethane groups), 2857–2925 cm^{-1} (CH₂ symmetric and anti-symmetric stretching vibrations) and 3378 cm^{-1} (free O–H and N–H stretching from urethane group stretching vibrations). These vibrational bands show the formation of urethane linkage, NH–COO in the synthesized polyurethane.

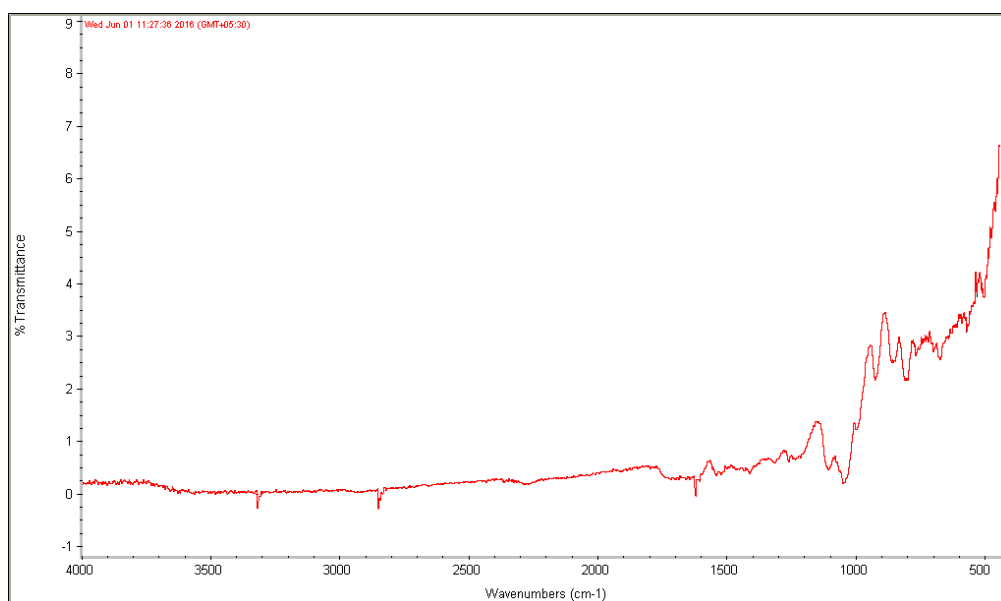


Fig. 4.3.1 FTIR Result of castor oil PU Foam

4.3.2. Iron dust filler (Fe_3O_4)

The FTIR transmission spectra of iron dust filler is depicted in the figure below. The absorption band at 584 cm^{-1} and 2923 cm^{-1} is due to Fe–O bending vibration mode and O–H stretching vibration modes respectively.

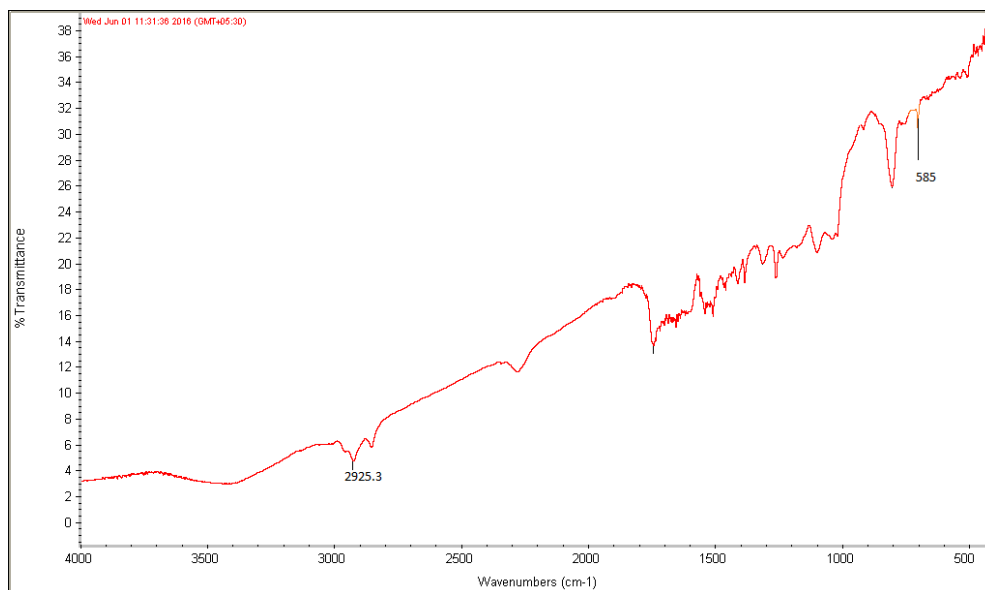


Fig. 4.3.2 FTIR Result of iron dust filler

4.3.3 Castor oil based PU foam containing iron dust filler

The FTIR spectra of the polyurethane foam containing iron dust filler shows absorption peaks at 3,300 cm^{-1} (hydrogen-bonded N–H stretching), 1550 cm^{-1} (N–H deformation), and 1,720–1,695 cm^{-1} (C=O stretching) as assigned to the urethane structure. The bands at 2,960 cm^{-1} are corresponding to the C–H asymmetrical stretching of the methylene hydrogen of polyether.

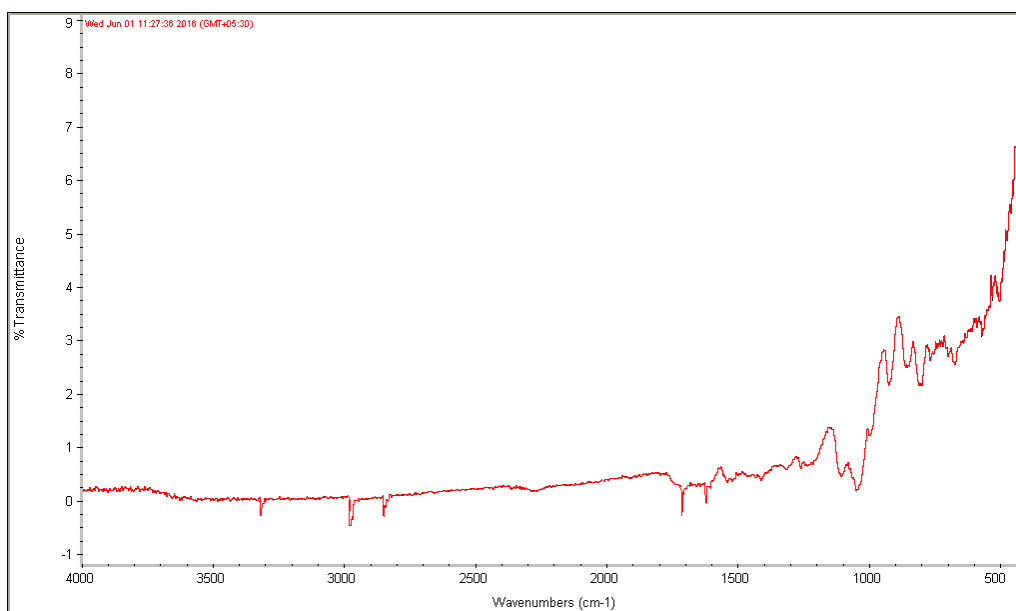
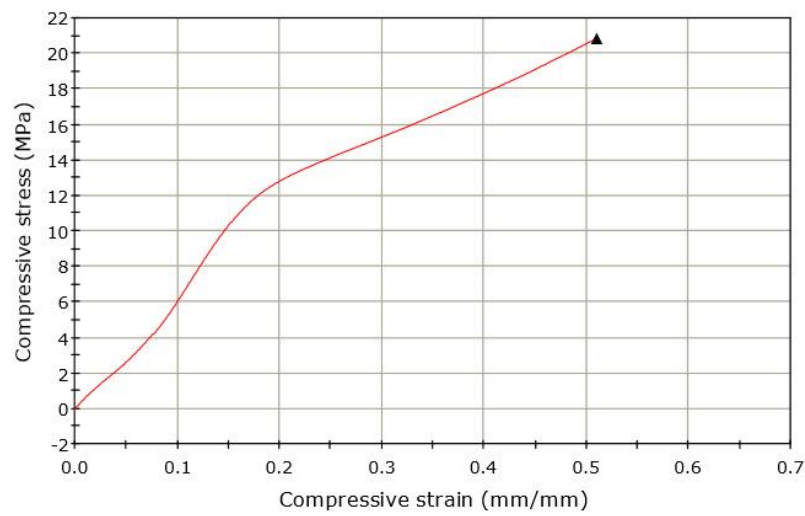
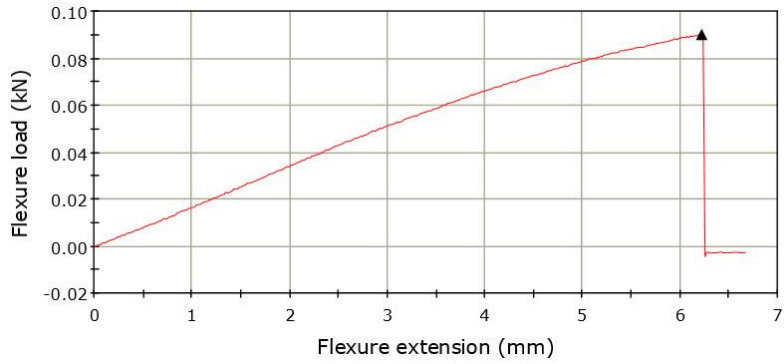


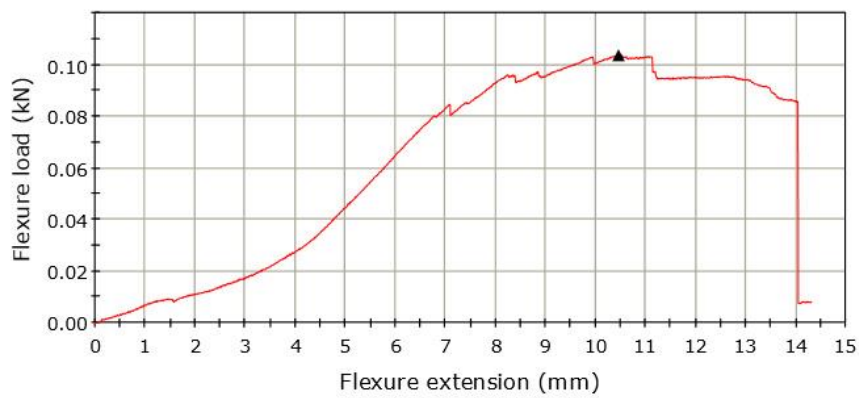
Fig. 4.3.3 FTIR result of PU foam with iron dust filler

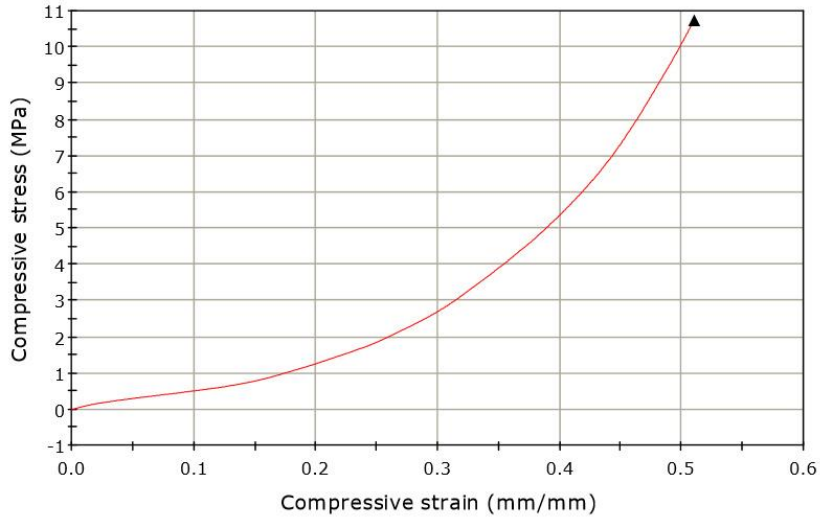
4.4 MECHANICAL PROPERTIES OF THE IRON DUST FILLED RPUF

1. Neat polyurethane foam

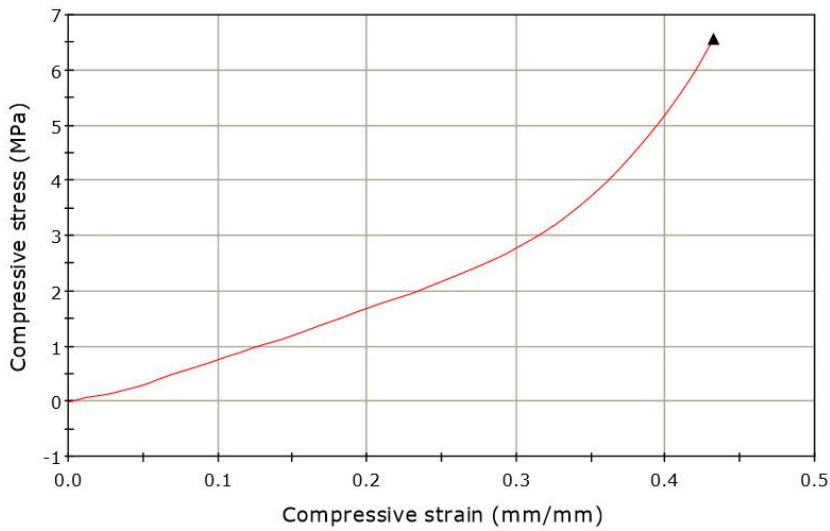
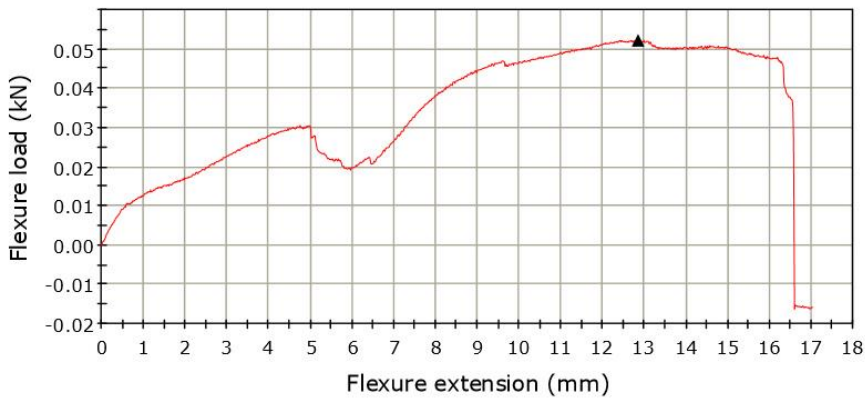


2. PU foam with 0.2 gm Fe dust

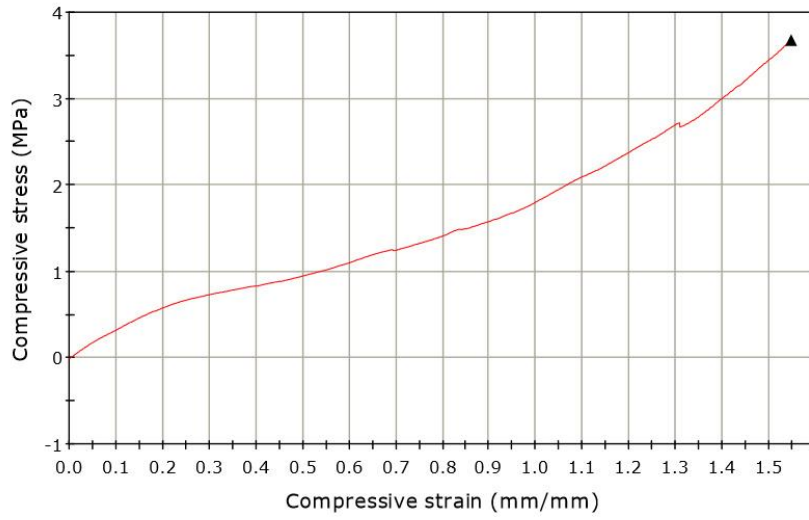
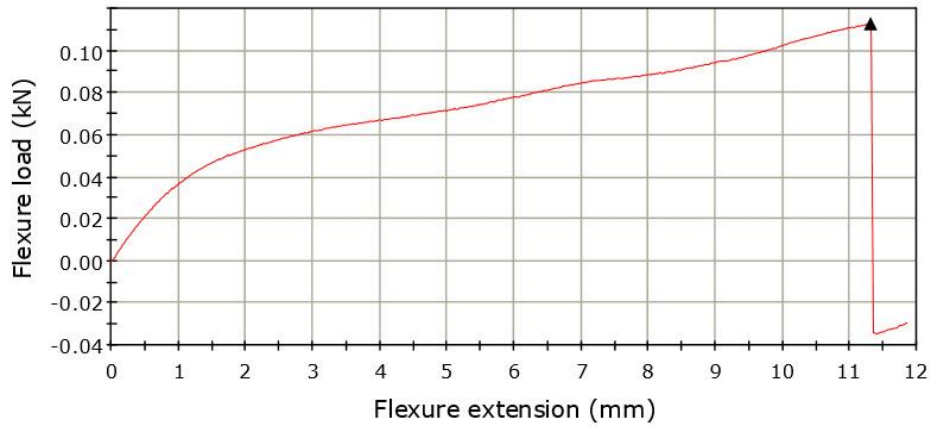




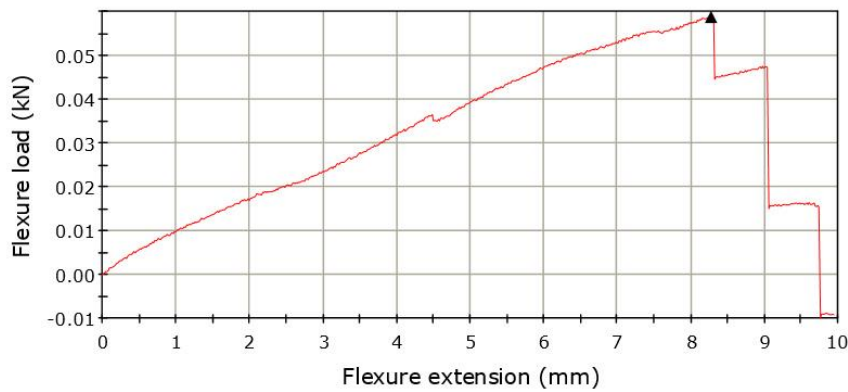
3. PU foam with 0.3 gm Fe dust

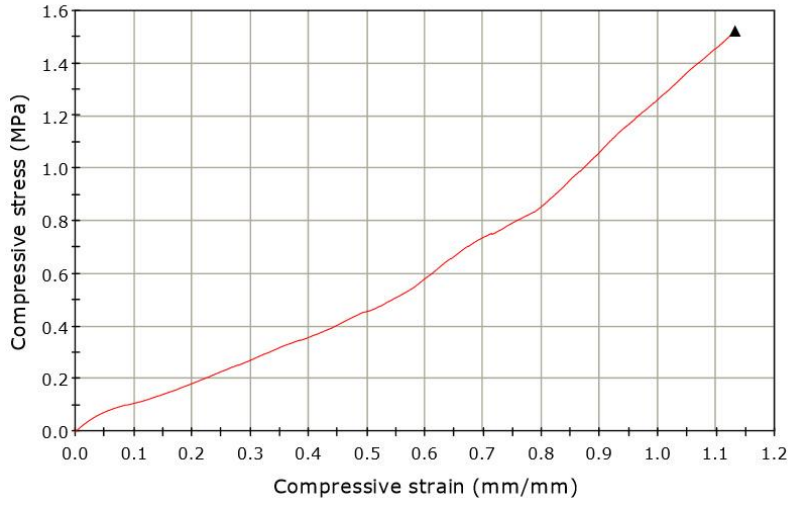


4. PU foam with 0.5 gm Fe dust

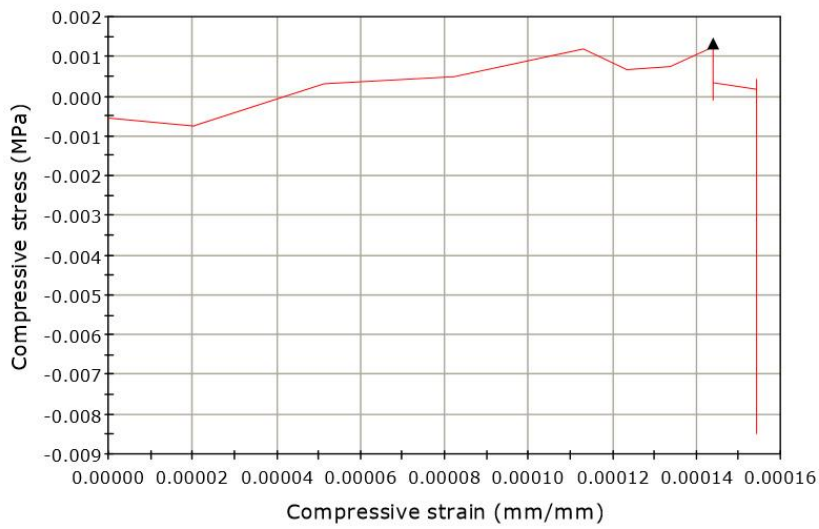
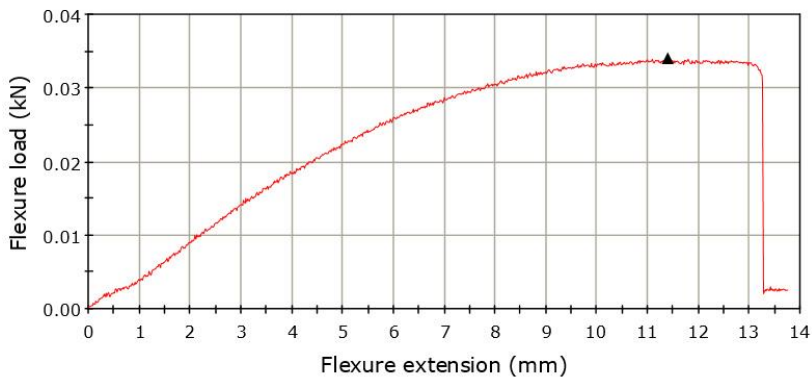


5. PU foam with 1.5 gm Fe dust

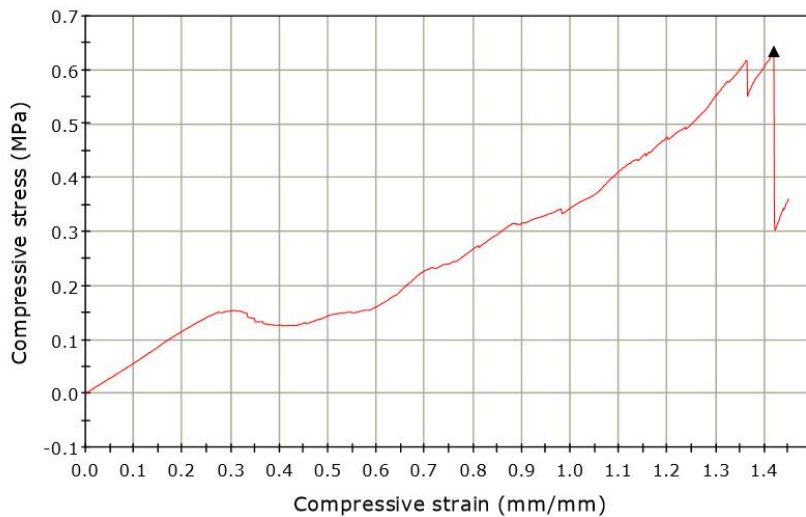
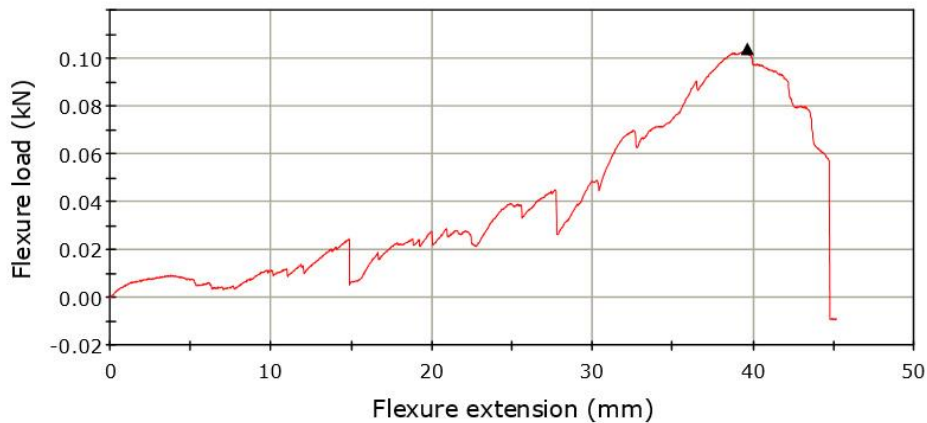




6. PU foam containing 2.0 gm Fe dust



7. PU foam with 2.5 gm Fe dust



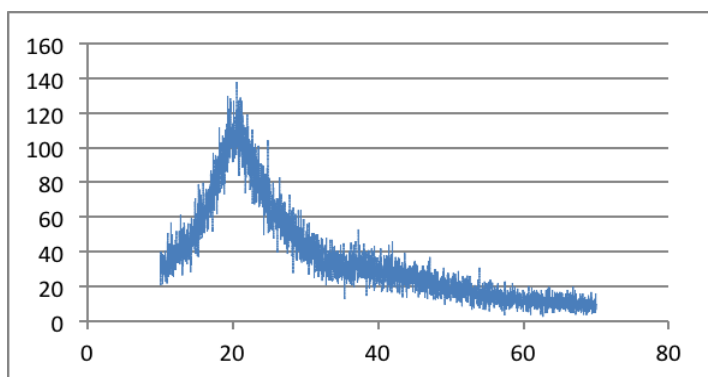
It can be concluded from the graph pattern that as the amount of filler loading i.e. Fe is increased there is an increase in the capability of the foam to withstand flexural load which could be because Fe dust fills the void space within the foam and helps it to withstand external breaking force.

From the graphs of compressive stress v/s compressive strain, it can be seen that on increasing the amount of Fe in the composite foam, there is an increase in the ability of foam to withstand more compressive force.

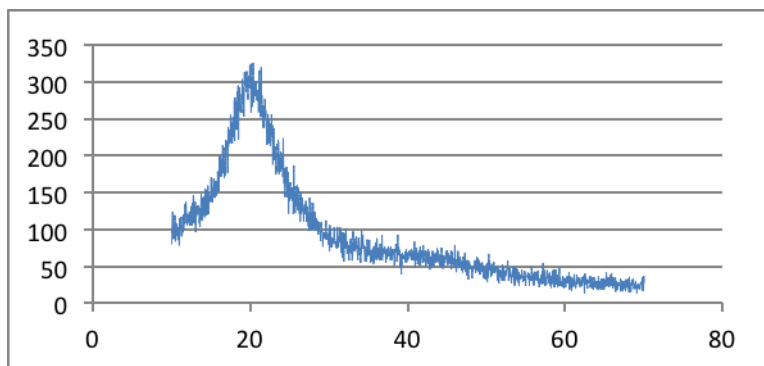
4.5 XRD ANALYSIS

1. Neat PU sample

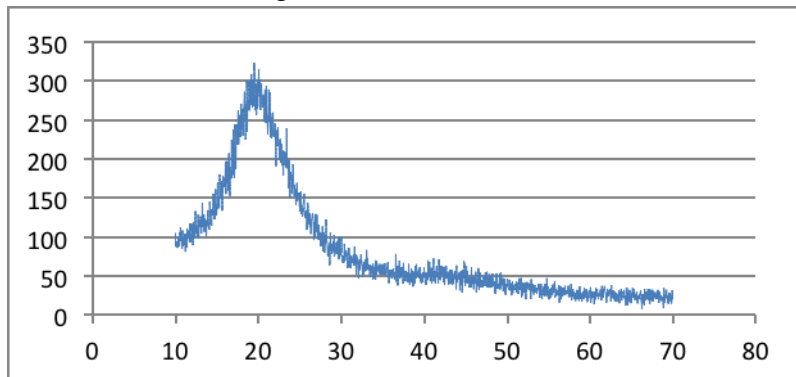
The XRD analysis was carried out using Bruker D8 Advance Diffractometer with Ni-filtered Cu $K\alpha$ radiation. The XRD of pure castor oil based PU foam is demonstrated by one peak at $2\theta = 20.42$ (d ang = 4.345) due to the difference in the chemical structure of the soft segment condition, such as the presence of mono-glyceride and di-glyceride. Also, the addition of MDI to the polyol mix results in the reaction between diisocyanate and $-OH$ groups (present in polyol) thus causing the formation of urethane linkages as the reaction proceeds.



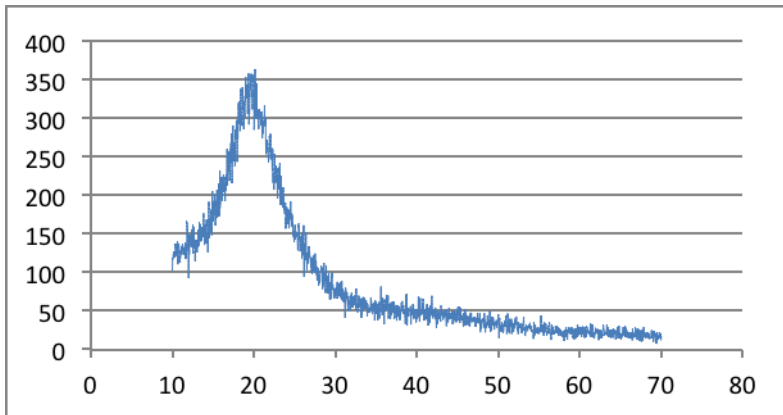
2. PU foam with 0.2 gm Fe dust



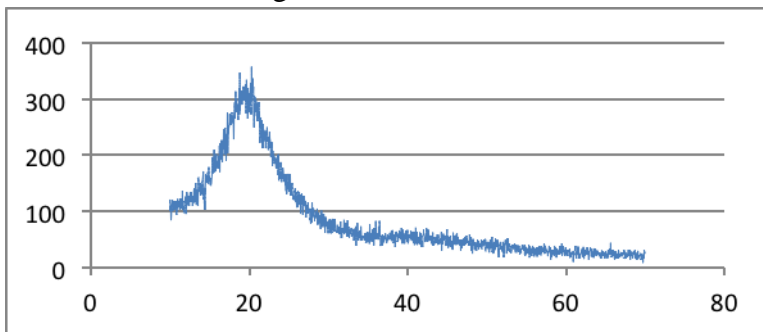
3. PU foam with 0.3 gm Fe dust



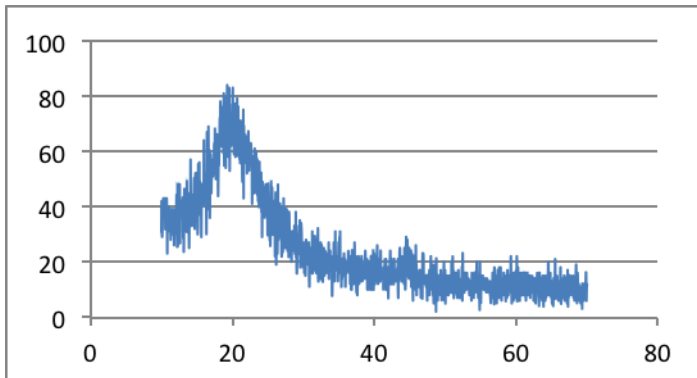
4. PU foam with 0.4 gm Fe dust



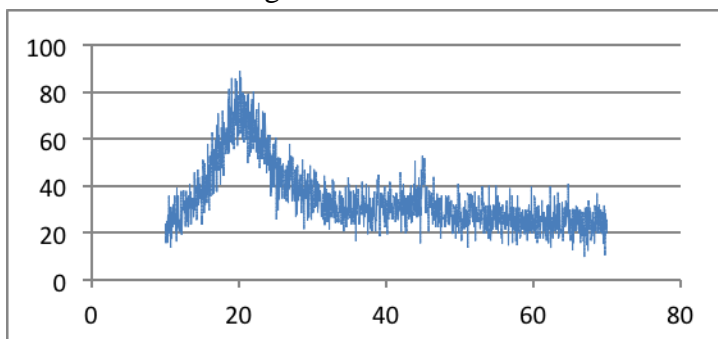
5. PU foam with 0.5 gm Fe dust



6. PU foam with 1 gm Fe Dust



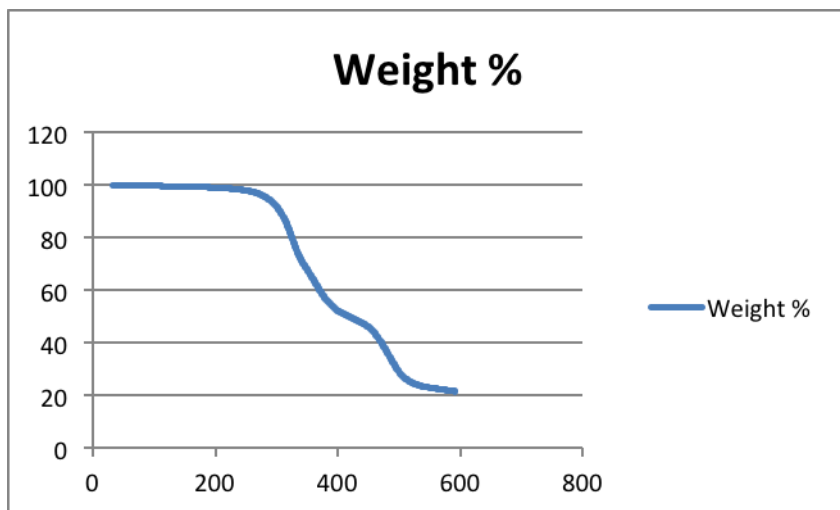
7. PU foam with 2.0gm Fe dust



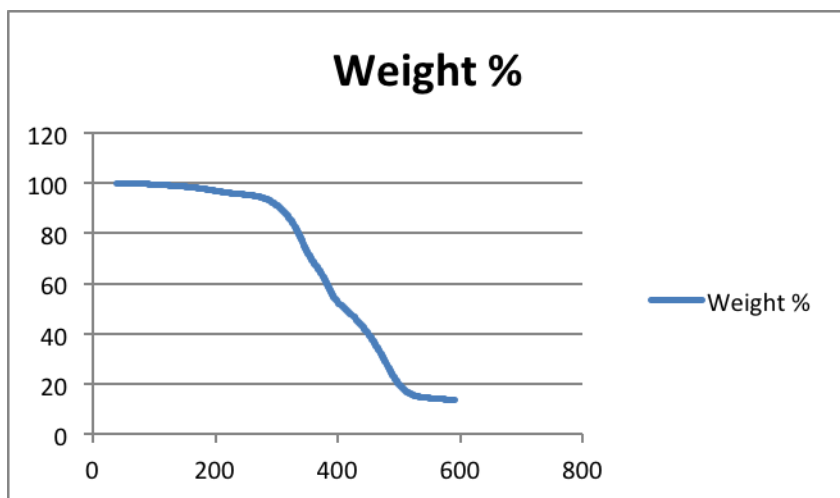
From the XRD graph, it can be concluded that as the amount of filler content i.e. Fe dust is increased an increase in the intensity of Fe peak at 44 can be seen.

4.6 TGA ANALYSIS

1. PU foam with 0.2 gm Fe dust



2. PU foam with 2.0 gm Fe dust



On observing the TGA graphs it can be said that as the amount of Fe filler is increased, larger amount of residue is left even after 500°C. Which shows that the residue left is a metal because the rest of hydrocarbons degrade till 600°C

4.7 PREPARATION OF POLYURETHANE FOAM INCORPORATED WITH IRON NANOPARTICLES

Magnetic nanoparticles (MNs), due to their unique physio-chemical properties and wide applicability in various field have garnered a lot of attention in recent years. These particles are used in field such as catalysis, controlled drug release, adsorption of dyes, wastewater purification, magnetic and electromagnetic wave absorption, magnetic recording media like audio and videotape, magnetic fluids, magnetic sensing, etc. Apart from their diverse uses in various industries, these nanoparticles help in improving thermal and mechanical properties of the polymer.

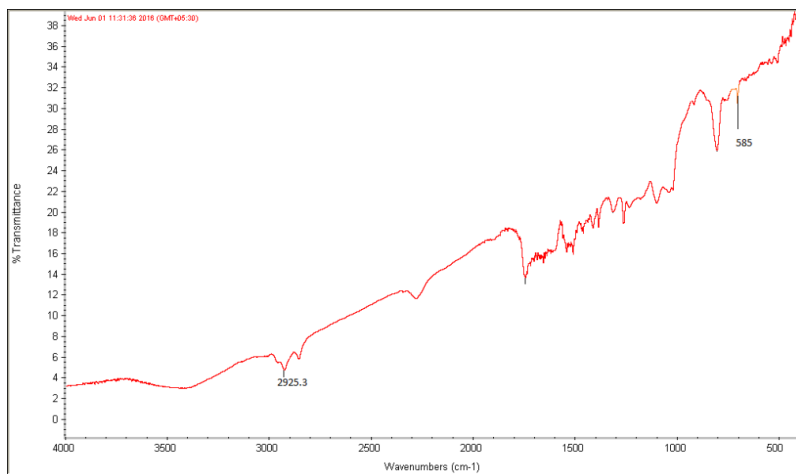
4.7.1 Synthesis of Fe₃O₄ nanoparticles by co-precipitation technique

Ultra fine particles of Fe₃O₄ were prepared by co-precipitating aqueous solutions of (NH₄)₂Fe(SO₄)₂ and FeCl₃ mixtures, respectively, in alkaline medium. (NH₄)₂Fe(SO₄)₂ and FeCl₃ solutions were mixed in their respective stoichiometry (i.e, ratio Fe +2: Fe +3 = 1:2). The mixture was kept at 80°C. This mixture was then added to the boiling solution of NaOH (0.5 mol. is dissolved in 600 ml of distilled water) within 10 second under constant stirring. Magnetite was formed by conversion of metal salts into hydroxides, which took place immediately, and transformed of hydroxides into ferrites. The solution was maintained at 100⁰C for 1.5 h. The Fe₃O₄ particles were washed several times by distilled water and then were divided into three parts. In the first part, the Fe₃O₄ particles were remained in the distilled water without any additives as prepared, in the second part, the Fe₃O₄ particles were just dried at 100⁰C for 1 h and the third part was centrifuged, then was redispersed in oleic acid.

4.7.2 Characterization of Fe₃O₄ Nanoparticles

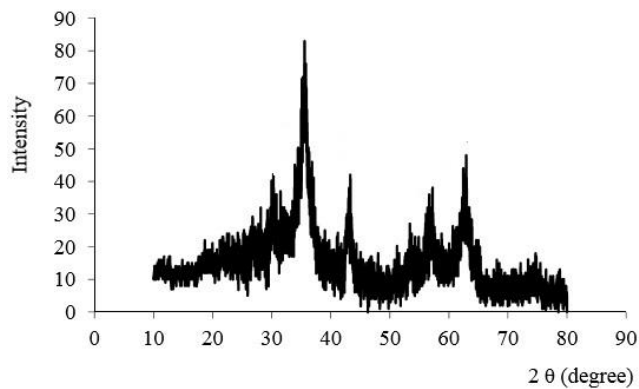
4.7.2.1. FTIR

It can be seen that the characteristic absorption of Fe-O bond is at 580 cm⁻¹ and 634 cm⁻¹, while that of -OH bond is at 3398 cm⁻¹. The absorptions at 1393 cm⁻¹ and 1587 cm⁻¹ are characteristic peaks of the COO-Fe bond, which may be due to the reaction of hydroxide radical groups on the surface of Fe₃O₄. The peaks at 2855 cm⁻¹ and 2924 cm⁻¹ are from the vibration of in long alkyl chain -CH₂ and -CH₃. Furthermore, the characteristic peak of -OH bond at 3378 cm⁻¹ is obviously enhanced..

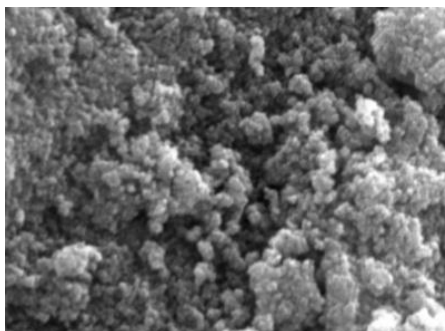


4.7.2.2 XRD ANALYSIS

Six characteristic peaks at 30.2° , 35.5° , 43° , 53.7° , 57.215° and 63° were observed. The peaks indicated that Fe_3O_4 was with a spinel structure and no characteristic peak of impurities were detected in the XRD pattern.



4.7.2. 3. SEM ANALYSIS



4.8. EFFECT OF FILLERS ON APPEARANCE IN PU FOAM

The method employed to add iron nanoparticles as filler in the polyurethane foam was the same as employed to add iron dust filler in the foam. Incorporation of nanoparticles resulted in a drastic change of appearance and color of the foam. Figures 1-3 indicate that as the content of filler amount increased, the color of the foam changed from pale red-orange to stark red.

1. PU foam with 0.1 gm Fe nanoparticle



2. PU foam with 0.2 gm Fe nanoparticle



3. PU foam with 0.3 gm Fe nanoparticle

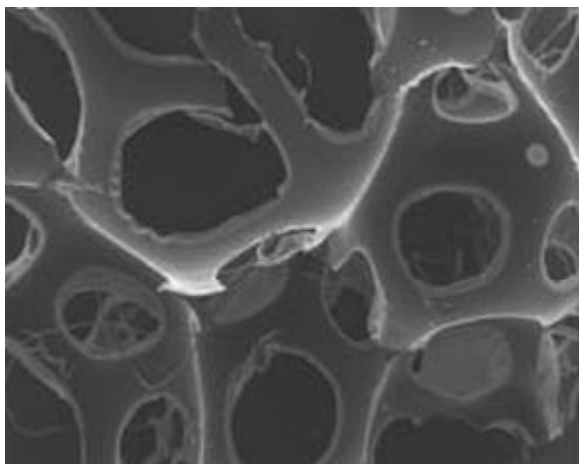


4.9 SEM ANALYSIS

SEM images of Fe_3O_4 incorporated in polyurethane foam with different contents of Fe_3O_4 nanoparticles are given below.

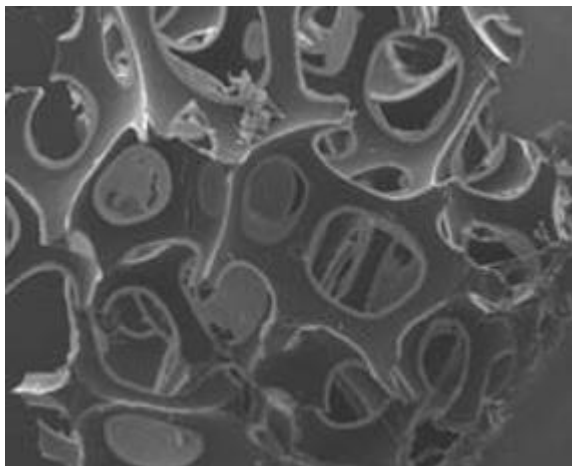
1. PU foam with 0.1 gm Fe_3O_4 NP

The SEM image when 0.1 gm of nanoparticle was added showed that the cell opening was quite large



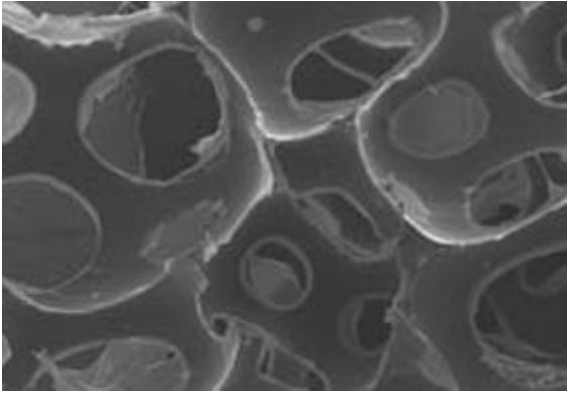
2. PU foam with 0.2 gm Fe_3O_4 NP

With the increase of the content of nano-particle Fe_3O_4 , the pore size became much smaller and the opening ratio slightly decreased, which had little influence on the pore structure of the foam.



3. PU foam with 0.3 gm Fe_3O_4 NP

When the amount of filler increased to 0.3, the foam structure became a little blurred i.e uniform pore structure and opening ratio was lost slightly.



CHAPTER 5

CONCLUSION AND FUTURE SCOPE

5.1 CONCLUSION

The use of iron dust as filler in the polyurethane foam based on castor oil has been evaluated. An attempt was made to develop foam that has superior mechanical properties and study the impact of filler on the conducting properties of the foam. The main purpose of this study was to distinguish between the impact of iron dust filler and nanoparticles (as used in previous studies) on the properties of foam. Since, the foam is derived from a natural vegetable oil i.e. castor oil, it is more environment friendly in nature as compared to foam synthesized using petroleum based polyol. The studies conducted in this project clearly indicate that castor oil has a great potential to replace foams made using commercial polyols as it resulted in the production of high rigidity PU foams. Addition of glycerol results in high cross-linking and stiffer structure of the foam. Also, addition of filler affected the mechanical properties of the foam. Higher the amount of filler loading, higher is the capability of the foam to withstand flexural load which could be attributed to the fact that Fe dust fills the void space within the foam and helps it to withstand external breaking force. Also, as the content of iron dust increased, the foam had the ability of foam to withstand more compressive force.

5.2 FUTURE SCOPE OF WORK

It is a well-established fact that nanoparticles apart from being expensive in nature, help in enhancing the mechanical properties of a material significantly. The future work of this study includes the study and synthesis of iron nanoparticles and to evaluate their impact on the physio-chemical properties of the foam and study the difference in the physical and chemical properties of iron dust and iron nanoparticles.

REFERENCES

- [1] <http://www.essentialchemicalindustry.org/polymers/polyurethane.html>
- [2] Babb DA (2012) Polyurethanes from renewable resources. In: Synthetic biodegradable polymers. Springer, Berlin
- [3] Johnson DT, Taconi KA (2007) The glycerin glut: options for the value-added conversion of crude glycerol resulting from biodiesel production. *Environ Prog* 26:338–348
- [4] Szycher's Handbook of Polyurethanes, Second Edition
- [5] Lu QW, Macosko CW. Comparing the compatibility of various functionalized polypropylenes with thermoplastic polyurethane (TPU). *Polymer*. 2004;45:198191.
- [6] D. P. Pfister, Y. Xia, and R. C. Larock, Recent Advances in Vegetable Oil-Based Polyurethanes. *ChemSusChem*, 201, 4, 703 – 717.
- [7] Gerard Lligadas*, Juan C. Ronda, Marina Galià, and Virginia Cádiz, Plant Oils as Platform Chemicals for Polyurethane Synthesis: Current State-of-the-Art, *Biomacromolecules*, 2010, 11 (11), pp 2825–2835
- [8] dos Santos D, Tavares L, Batalha G. Mechanical and physical properties investigation of polyurethane material obtained from renewable natural source. *Journal of Achievements in Materials and Manufacturing Engineering*. 2012;54(2): 211-6.
- [9] E. Hablot, D. Zheng, M. Bouquey, L. Avérous, Polyurethanes Based on Castor Oil: Kinetics, Chemical, Mechanical and Thermal Properties, *Macromol. Mater. Eng.*, 2008, 293, 922–929.
- [10] dos Santos D, Tavares L, Batalha G. Mechanical and physical properties investigation of polyurethane material obtained from renewable natural source. *Journal of Achievements in Materials and Manufacturing Engineering*. 2012;54(2): 211-6.
- [11] X. Kong, G. Liu, J. M. Curtis, Novel polyurethane produced from canola oil based poly (ether ester) polyols: Synthesis, characterization and properties. *European Polymer Journal*, 2012, 2097-2106
- [12] <https://en.wikipedia.org/wiki/Isocyanate>

- [13]http://dowac.custhelp.com/app/answers/detail/a_id/13361/~/~dow-polyurethanes---isocyanate-index-definition
- [14] http://dowac.custhelp.com/app/answers/detail/a_id/5700/~/~dow-polyurethanes---isocyanate-index-definition
- [15]http://dowac.custhelp.com/app/answers/detail/a_id/5659/~/~dow-polyurethanes---polyol-manufacturing
- [16] http://dowac.custhelp.com/app/answers/detail/a_id/5693/related/1
- [17] http://dowac.custhelp.com/app/answers/detail/a_id/3281/~/~surfactant-basics---definition-of-cloud-point-and-its-importance
- [18]http://dowac.custhelp.com/app/answers/detail/a_id/5693/~/~dow-polyurethanes---polyol-characterization
- [19] R. Pantani , V. Volpe, Foam injection molding of poly(lactic acid) with environmentally friendly physical blowing agents, *Journal of Materials Processing Technology* Volume 214, Issue 12
- [20] Thanapon Kattiyaboot, Chanchai Thongpin, Effect of Natural Oil Based Polyols on the Properties of Flexible Polyurethane Foams Blown by Distilled Water, *Energy Procedia*, Volume 89
- [21] Christian Hopmann, Simon Latz, Foaming technology using gas counter pressure to improve the flexibility of foams by using high amounts of CO₂ as a blowing agent, *Polymer* Volume 56
- [22]http://dowac.custhelp.com/app/answers/detail/a_id/13327/~/~dow-polyurethanes---amine-catalysts-role-in-foam-formulations
- [23]<http://www.airproducts.com/~~/media/Files/PDF/company/product-summary-polyurethane-amine-catalysts.pdf?la=en>
- [24] Sinadinović-Fišer S, Janković M, Petrović ZS (2001) Kinetics of in situ epoxidation of soybean oil in bulk catalyzed by ion exchange resin. *J Am Oil Chem Soc* 78:725–731
- [25] Petrović ZS, Zlatanić A, Lava CC, Sinadinović-Fišer S (2002) Epoxidation of soybean oil in toluene with peroxyacetic and peroxyformic acids-kinetics and side reactions. *Eur J Lipid Sci Tech* 104:293–299

- [26] Miao S, Zhang S, Su Z, Wang P (2010) A novel vegetable oil-lactate hybrid monomer for synthesis of high-Tg polyurethanes. *J Polym Sci Pol Chem* 48:243–250
- [27] Monteavaro LL, da Silva EO, Costa AP, Samios D, Gerbase AE, Petzhold CL (2005) Polyurethane networks from formiated soy polyols: synthesis and mechanical characterization. *J Am Oil Chem Soc* 82:365–371
- [28] Zlatanić A, Lava C, Zhang W, Petrović ZS (2004) Effect of structure on properties of polyols and polyurethanes based on different vegetable oils. *J Polym Sci Pol Phys* 42:809–819
- [29] Ionescu M, Petrović ZS, Wan X (2007) Ethoxylated soybean polyols for polyurethanes. *J Polym Environ* 15:237–243
- [30] Pfister DP, Xia Y, Larock RC (2011) Recent advances in vegetable oil-based polyurethanes. *Chem Sus Chem* 4:703–717
- [31] Guo A, Cho Y, Petrović ZS (2000) Structure and properties of halogenated and nonhalogenated soy-based polyols. *J Polym Sci Polym Chem* 38:3900–3910
- [32] Pan X, Webster DC (2012) New biobased high functionality polyols and their use in polyurethane coatings. *ChemSusChem* 5:419–429
- [33] Kiatsimkul PP, Suppes GJ, Hsieh Fh, Lozada Z, Tu YC (2008) Preparation of high hydroxyl equivalent weight polyols from vegetable oils. *Ind Crop Prod* 27:257–264
- [34] Guo Y, Hardesty JH, Mannari VM, Massingill JL Jr (2007) Hydrolysis of epoxidized soybean oil in the presence of phosphoric acid. *J Am Oil Chem Soc* 84:929–935
- [35] Wang CS, Yang LT, Ni BL, Shi G (2009) Polyurethane networks from different soy-based polyols by the ring-opening of epoxidized soybean oil with methanol, glycol, and 1,2-propanediol. *J Appl Polym Sci* 114:125–131
- [36] Zlatanić A, Lava C, Zhang W, Petrović ZS (2004) Effect of structure on properties of polyols and polyurethanes based on different vegetable oils. *J Polym Sci Pol Phys* 42:809–819
- [37] Guo A, Javni I, Petrović Z (2000) Rigid polyurethane foams based on soybean oil. *J Appl Polym Sci* 77:467–473

- [38] Hu YH, Gao Y, Wang DN, Hu CP, Zu S, Vanoverloop L, Randall D (2002) Rigid polyurethane foam prepared from a rape seed oil based polyol. *J Appl Polym Sci* 84:591–597
- [39] Tan S, Abraham T, Ference D, Macosko CW (2011) Rigid polyurethane foams from a soybean oil-based Polyol. *Polymer* 52:2840–2846
- [40] Zhang L, Jeon HK, Malsam J, Herrington R, Macosko CW (2007) Substituting soybean oil-based polyol into polyurethane flexible foams. *Polymer* 48:6656–6667
- [41] Lu Y, Larock RC (2008) Soybean-oil-based waterborne polyurethane dispersions: effects of polyol functionality and hard segment content on properties. *Biomacromolecules* 9:3332–3340
- [42] Lu Y, Larock RC (2007) New hybrid latexes from a soybean oil-based waterborne polyurethane and acrylics via emulsion polymerization. *Biomacromolecules* 8:3108–3114
- [43] Lu Y, Larock RC (2010) Aqueous cationic polyurethane dispersions from vegetable oils. *ChemSusChem* 3:329–333
- [44] Guo A, Demydov D, Zhang W, Petrović ZS (2002) Polyols and polyurethanes from hydroformylation of soybean oil. *J Polym Environ* 10:49–52
- [45] Petrović ZS, Guo A, Javni I, Cvetković I, Hong DP (2008) Polyurethane networks from polyols obtained by hydroformylation of soybean oil. *Polym Int* 57:275–281
- [46] Pfister DP, Xia Y, Larock RC (2011) Recent advances in vegetable oil-based polyurethanes. *Chem Sus Chem* 4:703–717
- [47] Desroches M, Escouvois M, Auvergne R, Caillol S, Boutevin B (2012) From vegetable oils to polyurethanes: synthetic routes to polyols and main industrial products. *Polym Rev* 52:38–79
- [48] Petrović ZS, Cvetković I, Hong D, Wan X, Zhang W, Abraham TW, Malsam J (2010) Vegetable oil-based triols from hydroformylated fatty acids and polyurethane elastomers. *Eur J Lipid Sci Tech* 112:97–102
- [49] Petrović ZS, Zhang W, Javni I (2005) Structure and properties of polyurethanes prepared from triglyceride polyols by ozonolysis. *Biomacromolecules* 6:713–719

- [50] Narine SS, Yue J, Kong X (2007) Production of polyols from canola oil and their chemical identification and physical properties. *J Am Oil Chem Soc* 84:173–179
- [51] Kong X, Narine SS (2007) Physical properties of polyurethane plastic sheets produced from polyols from canola oil. *Biomacromolecules* 8:2203–2209
- [52] Benecke HP, Vijayendran BR, Garbark DB, Mitchell KP (2008) Low cost and highly reactive biobased polyols: a co-product of the emerging biorefinery economy. *Clean-Soil Air Water* 36:694–699
- [53] Tran P, Graiver D, Narayan R (2005) Ozone-mediated polyol synthesis from soybean oil. *J Am Oil Chem Soc* 82:653–659
- [54] Narine SS, Kong X, Bouzidi L, Sporns P (2007) Physical properties of polyurethanes produced from polyols from seed oils: I. Elastomers. *J Am Oil Chem Soc* 84:55–63
- [55] Desroches M, Escouvois M, Auvergne R, Caillol S, Boutevin B (2012) From vegetable oils to polyurethanes: synthetic routes to polyols and main industrial products. *Polym Rev* 52:38–79
- [56] Caillol S, Desroches M, Carlotti S, Auvergne R, Boutevin B (2012) Synthesis of new polyurethanes from vegetable oil by thiol-ene coupling. *Green Mater* 1:16–26
- [57] Desroches M, Caillol S, Lapinte V, Auvergne R, Boutevin B (2011) Synthesis of biobased polyols by thiol-ene coupling from vegetable oils. *Macromolecules* 44:2489–2500
- [58] Chuayjuljit S, Maungchareon A, Saravari O (2010) Preparation and properties of palm oil-based rigid polyurethane nanocomposite foams. *J Reinf Plast Comp* 29:218–225
- [59] Stirna U, Cabulis U, Beverte I (2008) Water-blown polyisocyanurate foams from vegetable oil polyols. *J Cell Plast* 44:139–160
- [60] Campanella A, Bonnaillie LM, Wool RP (2009) Polyurethane foams from soyoil-based polyols. *J Appl Polym Sci* 112:2567–2578
- [61] an E, Küseföglü S, Wool RP (2001) Rigid, thermosetting liquid molding resins from renewable resources. I. Synthesis and polymerization of soy oil monoglyceride maleates. *J Appl Polym Sci* 81:69–77

- [62] Gryglewicz S, Piechocki W, Gryglewicz G (2003) Preparation of polyol esters based on vegetable and animal fats. *Bioresour Technol* 87:35–39
- [63] Dutta S, Karak N (2006) Effect of the NCO/OH ratio on the properties of *Mesua Ferrea* L. seed oil-modified polyurethane resins. *Polym Int* 55:49–56
- [64] Petrović ZS (2008) Polyurethanes from vegetable oils. *Polym Rev* 48:109–155
- [65] Lee CS, Ooi TL, Chuah CH, Ahmad S (2007) Synthesis of palm oil-based diethanolamides. *J Am Oil Chem Soc* 84:945–952
- [66] Yadav S, Zafar F, Hasnat A, Ahmad S (2009) Poly(urethane fatty amide) resin from linseed oil-a renewable resource. *Prog Org Coat* 64:27–32
- [67] Meshram PD, Puri RG, Patil AL, Gite VV (2013) High performance moisture cured poly (ether-urethane) amide coatings based on renewable resource (cottonseed oil). *J Coat Technol Res* 10:331–338
- [68] Abdelaziz*, A. I. M., Elamin**, I. H. M., Gasmelseed**, G. A., Abdalla*, B. K. (2014) Extraction, Refining and Characterization of Sudanese Castor Seed Oil, *Journal of Chemical Engineering*, ISSN 2166-4358 (Print) ISSN 2166-4366
- [69] Mutlu H, Meier MA (2010) Castor oil as a renewable resource for the chemical industry. *Eur J Lipid Sci Tech* 112:10–30
- [70] Stirna U, Lazdina B, Vilsone D, Lopez MJ, del Vargas-Garcia Carmen M, Suárez-Estrella F, Moreno J (2012) Structure and properties of the polyurethane and polyurethane foam synthesized from castor oil polyols. *J Cell Plast* 48:476–488
- [71] Corcuera MA, Rueda L, Fernandez dArlas B, Arbelaiz A, Marieta C, Mondragon I, Eceiza A (2010) Microstructure and properties of polyurethanes derived from castor oil. *Polym Degrad Stabil* 95:2175–2184
- [72] Lyon CK, Garrett VH, Goldblatt LA (1962) Solvent-blown, rigid urethane foams from low cost castor oil-polyol mixtures. *J Am Oil Chem Soc* 39:69–71
- [73] Yeganeh H, Mehdizadeh MR (2004) Synthesis and properties of isocyanate curable millable polyurethane elastomers based on castor oil as a renewable resource polyol. *Eur Polym J* 40:1233–1238

- [74] Yeganeh H, Moeini HR (2007) Novel polyurethane electrical insulator coatings based on amide-ester-ether polyols derived from castor oil and re-cycled poly(ethylene terephthalate). *High Perform Polym* 19:113–126
- [75] Das SK, Lenka S (2000) Interpenetrating polymer networks composed of castor oil-based polyurethane and 2-hydroxy-4-methacryloyloxy acetophenone. *J Appl Polym Sci* 75:1487– 1492
- [76] Kovaly, K.A., 1982. Biomass and Chemicals. *Chemtech.*, August, pp. 486–489.
- [77] Okagbue, R.N., 1993. Microbiological activity in traditional food processing in Nigeria. In: *International Conference on Uniting African World Scholars and Communities: Global Realities and Social Transformation*. Ghana National Theater, Accra, Ghana, 30th July–8th August.
- [78] Ghandi, V.M, Cherian, K.M., Mulky, M.J., 1994. Detoxification of castor seed meal by interaction with sal seed meal. *J. Am. Oil Chem. Soc.* 71, 827–831
- [79] Weiss, E., 1983. *Oilseed Crops, Tropical Agriculture Series*. Longman Scientific and Technical, London, pp. 530–564.
- [80] Kovaly, K.A., 1982. Biomass and Chemicals. *Chemtech.*, August, pp. 486–489.
- [81] Kirk-Othmer, 1979. *Encyclopedia of Chemical Technology*, vol. 5. John Wiley & Sons, New York.
- [82] Woodend, J.J., 1993. Genetic improvement and commercialization of the African perennial castor (*Ricinus communis* L.) plant. *Zimba-bwe Sci. News* 27, 42–45.
- [83] Xie, H.Q., Guo, J.S., 2002. Room temperature synthesis and mechanical properties of two kinds of elastomeric interpenetrating polymer networks based on castor oil. *Eur. Poly. J.* 38, 2271–2277
- [84] Yeadon, D.A., McSherry, W.F., Goldblatt, L.A., 1959. Preparation and properties of castor oil urethane foams. *J. Am. Oil Chem. Soc.* 36, 16–20.
- [85] Kim DK, Zhang Y, Voit W, Rao KV, Muhammed M (2001) Synthesis and characterization of surfactant-coated superparamagnetic monodispersed iron oxide nanoparticles. *J Magn Magn Mater* 225(1–2):30–36. doi:10.1016/s0304-8853(00)01224-5