SYNTHESIS AND CHARACTERIZATION OF ANTI FLAMMABLE CASTOR OIL BASED RIGID POLYURETHANE FOAM

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FOR THE AWARD OF THE DEGREE OF

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DECLARATION

This is to certify that the work presented in this thesis entitled **“Synthesis and Characterization of Anti Flammable Castor Oil Based Rigid Polyurethane Foam”** is original and has been carried out by me for the degree of **Doctor of Philosophy** under the supervision of **Dr. Raminder Kaur**, Assistant Professor, Department of Applied Chemistry. This thesis is contribution of my original research work. Wherever research contributions of others are involved, every effort has been made to clearly indicate the same. To the best of my knowledge, this research work has not been submitted in part or full for the award of any degree or diploma in Delhi Technological University or in any other University/Institution.

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CERTIFICATE

This is to certify that the thesis entitled **"Synthesis and Characterization of Anti Flammable Castor Oil Based Rigid Polyurethane Foam"** submitted to the Delhi Technological University, Delhi-110042, in fulfilment of the requirement for the award of the degree of **Doctor of Philosophy** by the candidate **Mr. Mukesh Kumar**, (Reg. No.:2K12/Ph.D./AC/04) under the supervision of **Dr. Raminder Kaur, Assistant Professor,** Department of Applied Chemistry. It is further certified that the work embodied in this thesis has neither partially nor fully submitted to any other university or institution for the award of any degree or diploma.

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Dedicated

To

My Parents

Late Sh. Shyam Sunder

And

Smt. Sudesh Rani

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At the end, I pray to Almighty God to give me the serenity to accept the challenges of life.

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ABSTRACT

The versatility of rigid polyurethane foam (RPUF) has made it an indispensable material in construction, insulation and automobile industry. The global growing interest in RPUFs is towards the exploring of novel renewable sources. Being relatively inexpensive and a renewable, vegetable oils are located as the potential candidates for RPUFs production. In the present research work an attempt has been made to develop rigid polyurethane foam from castor oil. The effect of different process parameters on the properties of the RPUFs have been are extensively studied. To study the effect of the MDI/Polyol ratio, different formulations of the foams with varying amount of MDI were tested. Mechanical strength of the resulted polyurethane foams was found to be increased with increase in the MDI content. SEM studies had also shown evidence for improved morphology and closed packing with increase in MDI content. Further the RPUF was examined for the different surfactant concentrations to establish its function. Silicon oil was found to have significant effect on the mechanical properties of the foam. It emulsify the incompatible foam ingredients and promote bubble generation during mixing which in turn regulates the foam structure and cell size, thus influence the foam properties.

As RPUFs suffer from drawbacks such as lack of mechanical strength and thermal stability, it had been loaded with the different amounts of glass fiber. The higher values of hardness, tensile and compressive strength, with a relatively linearly increasing trend were observed. SEM studies had also revealed improved cell morphology with dense packing in RPUGFs. The mechanical properties and process parameters of these RPUFs are needed to be optimized to control the reliability of the products and to make the resulted product more economic. For this, the most common statistical approach i.e. Taguchi DOE was studied because of its easiness and reliability. As RPUFs suffers from the problem of being highly combustible, so different anti-flamming agents were incorporated in the foam. It was observed that thermal and anti-flamming properties of RPUFs were found to be significantly increased by incorporating TDCPP due to well homogenization of the flame retardant materials and polyols.

The resulted castor oil based RPUFs due to their high strength, anti flammable nature and load bearing capacity are suitable to be used as light weight moldable engineering material for various applications.

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LIST OF ABBREVIATIONS

Symbol	Notations
RPUFs	Rigid Polyurethane Foams
MDI	4,4’-diphenylmethanediisocyanate
FTIR	Fourier Transform Infrared
TGA	Thermo Gravimetric Analysis
UTM	Universal Testing Machine
SEM	Scanning Electron Microscope
DOE	Design of Experiments
OA	Orthogonal array
ANOVA	Analysis of Variance
S/N	Signal to Noise Ratio
DOF	Degree of Freedom
N	Number of Trials
$\mathbf{CI_{POP}}$	Confidence Interval for the Population
$\mathbf{CI_{CE}}$	Confidence Interval for a Sample Group
$\mathbf{V_e}$	Error Variance
$\mathbf{f_e}$	Error DOF
R	Sample Size for Confirmation Experiments
RPUGF	Rigid Polyurethane Foam with Glass Fibre
TDCPP	Tris(1,3-dichloro-2-propylphosphate)
TCP	Tris(2-chlroethyl) phosphate
DBTL	Dibutyltindichlorate

CHAPTER 1

INTRODUCTION

Polyurethane (PU) is one of the leading contenders of the highly diverse family of polymers. The unending adaptability of polyurethane has led to its numerous applications i.e. from low density packaging products to high performance medical substances and, from thermally stable insulation for space exploration vehicles to extremely flame-retarded flexible cushioning. Some polyurethane markets are relatively grown fully whilst others are in their formative years. As per the reported studies, polyurethanes represent around 6% of the world manufacture of plastics [1–3]. APAC is the largest revenue generating region in the polyurethane market and is anticipated to account for around 46% of the total market share. Polyurethanes are synthesized by the process of polymerization that involves reaction between polyisocyanates and polyols which permits the design of polymers for various applications in their different roles like foams, elastomers, surface coating and adhesives [4].

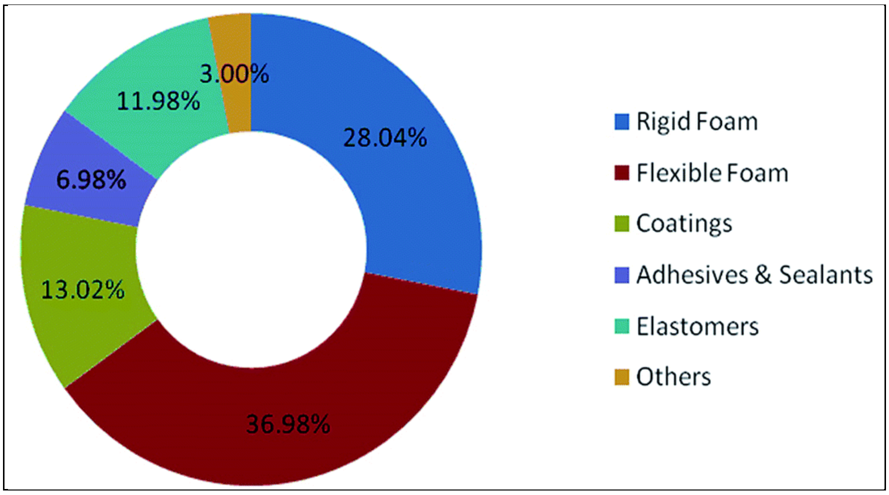


Figure 1.1: Contribution of Different Types of Polyurethanes in Global Market [5].

Due to its unique properties and flexibility of production, polyurethanes are employed in a variety of application like the insulation of buildings, refrigerators and freezers (rigid PU foams), as a filling material for seating cushions and mattresses (flexible PU foams), seats, armrests and headrests of automotive (both flexible and rigid PU), PU shoe soles (semi-rigid PU foams), PU coatings and varnishes, PU adhesives and sealants, PU elastomers, PU laminates and many others.

1.1 Applications of Polyurethane Foams

Polyurethane is a unique substance that offers the elasticity of rubber along with the toughness and durability of metal. It is one of the most versatile materials used today in different engineering and household applications, as follows:

1.1.1 Fridges and Freezers

Good insulation property of rigid polyurethane foams makes it suitable candidate in the refrigerator industries. Besides insulation, they are also economic to be used in energy efficient transportation as well as low temperature preservation, processing and supply of food to the consumers.

1.1.2 Buildings Insulation

Polyurethanes are inexpensive, long-lasting, and reduce the carbon emissions. Polyurethanes provide insulation that reduces heat loss in buildings during winter season and keep the buildings cool during summer season, thus saves electricity. Polyurethanes are used as insulations in buildings because of following reasons:

1) Due to the durability of polyurethanes, building last longer and require less maintenance.
2) Rigid insulation panels prepared from polyurethanes are physically powerful and easy to install.

1.1.3 Furniture and Bedding

Polyurathanes are widely employed in furniture and beddings. Flexible polyurethane foams are generally used for the cushioning purpose, as its density can be adjusted according to the requirement of the users.

1.1.4 Footwear

Polyurethanes allow designers to make footwear that should be restful, durable and fit for use. Polyurethanes with good abrasion resistant property are used to make shoe soles of high strength.

1.1.5 Automotive

Due to light weight and good insulating property of polyurethane foams, it is increasingly utilized in the automobile industries that are associated with several advantages such as comfort, protection and energy conservation. It is mostly utilized in the formation of seats, armrests and headrests of most of the car companies.

1.1.6 Coatings

Polyurethane based coatings are used for cables, floors, vehicles etc. which effectively covered exposed part from the different types of pollution. The durability, corrosion resistance and insulation property of polyurethane makes it excellent material for coating of all kinds of surfaces.

1.1.7 Sealants

Polyurethanes are used as sealants being very tough and can be employed under different environments. In addition, they also reduces the heat loss and thus, reducing energy bills, especially in winter season.

1.1.8 Elastomers

Two properties of polyurethanes i.e. resiliency and elasticity makes them to produce elastomers which are used where properties of long-lasting, chemical and oil resistance are needed.

1.1.9 Packing Foams

Packing foams provides protection and cushioning to packaged products. Polyurethanes foams are available in convoluted, flat and custom cut shapes and often used to pack highly sensitive equipment such as electronics and circuit boards.

1.1.10 Rafting Boats

Raft manufacturers use RPUFs to produce inflatable boats and surfboards, as it provides strength, buoyancy and sound deadening.

1.1.11 Adhesives/Binders

Polyurethanes can be used in the form of adhesives and glues for different types of subtrates such as glass, cardboard, wood, foams or rubber, so find application to in the houses and offices as binding agent. PU adhesives are commomly used in the manufacture of laminate packaging, construction of sandwich panels, flooring etc.

1.1.12 Textiles

PU is used in the manufacture of raincoats, shower curtains, diper linings, swimming suits etc. for being waterproof and light weight. Also PU fiber (spandex) is utilized in making stretchable clothings (in combination with other types of fibers) commercially known as Lycra.

1.2 Polyurethane Foams

PU foam is a versatile material and one of the most important classes of cellular plastics. Depending upon the chemical composition and the rigidity of the matrix material due to cross linking between the molecules, it may be categorized into rigid, semi-rigid or flexible. Polyurethane foam is infact a multipurpose polymeric material that is known for a series of engineering and industrial applications as listed above. The low density PU foam permits the design of many light weight structure such as sandwitch panels, crushing pads, composite materials for sports goods, tough material for interior panels of aircrafts and many more advanced materials. According to a survey carried out by Technavio in 2016, both flexible and rigid polyurethane has a significant share in global market. As, the foams behavior depends upon the type of cross-linking that exists between the molecules, open or closed cell structure of PU foam indicates its open or closed porous morphology [6]. Flexible polyurethane foam has open cell structure with interconnected pores as shown in Figure 1.3(a). This kind of foam has a relatively lower density and sponge like topography. They have sound absorbing properties along with their cushioning characteristics. They are mainly used in seats and interior of cars; cushioning and packaging; sports equipments and in mattresses and carpets manufacturing. Rigid foams have closed cell structure which does not have a network of connected cells, as shown in Figure 1.3(b). According to a study, the expected revenue earned by U.S. Polyurethane foam market (USD Million) is as shown in Figure 1.4.

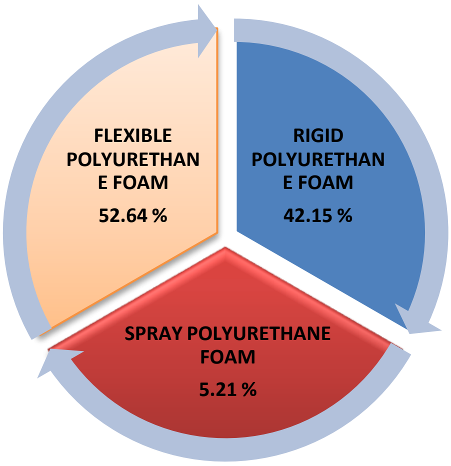


Figure 1.2: Global Polyurethane Foam Market by Type [7]**.**

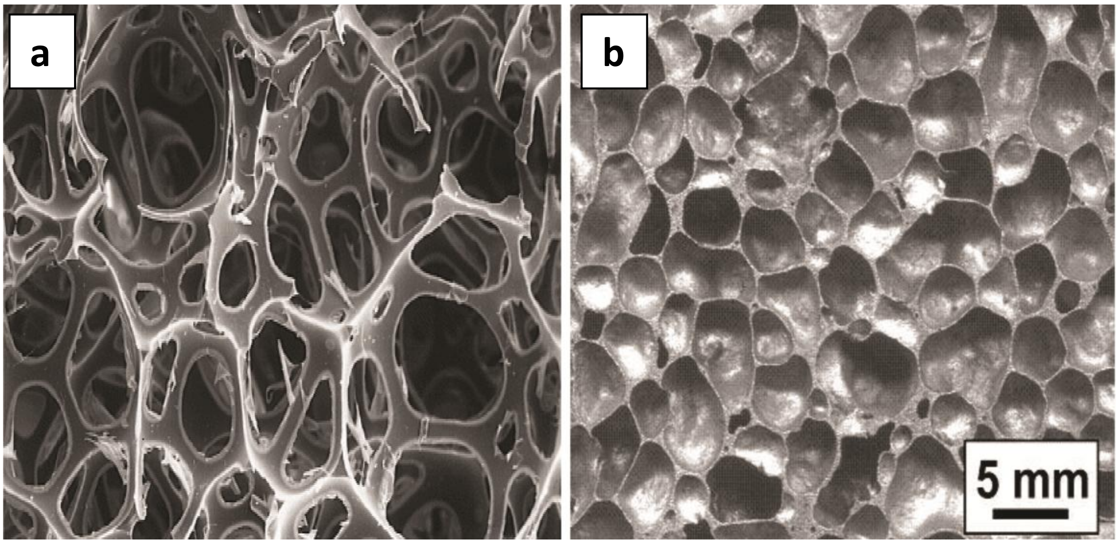


Figure 1.3 (a): Open Cell [8] **and (b) Closed Cell** [9] **Structure of Polyurethane Foam.**

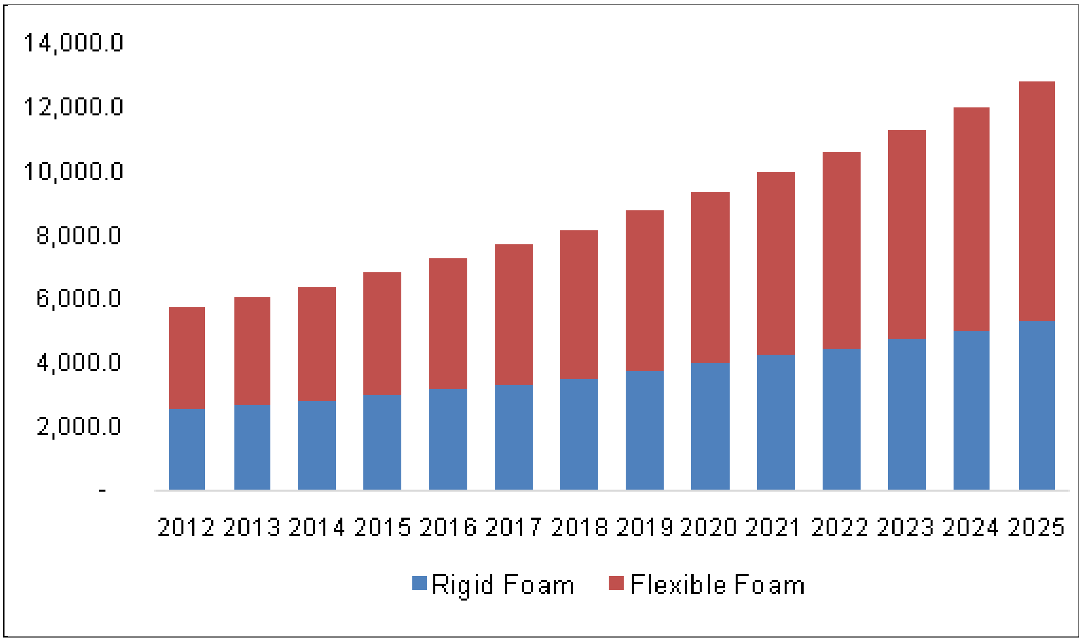


Figure 1.4: U.S. Polyurethane Foam Market Revenue by Product (USD Million) [10]**.**

1.2.1 Rigid Polyurethane Foams

Rigid polyurethane foams (PUFs) are one of the most widely used material in various engineering and industrial applications. Due to their light weight, excellent thermal insulation, good dimensional stability, low moisture permeability, easy processability, low density and high specific strength, they are the most suitable candidates for the manufacture of sandwich construction panel, false roofing and for thermal insulation of refrigerators and buildings [11-13]. RPUFs, in addition to being extremely energy-efficient, have very good mechanical properties, thus mainly used in sports equipment, horticulture, surface materials such as thermal insulation panels in buildings and for rock consolidation in mining [11–14]. Its structure makes it have a harder surface feel and makes it better at absorbing impacts.

Currently, RPUFs are the best thermal insulating materials available. Their thermal conductivity enables them one the most popular material for a range of applications.

Thus, thermal insulation is the key feature of RPUF for almost all of its applications. An add-on to this, due to wide range of density distribution and ability to adhere to different substrates enable RPUFs to be used as matrix material in composite production especially in construction industries. Due to their ease of processability, they can be produced directly in cavities, as desired. Due to its exclusive properties of extremely high thermal conductivity, high strength, low weight and easy processability, RPUFs are employed in a variety of applications at industries, buildings, houses and offices as insulants, sealants, polymeric concretes and as a substitute of wood.

1.3 Chemistry of the RPUF Formation

PUs are formed by step-growth polymerization reaction. During the reaction, monomers containing polyisocyanate groups (having more than one isocyanate functional groups; minimum two) react with another monomer containing polyol groups (having more than one hydroxyl groups; minimum two) in the presence of a catalyst and form urethane linkage (-NH-COO-). Reactivity of isocyanates determines the PU formation. Isocyanate group associated with arene is much more reactive and economical to use than the aliphatic one. The electron deficiency on the carbon atom of N=C=O group leads to the nucleophilic attack, thus the reaction is centered at the C=N bond, resulting in a urethane linkage (-NH-COO-) in the final product. During PU production, other materials such as catalysts, surfactants or blowing agents are also added to control the performance characteristics of the polymer to yield various forms of PUs like fibers, resins, elastomers, foams, coatings and adhesives. The generalized polyurethane reaction is:

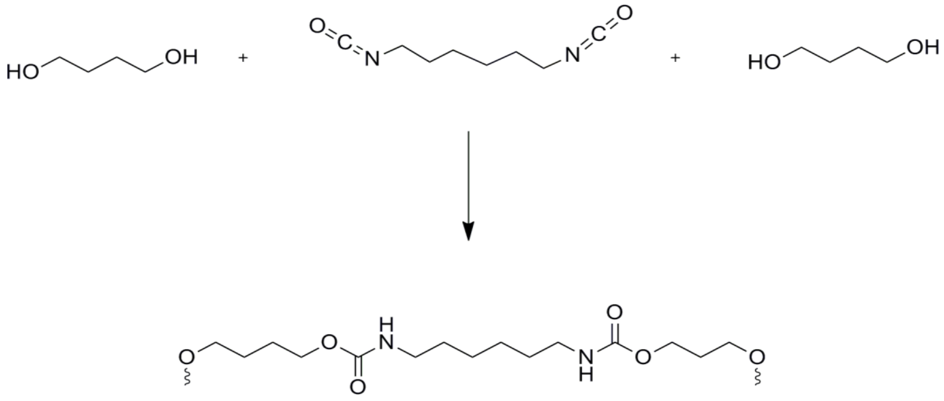


Figure 1.5: Generalized Polyurethane Reaction.

At laboratory scale, the polyurethane foam (PUF) can proceed in two steps. In the first step, all the ingredients i.e. Polyol, blowing agent and other additives (to induce specific properties) are mixed together into a premix, except diisocyanates and catalyst. In second step, premix is allowed to react with diisocyanates and catalyst to produce PUF. But in commercial processes all the reactants required for the polyurethane foam formulation are allowed to mix simultaneously in a single step [15]. Blowing agents present in the reaction mixture readily get evaporated due to the heat released and give rise to the cellular structure.

1.4 Reaction Profile

The formation of RPUF follows a defined reaction profile by ensuing successive steps of polymerization. The various characteristic stages define the progress of the RPUF formation.

1.4.1 Mixing Time

The mixing time, also known as stirring time corresponds to the time period required for mixing of reactants uniformally.

1.4.2 Cream Time

The cream or foaming time is the time duration between the start of mixing reaction mixture and the appearance of foaming. Generally, it is indicated by the change in color. It is characterized by cloudy appearance of reactants mixture and rise in volume.

1.4.3 Gel Time and String Time (Fiber Time)

The stage of the conversion of reaction mixure from the liquid state to the solid state represents the gel point (nearly 50% reaction is complete). Gel time is the time required for the formation of expanded foam having gel like texture after the completion of polymerization reaction. Further the String Time or Fiber Time is characterized by the formation of polymer strands or sting like cobweb after touching and pulling the foam with any tool.

1.4.4 Full Rise Time and Tack Free Time

Time required by the foam to reach its maximum height or largest rise is called Full rise time. It is the time lapse from the point of mixing of reaction mixture to the achievement of full rise of foam. Further, the moment of freedom from tack i.e. when the surface becomes free from tackiness, is called tack-free time.

1.4.5 Gas Release Time

The time duration between the start of mixing of the reaction mixture to the gas release by blowing agents is termed as the gas release time. This is common characteristics of open-celled foam.

1.5 PU from Vegetable Oil

The synthesis of vegetable oil based polyurethane has drawn great interest in the recent times [21-27] This growing worldwide interest is economically driven because vegetable oils are relatively inexpensive resource in comparasion to petrochemicals and also they are renewable. The rising environmental concern among the researchers and the scientist stimulates the use of vegetable oils and other renewable resources to produce polyurethane. Being agriculture based, they can be produced in abundance. Vegetable oils are composed of triglycerides of long chain fatty acids. By introducing hydroxyl functional groups into these enzymatically or chemically modified unsaturated fatty acid, vegetable oils can be converted into polyols. Several methods are identified i.e. transesterification, hydroformylation, ozonolysis followed by hydrogenation, etc. to add -OH group at the unsaturated sites to produce polyols. Different vegetable oils have been reported to be explored in the previous studies for PU production i.e. sunflower oil, soyabean oil, castor oil, palm oil and rice-barn oil. Many authors have used castor oil and lignins for the production of polyurethanes [16,17]. Ehrilich *et* al., 1959 and Leitheiser *et* al., 1969 reported that castor oil is an appropriate raw material which can be employed as a replacement to the petrochemical based polyol for PUFs production. RPUFs had also been reported to be synthesized from rhodium catalyzed hydroformylated polyols. It is reported that vegetable oil modified polyols based polyurethane rigid foams shows biodegradation behaviour [18–23].

Rigid polyurethanes foams (RPUFs) produced from the vegetable oil based polyols suffers from a drawback that they can display quite different properties as processing parameters may affect the overall properties of end products. Hence, the mechanical properties and process parameters of these RPUFs are needed to be optimized to control the reliability of the products and to improve cost. The most trustworthy and practical method to optimize the processing parameters is a statistical approach. To obtain the systematic data for the statistical approach, a good planning of the experiments with a range of varied parametric data is the main prerequisite. Taguchi DOE is one of most common statistical approach because of its easiness and reliability.

1.6 Optimization by Taguchi Method

Taguchi method is a consistent approach for knowing the finest grouping of inputs to give best product/service. Taguchi approach follows through DOE (design of experiments). Taguchi methods based techniques generally established on three basic concepts [24,25] i.e.:

- Quality is designed into the product instead of simply its inspection.
- Minimize the deviation from a target results into best quality.
- Losses should be determined system wide.

To categorize the working planes of the design aspects, system design play a vital role. The parameter design governs the factor levels that yield the finest presentation of the product. Tolerance scheme is employed to fine tune the results of parameter design by narrowing the factor tolerance with substantial impact on the product. Following this approach which leads to the identification of need for better materials, purchase of newer equipment and raising budget for inspection for end product.

1.7 Thesis Organization

The whole thesis is summarized in eight chapters. **Chapter 1** contains the technological significance of the field of this research. The principle, the technology, the potential applications along with scientific information related to this is summarized as introduction of thesis in this chapter. **Chapter 2** includes a comprehensive review of the available literature on Rigid Polyurethane Foam (RPUF) along with its characteristics, production and industrial applications has been conducted. A separate section is devoted to the Polyurethane derived from the renewable sources. The research aspects related to the PU production starting from the available source to the modification of the properties by the addition of reinforcing materials have been critically reviewed and gaps in the past research in the field are also highlighted in this chapter. As optimization is the best quantification tool for the design and developing of a system from the available resources, a comprehensive study on parametric optimization of mechanical properties using Taguchi Method has also been conducted and reported. Also, the aim of the research work is clearly highlighted. The research work and design is highlighted in the **Chapter 3**. This chapter describes the planning of the experimental studies starting from the study of physiochemical properties of raw materials. The challenges to achieve the aim, it is further bifurcated into specific experimental studies. This chapter also summarizes the scheme of work/methodology, characterization and design tools that have been utilized to achieve the desired objectives of the work. The experimental results and their significant findings to achieve specific objectives of the research work has been reported in Chapter 4, Chapter5, Chapter 6 and Chapter 7 respectively. **Chapter 4** is divided into two sections 4.1 and 4.2 respectively which deals with the effect of different formulation of MDI/Polyol on rigid polyurethane foams and function of silicon oil on the properties of foam. **Chapter 5** reports the reinforcement of RPUFs using glass fiber and its effects on mechanical properties of resulted foams are discussed in details. Further, effects of others fillers such as fly ash and calcium carbonate on properties of RPUFs has also been explored. **Chapter 6** discusses the parametric optimization of mechanical properties of rigid polyurethane foams by using Taguchi method. The chapter is sub divided into 4 sections i.e. Section 6.1, 6.2, 6.3 and 6.4 describing the parametric optimization of tensile, compressive and flexural strength and hardness of RPUFs respectively. Addition of the anti-flamming agents in the resulted optimized formulation of the RPUFs makes the studies complete. The experiment results and their significant findings by the incorporation of different anti-flammable agents in castor oil based RPUFs has been reported in **Chapter 7**. The comparative studies of the resulted anti-flammable foams have been presented with an emphasis on the properties of the developed material. Conclusion and future prospect of the study are included in the **Chapter 8,** which is followed by References. Supplimentry material is provided in the form of Appendix-I and Appendix-II giving details about the Physico-chemical study of raw materials and characterization tools employed to investigate the final RPUFs respectively. The material provided in as Appendixes is the standard procedure followed for the testing.

CHAPTER 2

LITERATURE REVIEW

The revolutionary work on polyurethanes was first carried out by Otto Bayer and his co-workers in the year 1937 [26]. The development of commercial polyurethane coatings and adhesives occurred between 1945 and 1947 which subsequently extended to the emergence of flexible foams in 1953 and followed by rigid foams in 1957 [27,28]. From such long time, polyurethane serves the mankind in its different roles such as adhesives, surface coatings, flexible foams, rigid foams and elastomers. Ever since the discovery of polyurethane, it has been used in the entire range of products from toys to aircraft parts and continues to get advanced with latest technology. PUs are a class of polymer that have urethane linkage between them and are formed by the reaction of isocyanates and polyols in the presence of catalysts and other additives. The type of the reactants i.e. isocyanates and/or polyols determines the physical state of final product i.e. solid, liquid or foamed. Polyurethane Foam (PUF) is one of the most important classes of cellular plastics which has been recognised for its multipurpose uses as cushioning material, structural panels, thermal insulations, packaging etc. The invention of the Polyurethane foams was the result of water accidentally introduced in the reaction mixture. Over the years a lot of successful industrial and engineering applications are added up to its achievements. Today, polyurethane foams represent the most important class of the cellular polymers and serves the mankind in its characteristics flexible and rigid foam, both having a boom in industrial application.

Taking in view of this industrially important cellular material, a detailed literature survey has been conducted on the rigid polyurethane foam (RPUF) starting from its raw materials and covering all aspects of its properties and industrial applications. Further, following the latest trend of environment friendly and renewable source based polyurethane especially the foams are also reviewed, as the present research is also based on the production of RPUF derived from vegetable oil i.e. castor oil and reported in the subsequent section. Since, the mechanical properties and process parameters of these RPUFs are needed to be optimized to control the reliability of the products and to make the resulted product more economic. For this, the most common statistical approach i.e. Taguchi DOE (design of experiment) is studied because of its easiness and reliability. A small section regarding the implementation of Taguchi DOE has been added as a section of this literature survey.

2.1 Rigid Polyurethane Foam

Rigid polyurethane foam (RPUF) is a cross-linked low density thermosetting polymeric cellular material that constitutes a high percent of closed cells [3]. Depending upon the volume occupied by them, they may be spherical or quasi spherical polyhedral [29]. RPUF is manufactured by the blowing of polyurethane matrix by means of a gas, released by a blowing agent. This PU matrix when solidify, it takes the state of foam. In RPUF polyurethane foam, the cells are made up of two structural parts: cell walls (called struts) and closed window areas (called voids). Due to closed windows in the cell walls, the air flow in the foam is restricted unlike flexible foams (with opened voids). This improves the thermal efficiency of RPUFs

[30]. Rigid polyurethane foams based materials are versatile, energy efficient and ecofriendly showing promising physical and mechanical properties [31]. The low thermal conductivity of rigid polyurethane foams makes it alternative option to conventional insulation product used for construction. Low thermal conductivity provides thinner insulation for any particular insulation level that is having a potential to fit easily in any building cavity. Moreover RPUFs based insulations are cost-effective and easy to install. Due to their ease in processability, Polyurethane based insulating materials are easily produced at the building construction sites. The excellent thermal insulation behaviour of rigid polyurethane foams attributed to closed cell structure which can be easily achieved using physical agents such as CO_2 or pentane [32]. Beside good insulation property, rigid polyurethane foam is also durable and dimensionally stable material and has an expected service life beyond 50 years. These light weight, energy efficient, moisture-resistant and eco-friendly rigid polyurethane foams having very good compressive and shear strength make it promising materials for building and construction fields, especially as insulation board for roofing, false ceiling, walls, floor, foam sealant and metal sandwich panels. RPUFs are reported to serve satisfactorily under extreme conditions of temperature without showing any deflection and deformation. They even resist the action of moisture due to condensation [33]. Due to extremely high compression strength, RPUFs may be used in many engineering applications such as a substitute of wood in the manufacture of decorating articles and in furniture and as roof support systems etc.

2.1.1 Preparation of Rigid Polyurethane Foams

High functionality polyols are mainly used to synthesize rigid polyurethane foams by the reaction with isocyanates and blowing agents. The additives are normally mixed to the polyol premix or isocyanate but they can also be put directly to the reaction vessel which is then filled with the reaction mixture [34]. For rigid foam preparation, high hydroxyl numbers of polyols are required i.e. 400-500 mg KOH/g [35]. PU foams are reportedly very combustible and hence to check their flammability, certain flame retardants are needed to be added in the polyol prior to the formation of foams. Fire retardancy can be gained by the use of halogen based compounds to the polyols. Melamine, aluminium trihydrate and phosphorous based FR reagents can be used in polyurethane products to gain fire retardancy. Standard stirrer is used to mix all the components. Normally RPUFs are foamed in moulds. Prepared foam can be used for various engineering applications.

2.2 Basic Components of Foams

Rigid Polyurethane foams are produced by reacting polyols with isocyanates using a catalyst, a physical or chemical blowing agent and other additives i.e. surfactant, etc. Different components to produce RPUFs are as given:

2.2.1 Polyol

In 1956, Dupont was the first commercialized different polyols such as polyether polyols, poly(tetramethylene ether glycol). In 1957, Low cost polyalkylene glycols were introduced by BASF and Dow chemical. Polyether polyols are wide spreadly used on commercial scale for the manufacturing of PU goods, as they are easy to handle, has good hydrolytic stability. Over the years, the polyols used for PU production have shown remarkable advancement. Today, in PU industry, two main types of polyols is used i.e. polyethers and polyesters. Propylene oxide is used with small quantity of ethylene oxide to make polyethers. Polyesters polyols are manufactured by the reaction of carboxylic acids and hydroxyl compounds. Properties of foams produced depend upon the functionality and molecular weight of polyols used during the reaction. It is easy to vary the functionality of polyether polyols as compared to polyester polyols that’s why the former is used to produce various types of foams such as rigid, semi-rigid, flexible and elastomers.

2.2.2 Isocyanates

Organic compounds that contain an isocyanate group (R-N=C=O) are referred to as isocyanates. They are very reactive compounds which enter several reactions with group containing active hydrogen. Nitro compounds are involved in the production of isocyanate compounds. Aliphatic and aromatic polyisocyanates are currently known which are used to produce resins, coatings, foams and fibres by polymerization reaction.

Isocyanate group associated with aromatic compounds is much more reactive and more economical to use than aliphatic one. For example: diphenylmethane diisocyanate (MDI), p-phenylenediisocyanate (pPDI), and toluene diisocyanate (TDI). MDI contains three isomers i.e. 4,4’-MDI, 2,2’-MDI and 2,4’-MDI which further on polymerization gives oligomers of functionality 3 and more. Insulated board stocks of polyisocyanurate are prepared by polymeric MDI (PMDI) due to presence of high functionality oligomers in it. Microcellular and flexible molded foams are synthesized by those PMDI which acquired high percentage of MDI monomers. For PU production, only a smaller volume of aliphatic isocyanates is reported to be employed. Hexamethylene diisocyanate (HDI) is mainly used to synthesize elastomers and light coatings. Aliphatic isocyanates are converted into dimers, prepolymers and biurets for commercial use due to their volatile nature.

2.2.3 Surfactant

Surfactants mainly play a major role in regulation of cell size, emulsification of liquid components and stabilization of cell structure. To get open and closed cell structures during PUF manufacturing, the role of surfactant is significant, as it greatly influence properties of the foam. Generally silicone surfactants which are copolymer of poly(dimethylsiloxane) $[-Si(CH_3)_2-O-]_n$, oxyalkylene chains, e.g. polyethylene oxide chains involved in urethane and related polymer foams.

2.2.4 Catalyst

Tertiary amines are compounds generally used to catalyze urethane reactions. Tetramehylbutanediamine (TMBDA) is also a catalyst that usually catalyzes gel reaction instead of blow reaction during polyurethane processing. The nature of reaction strongly depends upon the molecular structure of catalyst for example blow catalysts normally have either ether linkage and gel catalysts contain alkyl substituted nitrogen (e.g. triethylamine).

2.2.5 Blowing Agent

Blowing agents are used to produce gas bubbles in cellular polyurethanes. Generation of gas is one of the important parts of foam formation. Normally two types of gas generation technique are used i.e. physical and chemical. CO_2 gas is produced when isocyanate groups react with chemical blowing agents (CBA) [36]. Water, boric acid and enolizable organic compounds are used as CBA. On the other hand, physical blowing agents (PBA) exist in liquid form and possess low boiling point. PBA vaporize easily during foaming reaction and provide gas for the polymer expansion by undergoing physical change. Chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), n-pentane are physical blowing agents. Due to the threat of ozone layer depletion, the use of CFCs and HCFCs are restricted.

2.2.6 Flame Retardant

Polymers that are resistant to degradation at high temperature are known as fire safe polymers. Polyurethane products are highly flammable and during their use in the areas of public transportation strict fire regulations have to follow, due to fire threats. A high level of studies have been carried out to find effective flame retardant (FR) by many researchers but they did not get much success [37]. The major problems are heat release, surface flame spread and toxicity of gases. For polyurethane products, different types of flame retardants have been developed and are explored to be used in commercial PU products. Different anti-flamming agemnts work with probably different mechanism. During combustion halogen based FR reagents produced radical scavengers. Small quantities of flammable gases are produced when polyurethane products incorporated with phosphorous based FR reagents undergoes combustion reaction. Reactive type of FR reagents includes brominated polyethers, halogen or phosphorous containing polyethers while on the other hand non-reactive types include both organic as well as inorganic compounds.

A typical formulation for RPUFs is given in the Table 2.1.

Table 2.1: Typical Formulation of Rigid Polyurethane Foams

Sr. No.	**Components**	**Amount, pph**
1	Polyol	100
2	Crude MDI	Stoichiometric + 5 %
3	Blowing Agent	10-15
4	Catalyst (Triethylenediamine)	1-2
5	Surfactant (Silicone block copolymer)	1-3
6	Flame Retardant	15-20
Where pph – parts per hundred parts of polyol		

2.3 Application of Rigid Polyurethane Foams

Rigid polyurethanes foam is low density, light weight; dimensionally stable, strong materials that exhibited very good moisture resistance and a low vapor transmission behavior. The distinctive properties of RPUFs have make them popular to be used for different engineering applications [38].

1) Rigid polyurethane foams have been successfully utilized as thermal insulation materials in refrigerators, building panels as well as other similar insulating applications [39].
2) Now a day, rigid polyurethane foams utilized in packaging or crash padding to protect delicate objects because they have potential to absorb accidental impact significantly by undergoing large inelastic deformations[40].
3) In the field of construction rigid polyurethane foams have been used as sealants, polymeric concrete components and as insulant [31].

4) Beside the structural insulation and construction application, rigid polyurethane foam also utilized in horticulture, sports goods, furniture etc. [11].
5) They are also used in insulated pipes that are prepared by a casting technique, in which rigid polyurethane foam is filled inside the cavity between the inner pipe and outer jacket [41].

2.4 RPUF Derived from Renewable Sources

In recent years, an interest of synthesis of vegetable oil based polyurethane foams has increased significantly. Due to increasing prices of petrochemicals or due to environmental concern, recent research is more focussed on natural or renewable resources [48]. As polyols is one of the important raw materials in PU formation, it is desirable to obtain polyols from renewable resources rather than using petroleum based polyols which are disadvantageous in terms of production, energy and costs.

Due to increasing price of petrochemical feedstock’s as well as environmental safety point of view, vegetable oil derived polyols replacing increasingly petrochemical based polyols for the preparation of environmental friendly green products specially polyurethane [49,56-57]. Vegetable oils based polyurethane foams are relatively inexpensive because they are derived from renewable resources [42,43]. Vegetable oils contain triglycerides of long chain fatty acids with large number of unsaturated groups. With the help of chemicals and enzymes, that attak these unsaturated these unsaturated groups, vegetable oils could be converted into polyols. Although a number of vegetable oils such as soyabean oil, sunflower oil, castor oil, canola oil, rapeseed oil, palm oil, tung oil and rice-barn oil have been successfully utilized for polyols and polyurethane formulations [43–52] but castor oil is most economic and promising one that partially replace fossil fuel based polyols due to its volume and price stability. It is also found that castor oils have generally higher acetyl or hydroxyl value as compared to other biobased oils that will be beneficial for the synthesis of polyurethane foams. Many researchers have used castor oil and variety of lignin for the synthesis of polyurethanes, as the properties of the resulted product can be controlled by changing the hard and soft segment contents and utility of these products in biomedical industry [4,17,53,54]. Ehrilich *et* al., 1959 have successfully synthesized castor oil based polyurethane foams in place of petroleum based polyols [23]. Lu *et* al., 2005 have prepared polyurethane based biodegradable films using rapeseed oil based polyols and glycerol plasticized starch [55]. Similarly, soy flours incorporated rigid polyurethane foams was fabricated by Chang *et* al., in order to improve the physical properties and reduce the cost of the foams [56,57]. Rigid polyurethane foams had also been reported to be synthesized from rhodium catalysed hydroformylated polyols [58]. Structure & properties of vegetable oil based polyols and their subsequent application in polyurethane foams as well as biodegradation and thermal stability of the prepared foams extensively studied by various researchers (Petrovic *et* al, 2000 *et* al., Zlatanic *et* al., 2004) [42,59–61]. These vegetable oil based green polyurethane foams based products have been successfully utilized by Ford Motor Company [17].

Commercially available natural oils for synthesizing polyurethane foam are for example soyabean oil, castor oil, palm oil and rice-barn oil. Vitafoam Nigeria Plc, Lagos, Nigeria reported the extraction of castor oil from its seeds using a soxhlet extractor and further it was used wholly in the preparation of polyurethane foam. Also

PU forms were reported to be prepared from mixtures of castor oil and polyol (hydroxy-terminated polyether). The mechanical properties of the foams are comparable to that of 100% of commercial polyol. The foam synthesized by using pure castor oil was reportedly a semi-rigid foam [5]. Watsamon Saetae prepared glycerol based polyurethanes (GPUs). Polyol was produced from glycerol by reacting with a non polar group, such as castor oil, palm oil in order to modify properties of polyurethane [31]. It was found that types of oil affected the morphology of GPUs. GPUs from palm oil polyols and castor oil polyols had less bubbles in the foam structure. Table 2.2 gives the various renewable sources of polyols and the hydroxyl and acid values of the polyols derived. A work outcome by researchers on biobased polyurethane foams is given in the Table 2.3.

Table 2.2: Various Renewable Sources of Polyols

Sr. No.	Source of Polyols	Hydroxyl Value (mg KOH g^{-1})	Acid Value (mg KOH^{-1} g)	Reference
1	Ricinus Communis (RC) oil	160–168	2.45	[62]
2	CO-2ME MCO-AA MCO-HEA	286 258 218	0.98 2.74 4.94	[35]
3	Kraft Lignin	365	-	[63]
4	Rosin based polyester polyol	445	-	[64]
5	Coffee grounds wastes + PEG	287.2	9.8	[65]
6	N-635 polyether polyol	498	-	[66]
7	Mannich Polyol	452	0.76	[67]
8	Petrochemical polyol Rokopol Polyglycerol Pole Polyglycerol PGK	420 190 290	0.02 0.4 0.7	[68]
9	Polyether polyol 635 c Polyester polyol 3152	500 315	0.10 0.20	[69]
10	Jatropha oil Linseed oil	- -	2.1 2	[70]
11	Rapeseed oil	-	2.1	[46]
12	Liprol™ 270 Liprol™ 320	275 ± 1 323 ± 2	0.7 ± 0.1 2.0 ± 0.1	[51]

Where, CO: Castor oil, 2ME: 2-Mercaptoethanol, AA: Allyl Alcohol, HEA: 2-Hydroxyethylacrylate, PEG: Polyethyleneglycol, MCO: Mercaptanized castor oil

Table 2.3: Work Outcome by Researchers on Biobased Polyurethane Foams

Sr. No.	Author's Name	Year of Publication	Outcome	References
1	Ionescu, M. *et* al.	2016	Casted polyurethane resins were elastomeric or leathery when cured with aliphatic diisocyanate but moderately rigid when cured with HMDI and MDI. Castor oil based RPUFs demonstrated better strength.	[35]
2	Mahmood, N. *et* al.	2015	Compared with reference foams, bio-based rigid polyurethane foams synthesized from hydrolytically depolymerized Kraft lignin exhibit good mechanical properties. Foams produced are stable at temperature up to 200 °C.	[63]
3	Gama, N.V. *et* al.	2015	Mechanical properties, density, and thermal conductivity of viscoelastic bio-based polyurethane foams were assessed by using different concentration of surfactant, blowing agents and catalysts. By optimization of formulation good mechanical properties, thermal stability and conductivity have been obtained.	[65]
4	Gupta, R.K. *et* al.	2015	Rigid polyurethane foams were prepared by using bio-based mannich polyol showed thermal stability upto 250 °C and possessed high glass transition temperature (~200 °C). More than 90 % content of cells were found in closed state.	[67]
5	Gama, N.V. *et* al.	2015	Rigid polyurethane foam based on liquefied cork exhibited cellular structure with low value of density and thermal conductivity. And this foam was thermally stable up to 200 °C and presented Tg around 27 °C.	[71]
6	Piszczyk, L. *et* al.	2014	By increasing the number of polyglycerols in foams, it is found that there is increase in density and compressive strength of foam.	[68]
7	Pauzi, N.N.P.N. *et* al.	2014	Involvement of diaminopropane montmorillonite (DAP-MMT) nanoclay contents up to 4 wt% into palm oil increase the thermal stability and compressive strength of foams.	[72]
8	Li, X. *et* al.	2014	Lysine based ow density, closed cell foams	[69]

			were produced that had low density, high thermal stability and very high compressive strength.	
9	D’Souza, J. *et* al.	2014	Bark base foams showed lower modulus due to lack of cell membrane elastic stretching but possessed similar foaming kinetics and T_g compared with polyethylene glycol based control foam.	[73]
10	Ribeiro Da Silva, V. *et* al.	2013	Incorporation of rice husk ash into Tung oil based polyurethane foams showed some noticeable changes foam properties such as thermal conductivity (TC), density, and foam morphology. Higher value of TC was observed but there was no change found in thermal stability by the addition of rice husk ash content into foams.	[74]
11	Suresh, K.I. *et* al.	2013	Cardanol based rigid polyurethane foams were prepared which showed good physical and mechanical properties.	[75]
12	Li, Y. et al	2012	Involvement of cellulose nanowhiskers (CNWs) into lignin based polyurethane foams showed good thermal and mechanical properties.	[76]
13	Cardoso, G.T. *et* al	2012	In heat conditions, based on dynamic climate approach, the response of the thermal insulation lining of rigid polyurethane foam was studied. PU foam derived from castor oil showed decomposition at approximately 170 $^{\circ}$C and can be applied to thermal insulation of roof system.	[77]
14	Fan, H. *et* al	2012	Microsphere and nanoclay fillers (1-7%) were incorporated into soybean oil based polyurethane foams. Resuls showed a decrease the density of foam. With the increase in the content of microspheres, the compressive strength of the resulted foam receded. But with further increase in the microsphere, compressive strength was reportedly enhanced. At 7% amount of microsphere, the foams produced had significantly high compressive strength comparable to that of 100 % of petroleum based polyol foam.	[78]
15	Yang, L.T. *et* al	2012	Epoxidized soybean oil based PUFs reportedly had higher density and compressive strength.	[43]
16	Tan, S. *et* al.	2011	Soybean oil based polyol (SBOP) was used to synthesize the polyurethane foams which showed good thermal conductivity and closed cell content, higher Tg and compressive strength.	[79]

17	Palanisamy, A. *et* al.	2011	Karanja oil based polyols were used to prepare PU foams by water blown process. The resulted foams exhibited good mechanical properties such as compressive and flexural strength.	[80]
18	Kashif, M. *et* al.	2011	Castor oil base polyurethane presented antibacterial activity.	[62]
19	Ghosh, S.B. *et* al.	2010	Soy polyol based PU foams showed polygonal cell structure and good density and compressive strength.	[81]
20	Zhi-ming, L. *et* al.	2009	Lignin based polyurethane foams exhibited lower value of mechanical properties than that of the control sample.	[82]
21	Lim, H. *et* al.	2008	PU foams prepared from crude 4,4-diphenylmethanediisocyanate (CMDI) and polypropylene glycols (PPGs) for a different range of surfactant concentration showed improved reaction profile. Density of foam reduced quickly to a minimum at 0.5 pphp (part per hundred polyols) surfactant due to the increased blowing efficiency with surfactant.	[11]
22	Lee, C.S. *et* al.	2007	Mechanical and thermal properties of polyurethane foam showed improvement by the addition of epoxidized diethanolamides and oxazolidone heterocyclic rings.	[31]
23	Husic, S. *et* al.	2005	Soypolyol based polyurethane showed comparable tensile and flexural strength with those composite based on petrochemical polyol.	[83]
24	Armenta, J.L.R. *et* al.	2004	It was found that in polyurethane with increasing number of cellulose derivatives higher value of storage modulus observed and also the capacity of foam to dissipate energy increased.	[84]
25	Mythili, C.V. *et* al.	2004	Cardanol based polyurethane rigid foams (PURFs) and commercially available polyol based tough polyurethane were prepared. It was found that cardanol based PURFs possessed higher hardness and more stable in chemical reagents than tough polyurethane.	[85]
26	Swamy, B. K. K. *et* al.	2003	High density chain extended PUs were produced. 1,6-hexane diol system yields higher dimensional stability and lower tensile strength compared to 1,4-butane diol system. The variation of tensile strength with respect to diisocyanate is in the order: MDI > TDI > HMDI.	[17]

The investigations show that the forms synthesized from castor oil polyols compare favourably with semi-rigid forms (synthesized using petrochemical based polyols). The desired properties can be enhanced using additives and fillers. The rigid polyurethane produced from these bio-based sources have mechanical and thermal properties comparable to that of petrochemical based PUFs and may be used in many engineering applications.

2.5 Optimization

The need for optimization is to enhance the reliability of the products and to produce it more economically with financial gain. In simple words optimization of a product and its parameters aid in its quality and reduce in its cost. Statistical approach for optimization is accomplished through DOE (design of experiments). A mathematical model was developed by Arun kumar N. *et* al using response surface methodology (RSM) to optimize the procedure of polyurethane coatings. With the help of RSM they optimized the parameters such as paint flow rate, applicator distance, and paint viscosity to get the minimal value of dry film thickness (DFT) and high value of distinctness of image (DOI) and rating value (R) to decrease overall method cost [86]. Taguchi DOE was also used to synthesize thermoplastic polyurethane based nanocomposite reinforced with organoclay [87]. Recently, optimization phenomenon was used by Bil M. *et* al for bone tissue to optimize the PU structure [88]. Bratov A. *et* al optimized the composition of ammonium ion sensitive membrane based on a photocurable aliphatic urethane diacrylate oligomer for proper functioning of membrane [89]. Multi-layered noise control systems are widely used in production vehicles to reduce interior noise level. M. K. Ling examined the design optimization of polyurethane cored three layered carpeting which allows performance to be assessed before expensive road trials are carried out [90]. Eslick J. *et* al used stochastic optimization method for predicting the physical and chemical properties of polyurethane structures. They described an extension of the use of connectivity indices within a computational molecular design framework to the design of novel polyurethane structures [91]. Im E.J. *et* al used optimization method to get a solid product with a high I_2 number under pyrolysis conditions of polyurethane [92]. Nouranian S. *et* al used Taguchi L_{27} orthogonal array to study the effect of parameters on the adhesion between plasticized PVC layers and polyurethanes [93]. Portugal F. C. M. *et* al optimized PU foams to increase the sorptive extraction of herbicides in water matrices [94]. El-Shekeil Y. A. *et* al employed Taguchi L_9 orthogonal array to optimize the fiber amount of cocoa pod husk fiber in polyurethane composite [95]. With the use of RSM and central composition design, Wen T.C. *et* al studied optimization of conductivity for polyurethane and liquid electrolytes [96]. Dynamic optimization was performed by Zavala *et* al. for polyurethane production [97]. Nuclease P1 was produced by Zhu Y. *et* al from Penicillium citrinum by the process of optimization [98].

2.6 Gap in Literature

Presently, most of petrochemical based materials are used to produce polyols in PU manufacturing. But these materials are expensive and require high technology processing systems. Moreover, the formation of polyols from petrochemical uses huge amount of energy, in form of heating, carried out in 3-4 steps. Due to the harmful effects of petrochemicals, there is a need to develop such novel polymeric materials that could replace these non-ecofriendly raw materials with such materials that fulfil our requirements, exhibiting similar or better properties. After a few simple treatments, they can be converted into polyols for making polyurethane. Vegetable oil based polyols are gaining attention, because

- Petrochemicals based materials are non-renewable and the costs of petrochemical feedstocks are rising due to depleting fossil fuel resources.
- Petrochemicals based materials require high technology processing systems and involves a huge amount of energy.
- Polymers derived from petroleum sources do not undergo biodegradation on disposal, thus causing unnecessary waste which end up in landfills or create large amounts of pollution and greenhouse gases if incinerated.
- Boosted public wish for eco-friendly green products.

As PUs formed by vegetable oil is bio-based, so they do not pose much hazard to the environment. But, as the various studies reveal, it is observed that the properties of these products are not as good as that of the foam derived from petroleum based raw materials. So, the properties especially mechanical, thermal, and anti-flammability properties of these foams are needed to be enhanced by incorporating various reinforcing fillers and anti-flamming agents. To develop a high-quality material with just right properties, the right ingredients should go together, which might be quantified through design of experiments (DOE). For this, there is a requirement of suitable optimization tool.

2.7 Objective of the Research Work

During this PhD programme, we synthesized bio-based rigid polyurethane foam with anti-flammable properties using castor oil. The castor oil was used specifically, as it is found to be the most promising agriculture based product that contains hydroxyl groups naturally and shows a competence to replace petroleum in the formation of polyols, due to its abundance and price stability. Moreover, the modern trend of using bio-based and renewable materials in apprehension to the environmental issues also supported the idea. Here I summarise my objectives of the research programme.

The targeted objectives of the work were as follows:

a) Development of Castor Oil based Rigid Polyurethane Foam (RPUF) and to investigate the variation of process parameters like MDI/Polyol ratios and function of silicon oil on the properties of the foam.

b) To enhance the mechanical properties of RPUFs by the addition of reinforcing materials.

c) Optimization of reinforcing material composition in castor oil based RPUFs by Taguchi Method, using design of experiment (DOE) to propose an Engineering material with enhanced mechanical properties.

d) To enhance the anti-flammability of the castor oil based RPUFs using different types of flame retardants and studies their effects.

CHAPTER 3

RESEARCH WORK AND DESIGN

3. Experimental Section

The experimental section of the study is undertaken in the following heads:

3.1 Raw Materials/Chemicals

3.2 Research Design/Methodology

3.1 Raw Materials/Chemicals

In the present study, following raw materials/chemicals are used:

1) Castor oil (source of –OH- group)
2) Glycerol (for the modification of castor oil)
3) 4,4’-diphenylmethanediisocyanate Methylene chloride (MDI)
4) Cobalt octoate (Catalyst1)
5) Triethylenediamine (Catalyst 2)
6) Silicon oil (Surfactant)
7) n-Pentane (Blowing agent)
8) Chopped Glass fiber (Filler1)
9) Flyash (Filler 2)
10) Calcium carbonate (Filler 3)
11) A-189 gamma- Mercaptopropyltrimethoxysilane (Coupling agent)
12) Melamine (Anti-flamming agent 1)
13) Tris(1,3-dichloro-2-propylphosphate) (Anti-flamming agent 2)
14) Tris(2-chloroethyl)phosphate (Anti-flamming agent 3)

3.1.1 Specification and Sources of Raw Materials/Chemicals

Specification and sources of raw materials/chemicals used in the studies are given in Table 3.1.

3.1: Specifications and Sources of Raw Materials/Chemicals

Sr. No.	Chemicals	Source	Specification
1	Castor oil	Shivathene Linopack Ltd. Parwanoo, Himachal Pardesh	AR Grade
2	4,4’-diphenylmethanediisocyanate	Shivathene Linopack Ltd. Parwanoo, Himachal Pardesh	AR Grade
3	Methylene chloride	Standard Chemicals (ISO 9001:2008 certified), Delhi	AR Grade
4	Cobalt octoate	Standard Chemicals (ISO 9001:2008 certified), Delhi	AR Grade
5	Triethylenediamine (TEDA)	Standard Chemicals (ISO 9001:2008 certified) Delhi	AR Grade
6	Flyash	Standard Chemicals (ISO 9001:2008 certified) Delhi	Commercial Grade
7	Chopped Glass fiber (25µm in diameter)	Standard Chemicals (ISO 9001:2008 certified) Delhi	Commercial Grade
8	A-189 gamma-Mercaptopropyltrimethoxysilane	Standard Chemicals (ISO 9001:2008 certified) Delhi	AR Grade
9	Melamine	Standard Chemicals (ISO 9001:2008 certified) Delhi	AR Grade
10	Tris(1,3-dichloro-2-propylphosphate)	Standard Chemicals (ISO 9001:2008 certified) Delhi	AR Grade
11	Tris(2-chloroethyl)phosphate	Standard Chemicals (ISO 9001:2008 certified) Delhi	AR Grade
12	Silicon oil	Central Drug House (P) Ltd., Delhi	AR Grade
13	Calcium carbonate	Central Drug House (P) Ltd., Delhi	AR Grade
14	n-Pentane	Central Drug House (P) Ltd., Delhi	AR Grade
15	Glycerol	Sisco Industries Pvt. Ltd.	AR Grade

3.1.2 Purification of Raw Materials/Chemicals

The precision of the results is not only dependent on the instrument and experiment performed, but also to some extent to the purity of the substance/materials used. The percentage purity of the chemicals used in experimentation is given in Table 3.2.

3.2: Percentage Purity of the Chemicals

Sr. No.	Chemicals	Percentage Purity
1	Castor oil	99 %
2	4,4’-diphenylmethanediisocyanate	Approx. 99%
3	Methylene chloride	Approx 99%
4	Cobalt octoate	99 %
5	Triethylenediamine (TEDA)	99 %
6	Flyash	99 %
7	Chopped Glass fiber (25μm in diameter)	99 %
8	A-189 gamma-Mercaptopropyltrimethoxysilane	99 %
9	Melamine	99 %
10	Tris(1,3-dichloro-2-propylphosphate)	99 %
11	Tris(2-chloroethyl)phosphate	99 %
12	Silicon oil	99 %
13	Calcium carbonate	99 %
14	n-Pentane	99 %
15	Glycerol	99.9 %

3.2 Research Design/Methodology

The systematic methodology highlighting how the progress of proposed work towards achieving desired objectives was proceeded, involves the following steps:

- Physicochemical studies of raw materials
- Chemical modification of Castor oil by using Glycerol
- Synthesis of Rigid Polyurethane Foams (RPUFs) with an aim to investigate the:
    - ➢ Effect of Different Formulations of MDI on RPUFs
    - ➢ Function of Silicon oil on the Castor oil based RPUFs
    - ➢ Outcomes of the Addition of Reinforcing Filler i.e. Glass Fiber on the properties of RPUFs
    - ✓ Optimization of reinforcing material composition in RPUFs by Taguchi Method, using design of experiment (DOE)
    - ✓ Effect of Different Anti-flamming Agents on RPUFs.

3.2.1 Physicochemical Studies of Raw Materials

The properties of the final product are very much dependent on the raw materials used. Thus, the study of physiochemical properties of raw materials is an important step in the RPUF production. The following properties were studied during our research.

3.2.1.1 Determination of Acid Value of Vegetable Oil

Acid value of oils were determined as per the standard ASTM D 4662-98 procedure [51]. Acid value of the oils gives an idea about the oxidative behaviour of the oils. The detailed procedure for the calculation of acid value of the oil is as given in Appendix-I.

3.2.1.2 Determination of Hydroxyl Value of Vegetable Oil

The standard process followed for determining the hydroxyl value is as per ASTM D 1957-86 [99,100]. The final state of polyurethane foam produced depends upon the hydroxyl value of polyol used. Rigid polyurethane foam shows good physical and mechanical properties with higher hydroxyl value of polyols. The detailed procedure for the calculation of hydroxyl value of the oil is as given in Appendix-I.

3.2.1.3 Determination of Viscosity of Oil

Viscosity is the property of a fluid which enables the adjacent layers of fluid to slide over each other under the action of frictional forces. It is a property arising from collisions between neighboring particles in fluid that are moving at different velocities. Sample viscosity was determined by using Brookfield viscometer (ASTM D 4878 -98). The detailed procedure for the determination of viscosity of oil is as given in Appendix-I.

3.2.1.4 Determination of Specific Gravity

It is a dimensionless quantity. The standard way to measure the specific gravity is ASTM D 4669-98. The procedure followed for the determination of specific gravity of oil is as given in Appendix-I.

3.2.1.5 Determination of Percentage NCO

The % of NCO content is the unique property of polyisocyanates and measured by standard ASTM D 1638-74. The detailed procedure for the calculation of percentage of NCO is as given in Appendix-I.

3.2.2 Chemical Modification of Vegetable Oil

By introducing hydroxyl functional groups into enzymatically or chemically modified unsaturated fatty acid, vegetable oils could be converted into polyols. There are different techniques which are used to introduce -OH group to the unsaturated system.

a) Transesterification.
b) Reaction of CO & H_2 with unsaturated system to introduce formyl group tracked by hydrogenation.
c) Reaction of Peroxide acid with unsaturated system to form epoxide tracked by oxirane opening.
d) Reaction of unsaturated system with O_3 tracked by hydrogenation.

All these approaches produce polyols [68,101–104].

In our research work we used transesterification method to introduce hydroxyl group in castor oil.

3.2.2.1 Transesterification of Castor Oil using Glycerol

Transesterification process was employed to introduce more hydroxyl groups in castor oil. Glycerol is used to enhance the hydroxyl number of castor oil. The modification of castor oil was carried out under the inert atmosphere i.e. in the presence of nitrogen. The reactor used for oil modification has four-necked glass reactor of 500 mL capacity with 180 mm height and 90 mm diameter 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 an oil bath.

Reactor was supported on a circular copper plate with in the oil bath. Nitrogen gas was used at a constant flow rate to avoid any oxidation reaction within the reactor. Reflux condenser was also used to minimize the carry over losses. The reaction kettle was charged with castor oil and glycerol. The reacting contents were heated to a temperature of 220 ± 10 °C. The stirring speed is kept constant at 1000 rpm.

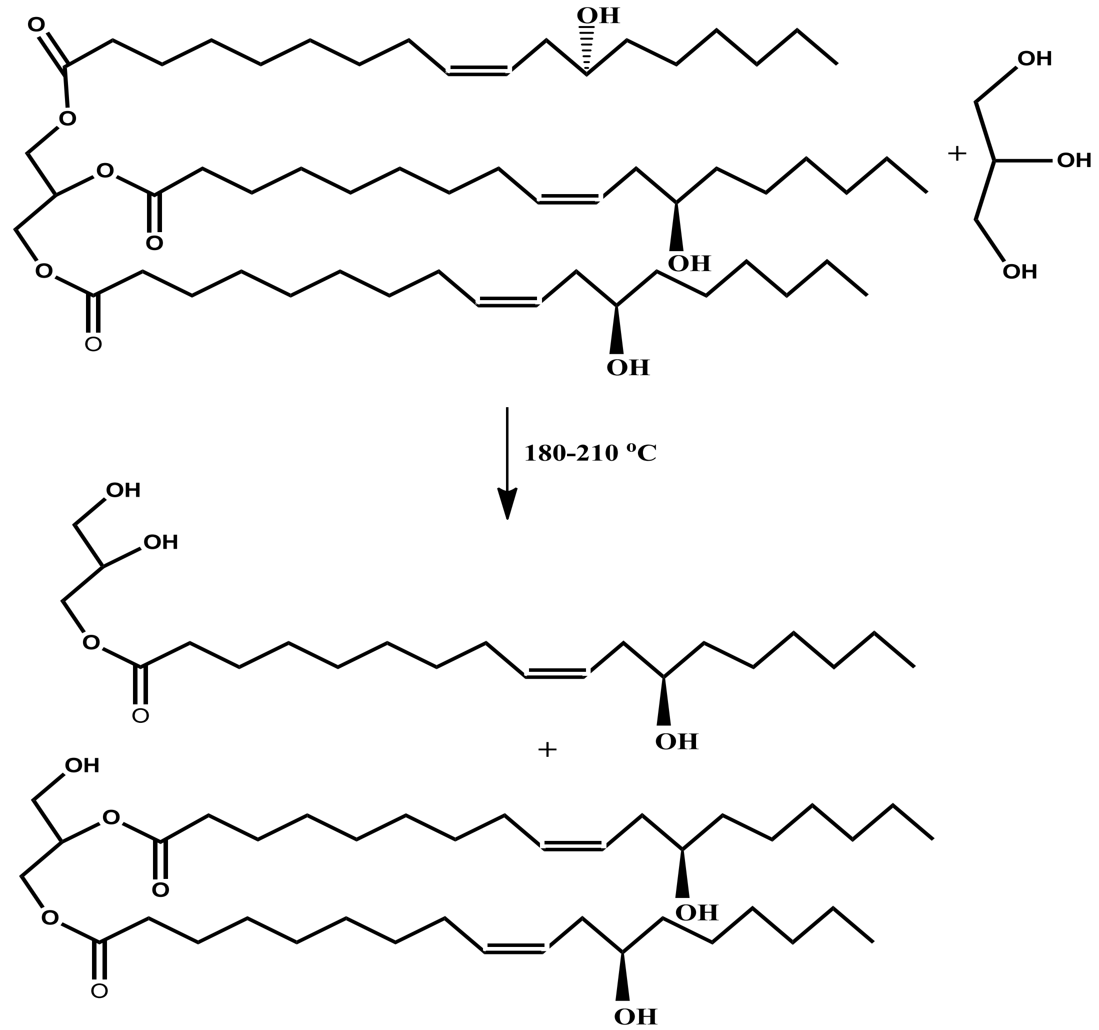


Figure 3.1: Polyol Based on Glycerol -Castor Oil Formulation.

The progress of reaction was confirmed by checking the hydroxyl value of the reaction mixture. 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 390-410 mg KOH/g is achieved. Approximately time 4-5 h was required to complete the reaction. The modified polyol was stored in dark bottles away from direct sun light. Figure 3.2 represents the polyol based on glycerol – castor oil formulation.

3.2.3 Synthesis of Rigid Polyurethane Foams (RPUFs)

The polyols (Mpol), catalyst, blowing agent, filler or reinforcing material, silicon oil and anti-flamming agent were added in the reaction kettle and thoroughly mixed under controlled temperature conditions at 35 ± 2 $^{\circ}$C. Calculated amount of MDI based on NCO/OH ratio was taken and mixed carefully by high-speed mechanical stirrer at 1200 rpm. A metal mould (100x100x10 mm^3) coated with releasing agent i.e. silicon oil was used to pour the resulting reaction mixture. The mould was thus closed and kept under a load of about 10 kN. To ensure complete curing, the foam thus produced was left to stand for 24 hours before it was tested. After demoulding, the resulted foam was cut into desired dimensions and tested for its visual colour, tensile strength, compression strength, flexural strength, hardness, density, water absorption, thermal stability, antiflammability and morphology. The selected range of the RPUFs formulations for studying the effects of different parameters (as reported in section 3.2) is given in Tables 3.3 – 3.6.

Table 3.3: Formulations to Study the Effect of MDI: Polyol Ratio (in pbw) on RPUFs

Samples	MDI	Mpol	Cobalt octoate	n-Pentane	Silicon oil
Formulation 1	30	30	2	20	3
Formulation 2	60	30	2	20	3
Formulation 3	90	30	2	20	3

Table 3.4: Formulations to Study the Effect of Surfactant (in pbw) on RPUFs

Samples	MDI	Mpol	Cobalt octoate	Methylene chloride	Silicon oil
Formulation 1	110	100	3	20	3
Formulation 2	110	100	3	20	6
Formulation 3	110	100	3	20	9

Table 3.5: Formulations to Study the Effect of Incorporation of Glass Fiber (in pbw) in RPUFs

Samples	Glass Fiber (wt %)	Mpol	TEDA	C-109-66-0	C-63148-62-9	MDI
GF-00	00	100	2	15	3	110
GF-05	05	100	2	15	3	110
GF-10	10	100	2	15	3	110
GF-15	15	100	2	15	3	110

Table 3.6: Formulations to Study the Effect of Anti Flamming Agents (in pbw) on RPUFs

Samples	Flame Retardants	Mpol	TEDA	n-Pentane	Silicon oil	MDI
AF-00	Neat	100	2	15	3	110
AF-01	Melamine	100	2	15	3	110
AF-02	TDCPP	100	2	15	3	110
AF-03	TCP	100	2	15	3	110

Where pbw: parts by weight

3.2.3.1 Characterization of the Synthesized RPUFs

Characterizations of the final products formed were done by using FTIR, TGA, XRD, UTM, SEM, Durometer (Shore) Hardner and UL-94. The detailed procedures followed for the characterization of RPUFs along with the instrument used is given in Appendix-II.

3.2.4 Optimization of Reinforcing Material Composition in RPUFs

Mankind has always had a fascination with quality. Today’s technology bears testimony to man’s incessant desire to provide a higher level of quality in products and services to increase market share and profits. In the present studies, Taguchi design of experiments L_{18} orthogonal array has been used for the optimization of reinforcing material composition in resulted Rigid Polyurethane Foams (RPUFs). Due to reliability, the most common statistical approach used is Taguchi Design of Experiment (DOE).

3.2.5 Experimental Design Strategy

Experiment Design Strategy, as suggested by Taguchi deals with the study of orthogonal array to examine the consequences of applied processing limits used in a small set of experiments [24,25,105]. There are two dissimilar ways to conduct the entire analysis. The result of single run is managed through key effects via ANOVA is the first way and the second one is to apply S/N ratio (signal to noise ratio) for multiple runs for the similar step [106]. The S/N ratio gives a synchronized value.

3.2.6 Steps in Experimental Design and Analysis

The important steps are involved in design and their analysis is as follows:

3.2.6.1 Choice of Orthogonal Array (OA)

- Choice of process limits or parameters to be assessed
- Choice of number of levels for the selected limits

Table 3.7 Selected Process Limit and their Levels

Representation	Process Limit	Unit	Level 1	Level 2	Level 3
A	Filler	-	Flyash	$CaCO_3$	-
B	Polyol	-	2:1	3:1	4:1
C	Surfactant	-	1%	3%	5%
D	Catalyst	-	Cobalt Octoate	TEDA	DBTDL
E	Blowing Agent	-	5%	10%	15%
F	Antiflamming Agent	-	Melamine	TDCPP	TCP

Table 3.8 L_{18} OA (Limit Allotted) with Response

Exp. No.	Run Order	Limits Trial Conditions							Response (Raw Data)			S/N ratio (db)
		A	B	C	D	E	F	e	R_1	R_2	R_3	
		1	2	3	4	5	6	7				
1		1	1	1	1	1	1	-	X_{11}	X_{12}	X_{13}	S/N (1)
2		1	1	2	2	2	2	-	X_{21}	X_{22}	X_{23}	S/N (2)
3		1	1	3	3	3	3	-	-	-	-	-
4		1	2	1	1	2	2	-	-	-	-	-
5		1	2	2	2	3	3	-	-	-	-	-
6		1	2	3	3	1	1	-	-	-	-	-
7		1	3	1	2	1	3	-	-	-	-	-
8		1	3	2	3	2	1	-	-	-	-	-
9		1	3	3	1	3	2	-	-	-	-	-
10		2	1	1	3	3	2	-	-	-	-	-
11		2	1	2	1	1	3	-	-	-	-	-
12		2	1	3	2	2	1	-	-	-	-	-
13		2	2	1	2	3	1	-	-	-	-	-
14		2	2	2	3	1	2	-	-	-	-	-
15		2	2	3	1	2	3	-	-	-	-	-
16		2	3	1	3	2	3	-	-	-	-	-
17		2	3	2	1	3	1	-	-	-	-	-
18		2	3	3	2	1	2	-	X_{181}	X_{182}	X_{183}	S/N (18)
Total									$\sum$	$\sum$	$\sum$	

3.2.6.2 Experimentation and Data Collection

The experiments were conducted for every single trial condition. Each experiment at a trial state is repeated and the data (raw data) are recorded against each trial condition and S/N ratios of the repeated data points are calculated and recorded against each trial condition.

3.2.6.3 Data Analysis

Out of various methods of data analysis suggested by Taguchi, the following methods are explored in the present studies:

1) ANOVA applied for raw data
2) ANOVA applied for S/N data
3) Graphs for S/N response

And the plot of plots of average response curves are drawn for each level of a parameter is drawn to indicate the trend followed.

3.2.6.4 Prediction of Mean

The mean is assessed from the significant parameters given by ANOVA. If A and B are significant parameters, A_2B_2 (2^{nd} level of A i.e. A_2 and 2^{nd} level of B i.e. B_2) is the optimal condition. The optimal value of the response i.e mean at the optimal condition can be give [24,106]as:

$$\mu = \bar{T} + (\bar{A}_2 - \bar{T}) + (\bar{B}_2 - \bar{T})$$

$$\mu = \bar{A}_2 + \bar{B}_2 - \bar{T}$$

Where,

$\bar{T}$ = Overall response mean

$\bar{A}_2$, $\bar{B}_2$ = Average response at the 2^{nd} levels of parameters A and B respectively.

3.2.6.5 Confidence Interval

Two categories of confidence interval are suggested by Taguchi in r/o the estimated mean of optimal conditions.

1) Estimated average of a treatment condition based on the experiment, designated as CI_{POP} (confidence interval for the population).
2) Estimated average of a treatment condition based on the confirmation experiment (for the verification of the predicted values), designated as CI_{CE} (confidence interval for a sample group).

The confidence interval are calculated [34,109] as:

$$CI_{CE} = \sqrt{F_a\ (1, f_e\ )V_e\ [\frac{1}{n_{eff}} + \frac{1}{R}]}$$

$$CI_{POP} = \sqrt{\frac{F_a\ (1,f_e)V_e}{n_{eff}}}$$

Where,

$F_a(1, f_e)$ is the ratio at the confidence level of (1-α) against DOF 1 and error DOF f_e.

$$N_{eff} = \frac{N}{1+[DOF\ associated\ in\ the\ estimate\ of\ mean\ response]}$$

N: Total number of results

R: Sample size for confirmation experiments

V_e: Error variance

3.2.6.6 Confirmation Experiment

The confirmation experiments are conducted to confirm the conclusions drawn from prior set of experimental studies. These finally confirm the significant parameters for ideal situations, as these are based on the selected number of tests conducted under definite conditions. Also, the insignificant parameters are set and implemented at economic levels. The average of the results of confirmation experiments is compared with the anticipated average taking parameters and levels as basis. To reach to the conclusion, the carrying out of confirmation experiments is highly suggested.

CHAPTER 4

INVESTIGATION OF DIFFERENT PROCESS PARAMETERS

Studies have been conducted to investigate the effect of varying parametric conditions on the properties of castor oil based polyurethane foams (RPUFs) with a purpose to design and develop an environment friendly high strength light weight material for multipurpose use. This Chapter is divided into two sections 4.1 and 4.2 respectively which deals with the effect of different formulation of MDI/Polyol on rigid polyurethane foams and function of silicon oil on the properties of foam.

4.1 Effect of Different Formulations of MDI on RPUFs

The rigid polyurethane foams (RPUFs) had been produced by the reaction of MDI with castor oil based modified polyols. The studies had been conducted to investigate the effect of varying the MDI:Castor oil ratio on the properties of RPUFs. The various polyurethane formulations used are as reported in Table: 3.3. Results and Discussion of effect of different formulation of MDI:Castor oil ratio is given here.

4.1.1 Visual Studies

Formulation 1 constitutes a conventional polyurethane composition and it contains MDI and Polyol in the ratio 1:1. The product of this formulation has a spongy texture and it is quite weak. Formulation 2 contains MDI : Polyol ratio as 2:1 and consequently found somewhat better in terms of strength and formulation 3, containing MDI : Polyol ratio of 3:1 is very strong and stiff. It was observed that in all the products obtained, the intensity of the yellow color was more. The reason behind this is the yellow colour of natural castor oil itself. However, if castor oil is bleached prior to the formation of foams, the resulted foam produced would range from colourless to white. In addition, the foam can be made coloured by the addition of dyes or pigments during the processing itself.

4.1.2 FTIR Spectra

A Fourier Transform Infrared (FTIR) spectrometer was employed to analyze the structure of polyols and polyurethanes. Spectra were recorded on Nicolet 380 spectrometer in the range 400-4000 cm^{-1}. Sample was tested in the form of pallets made with KBr. Figure 4.1.1 (a) shows the characteristic absorption peaks of polyols and MDI at 3402 cm^{-1} (O-H stretching frequency), 2925-2851 cm^{-1} (-CH_2 and -CH_3 stretching frequency) and 2268 cm^{-1} (-NCO stretching frequency).

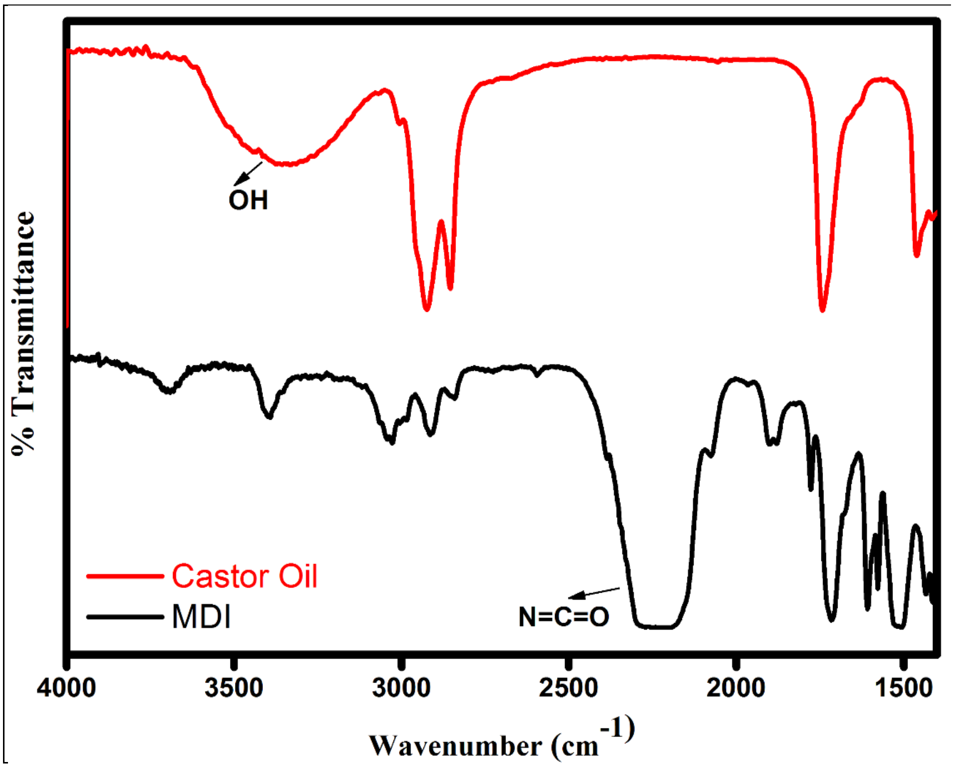


Figure 4.1.1(a): FTIR Spectra of Polyol and MDI

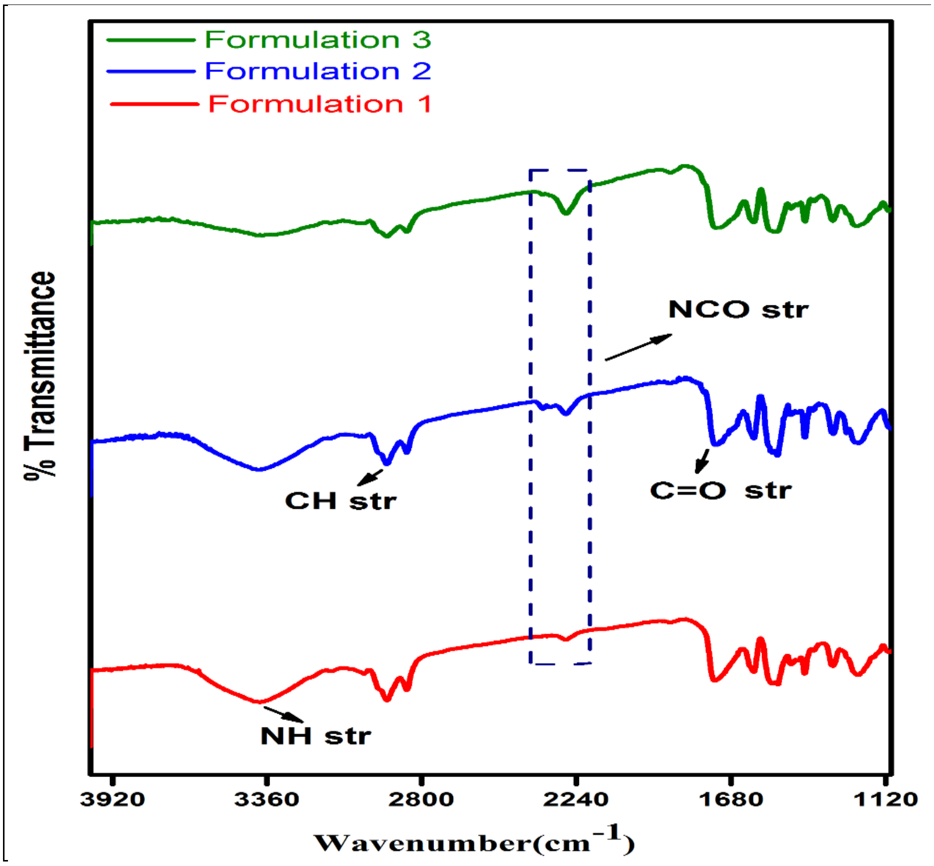


Figure 4.1.1(b): FTIR Spectra of Formulations 1, 2 and 3

In Figure 4.1.1 (b) formulation 1 shows absence of peak at 2268 cm^{-1} (-NCO stretching frequency) which confirms that all the MDI have been used in the curing reaction. But Formulation 2 and 3 shows peaks at 2268 cm^{-1} (-NCO stretching frequency) which indicates that there is some unreacted MDI.

4.1.3 XRD Analysis

Powder XRD patterns for formulation 1, 2 and 3 were obtained using D-8 Advance, Bruker diffraction as shown in Figure 4.1.2. From Figure 4.1.2 it is evident that all types of samples having broad amorphous peak at $2\theta = 20^{\circ}$. As expected all the PU foam formulations shows amorphous structure. Peaks obtained are not sharp because of absence of the crystalline behavior.

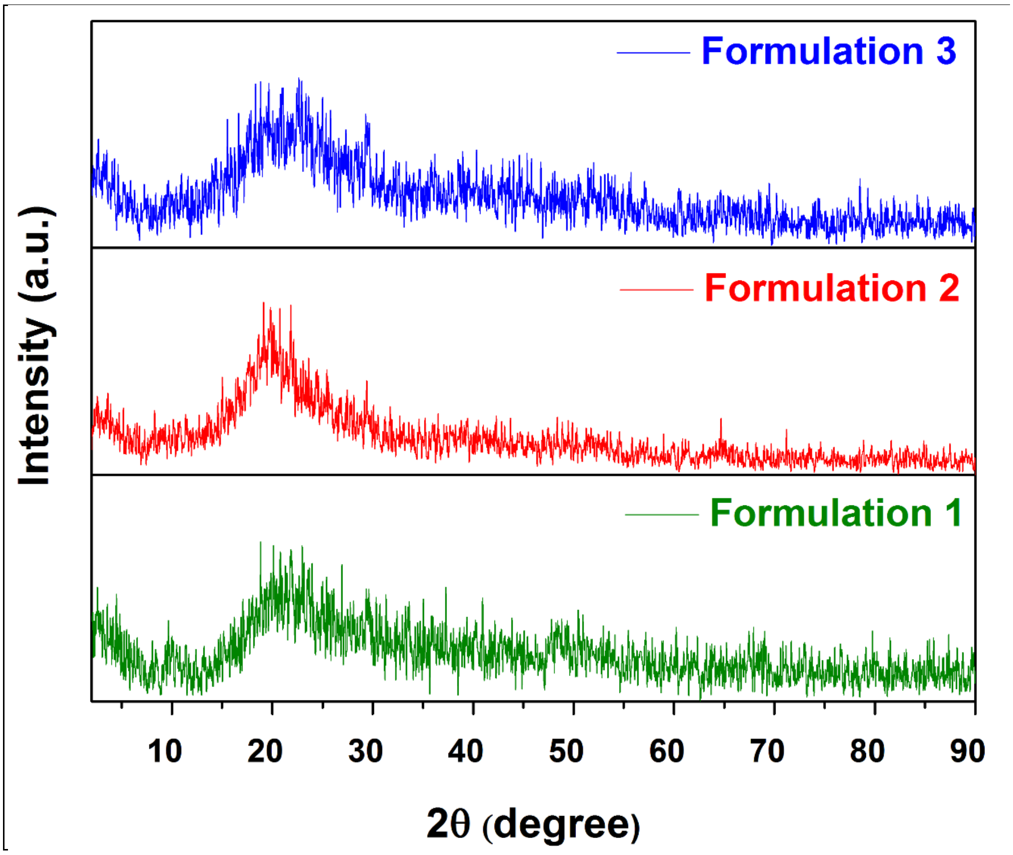


Figure 4.1.2: XRD Spectra of Formulations 1, 2 and 3

4.1.4 Mechanical Properties

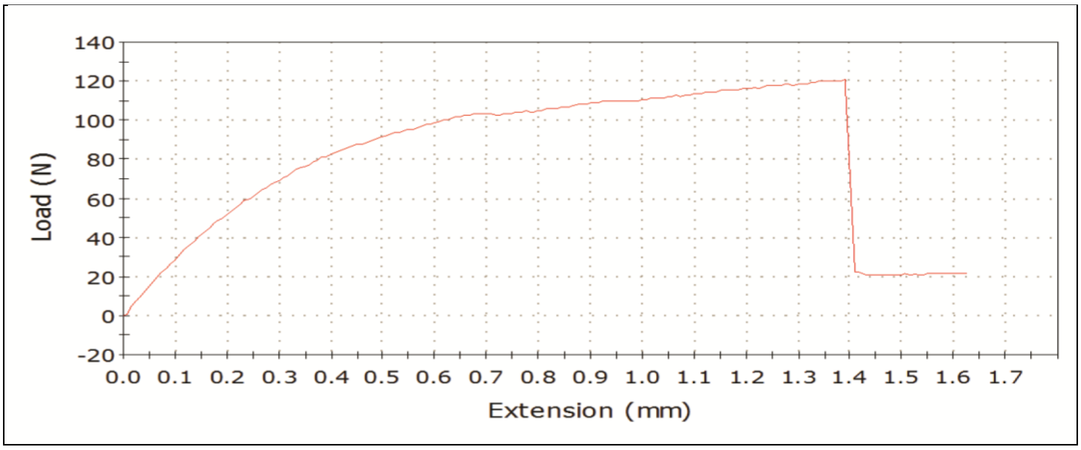
The mechanical characterization of RPUFs was conducted as per the standard procedures. Samples were prepared as per the requisite dimensions. Tensile and compressive properties of the resulted foams were measured at using Instron (model No.: 3369) universal testing machine at room temperature as per ASTM D-638 and ASTM D 695 respectively. The tensile stress at maximum load (MPa) and maximum compressive load (kgf) for different formulations are as given in Table: 4.1.3. The tensile stress at maximum load as well as maximum compressive load was observed to be increased with increase in MDI : Polyol ratio, thus indicating a significant improvement in overall mechanical properties of the foamed samples, with MDI.

Table 4.1.1: Mechanical Properties of Castor Oil Based Rigid Polyurethane Foams

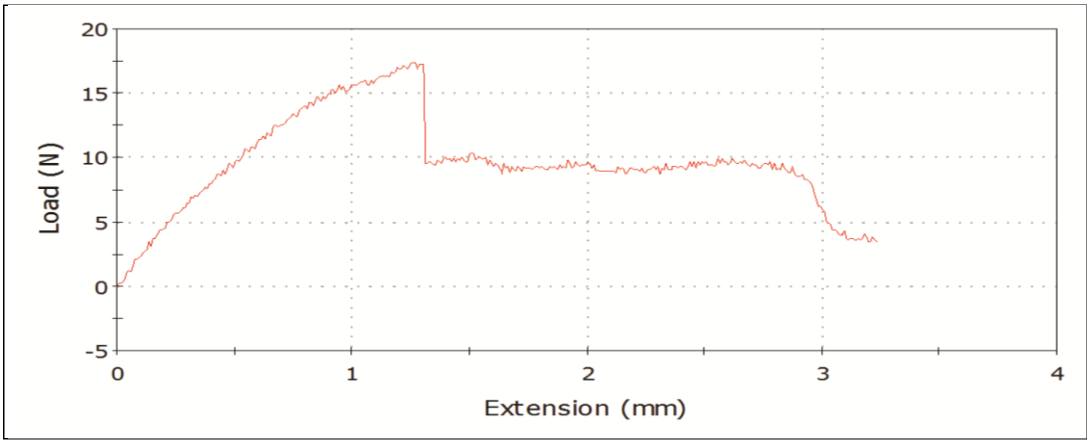
S No.	Tensile stress at Maximum Load (MPa)	Maximum Compressive Load (kgf)
Formulation 1	0.12903	1030.18514
Formulation 2	0.29220	1082.10801
Formulation 3	0.35285	1091.64952

4.1.4.1 Tensile Strength

The tensile strengths of the resulted foam samples were obtained good and was found increased with increase in MDI: Polyol ratio. Test results are plotted in the graphs between tensile load and extension, which shows almost a linear response that subsequently diverted toward nonlinearity prior to the fracture. Tensile strength was determined from the gradient of the linear portion and the maximum stress prior to failure. The relationship between tensile load and extension for the castor oil based rigid polyurethane rigid foams is as shown in Figure 4.1.3 (a) to (c). From Figure 4.1.3 (a) to (c), value for tensile modulus for formulation 1 (i.e. MDI:Polyol::1:1) is seemed to be less as compared to that observed in case of formulation 2 (MDI : Polyol::2:1), which in turn is lesser than for formulation 3. It is very clear from Figure 4.1.3 (a) that extension is very high in formulation 1, before the breaking point arrived and it shows elasticity within the material. The formulation 2, as seen from Figure 4.1.3 (b) shows elasticity but to a less extent and breaks under the applied load. The formulation 3, as indicated by Figure 4.1.3 (c) has not extendibility at all and breaks under the condition of maximum applied load thus representing that sample is very tough.



(a)



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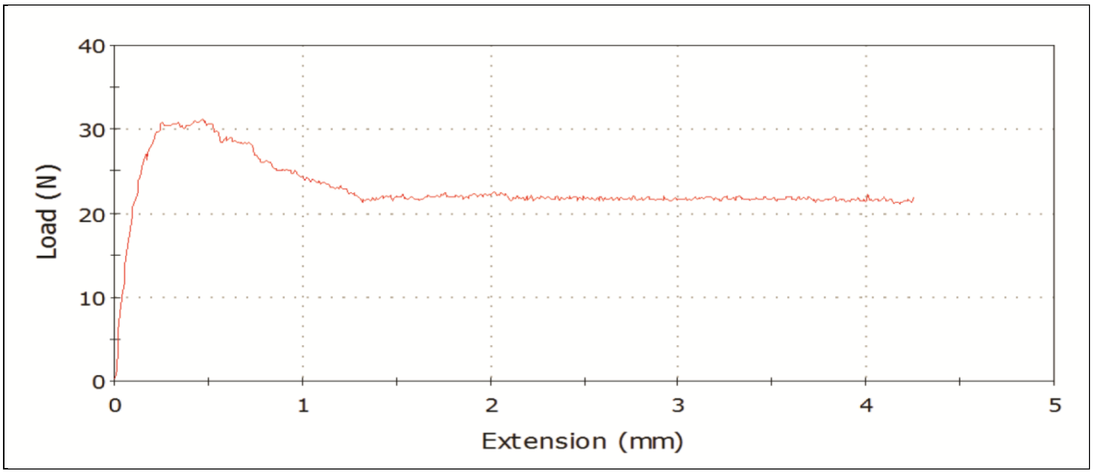

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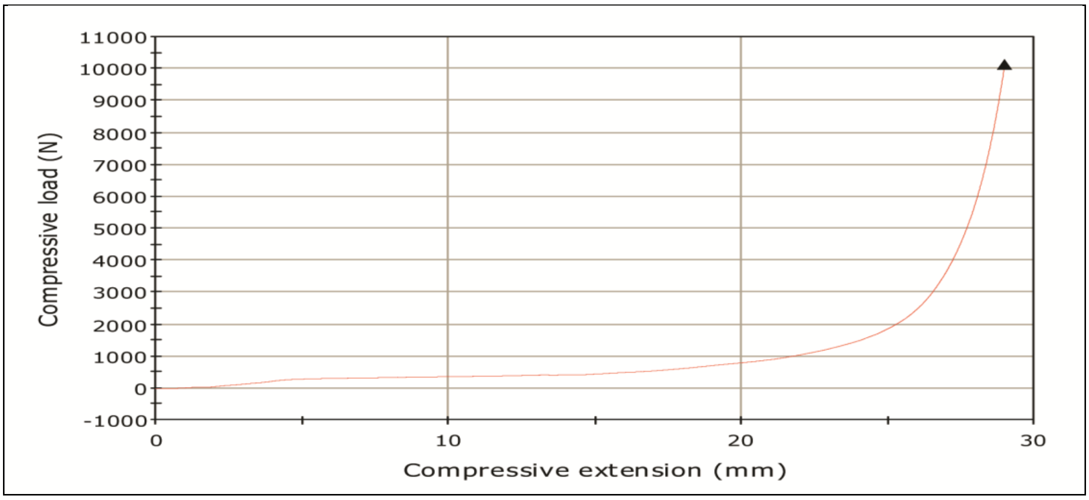
Figure 4.1.3: Relationship between Load and Extension for (a) Formulation 1 (b) Formulation 2 and (c) Formulation 3

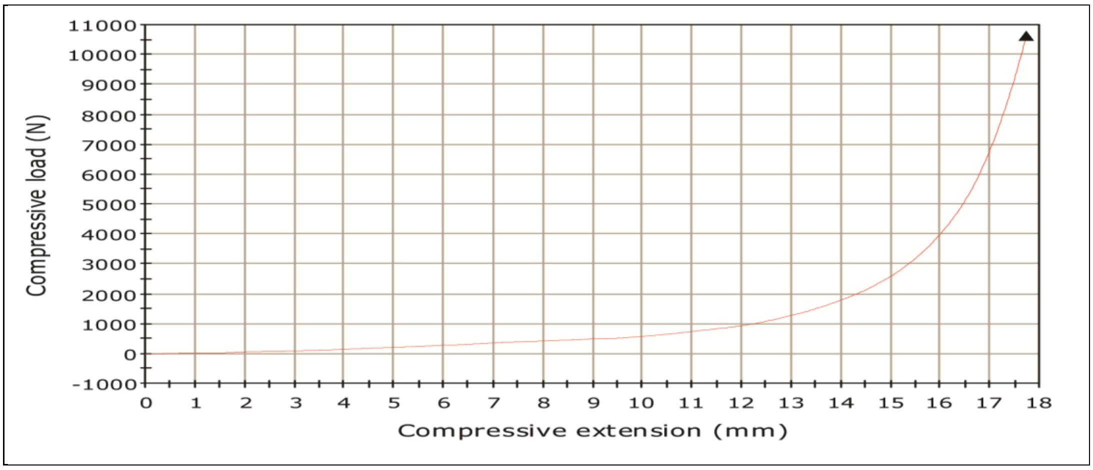
The load bearing capacity of the resulted castor oil based rigid polyurethane foam increases with increase in MDI : Polyol ratio. From the above discussions, it is clearly evident that both tensile strength and hardness get enhanced while elongation get receded increase in NCO/OH ratio. Low molecular weight of PU has been reported for high NCO/OH ratio[107] and higher levels of covalent crosslinking [108], which in turn increases the modulus as per the theory of rubber elasticity. This clearly justifies the higher tensile strength and hardness of formulation 2 as compared to formulation 1 and further increased tensile strength and hardness of formulation 3 as compared to formulation 2. The more load is needed to be applied to break the samples from the formulation 3, probably due to the requirement of cleavage of rigid crosslinks that were formed between castor oil and MDI.

4.1.4.2 Compressive Strength

The compressive strengths of the resulted rigid polyurethane samples were found good. The relationship between compressive load and compressive extension for the castor oil based rigid polyurethane foams is as shown in Figure 4.1.4 (a) to (c). It is seen from Figure 4.1.4 (a), for formulation 1 (MDI : Polyol :: 1:1) for a maximum compressive load of 1030.18514 kgf, an extension up to 26 to 29 mm is there. Similarly for formulation 2 (MDI : Polyol :: 2:1), for a maximum compressive load of 1082.10801 kgf, an extension up to 17 to 18 mm had been observed. And for formulation 3 (MDI : Polyol :: 3:1), for maximum compressive load of 1091.64952 Kgf, an extension of 15-16 mm is there. Thus, it is very clear that with increase in MDI content in polyurethane foams, the load bearing capacity i.e. stiffness was increased and the extension was reduced.



(a)



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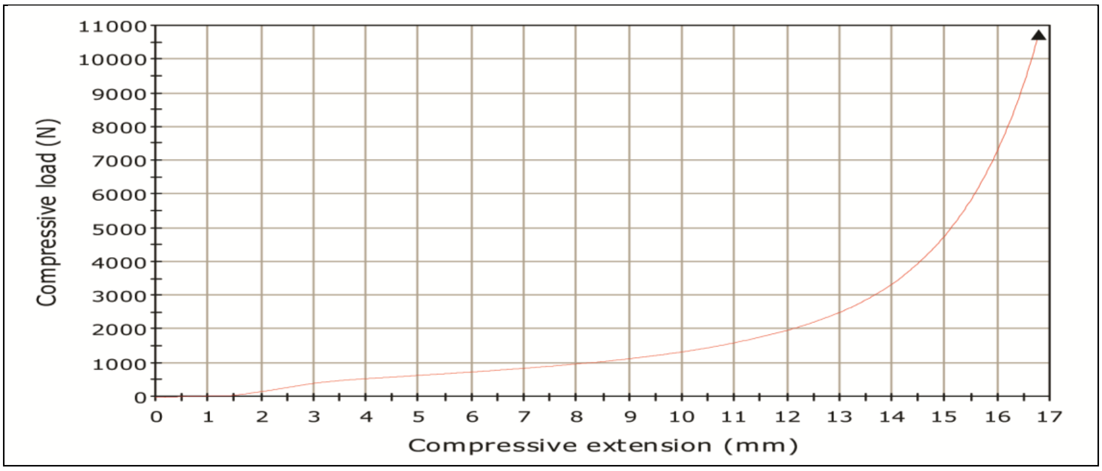


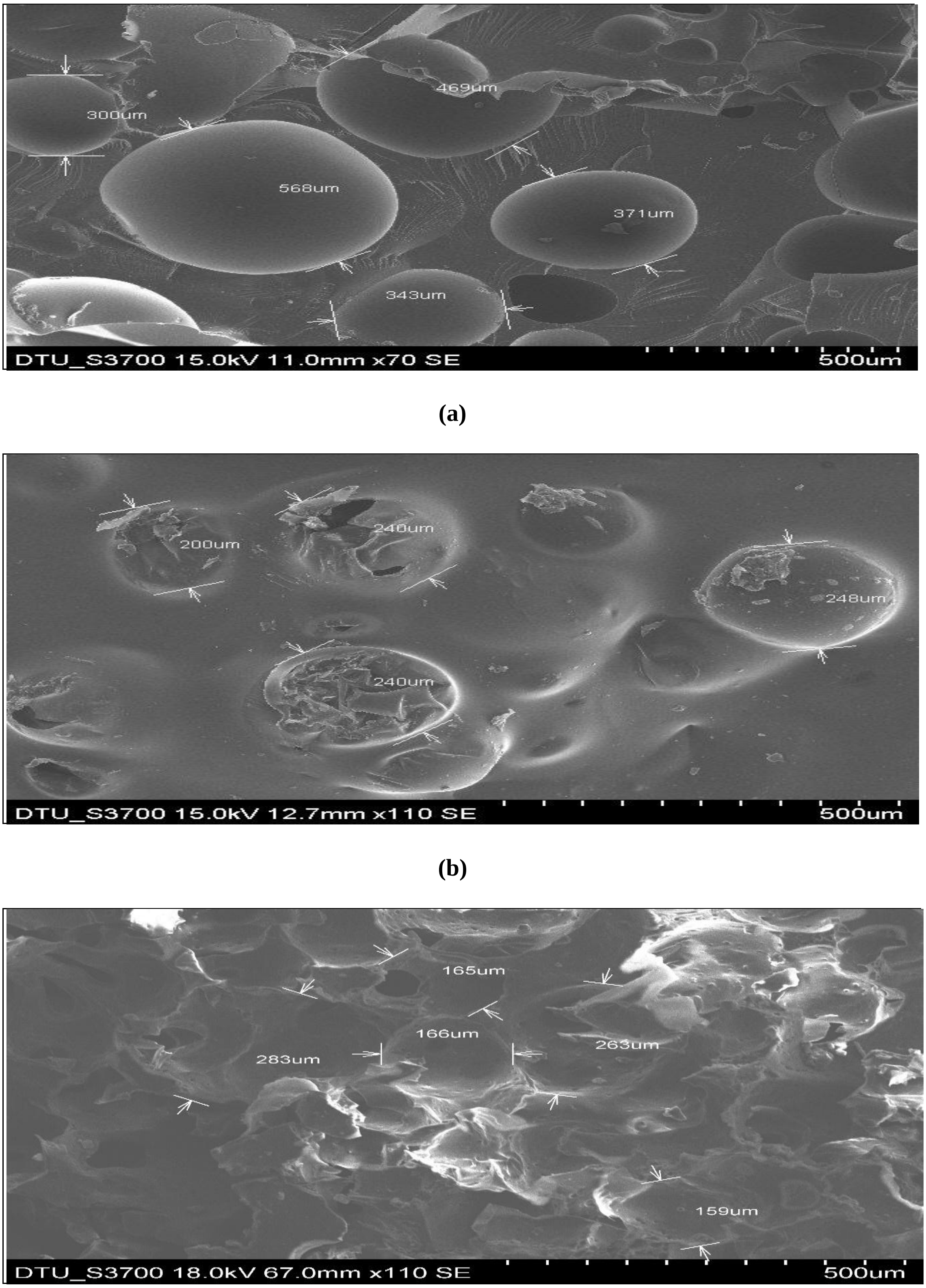
(c)

Figure 4.1.4: Relationship between Compressive Load and Compressive Extension for (a) Formulation 1 (b) Formulation 2 and (c) Formulation 3

This result is in accordance with that reported in literature. Tu *et* al., 2007 reported that with increase in the isocyanate index or the increase in the isocyanate usage in the polyurethane foam, there is increase in the foam's cross-linking density which leads to a higher compressive strength [12]. The increase in compressive strength is also favoured by the fact that with increased content of MDI, a more closely packed structure is obtained, as reported under the section for SEM studies of the resulted foams, which may probably be due to formation of rigid crosslinks formed between castor oil and MDI. Because of a restricted airflow in a closely packed foam, results in a higher compressive load bearing. Due to rigid cross links with in the foam structure, elastic recovery (that is more common in case of flexible foams) is restricted thus making foams rigid and stiff. This result is according to the theory of rubber elasticity, as stiffness or modulus of the polymer is supported by the higher levels of covalent crosslinking.

4.1.5 SEM Analysis

Cell structure also determines the physical properties of the foams. The cell structures of the samples were characterized with a Hitachi S3700 SEM (Scanning Electron Microscope) using an acceleration of 15 kV. Figure 4.1.5 (a) to (c) show the scanning electron micrographs of the castor oil based rigid polyutrthane foams with different MDI contents. As seen in Figure 4.1.5 (a), for the formulation 1, i.e. for MDI : Polyol ratio 1:1, the foams present a smaller cell density with a higher pore size. The size of pores is mostly in range of 300-400 µm and a few are in the range of 500 µm, with an average pore size equal to 410.2 µm and it subsequently get reduced for other two formulations.



(a)

(b)

(c)

Figure 4.1.5: SEM of Castor Oil Based Rigid Polyurethane Foams for (a) Formulation 1 (b) Formulation 2 and (c) Formulation 3

For Formulation 2 (MDI : Polyol ratio equal to 2:1), it is clearly indicated that pore size is reduced to an average pore size of 232 µm. And, with further increase in MDI content, i.e. for Formulation 3 with ratio of MDI : Polyol equal to 3:1, average pore size was reported to be 207.2 µm only (Figure 4.1.5 (c)). Thus, there is nearly 44% reduction in pore size when MDI content is made double and nearly 50% reduction in the case where MDI content is tripled. The reduced pore size, as in case of Formulation 2 and Formulation 3 indicated that the 3-D structure of foam was more packed and consequently resulted in increased density and increased compressive strength. The same result i.e. increased compressive strength was reported in the former section (where results of compression testing are reported).

4.1.6 Water Absorption in Foams

Results for water absorption tests for castor oil based rigid polyurethane samples are as given in Table 4.1.4. It had been observed that percentage of the water absorbed in the resulted foamed samples was decreased with the increase in MDI concentration. With increase in MDI content, the pore size was found to be decreased (as confirmed by SEM studies) and foamed structure was found to be more closely packed, which in turn reduced the water absorption capacity of the foam especially in the formulation 3. The water absorption capacity can be further reduced by adding suitable fillers.

Table 4.1.2: Water Absorption in Different Formulations

Sample no.	Initial weight (g)	Final weight (g)	Water absorption (%)
Formulation 1	1.1813	1.642	38.99
Formulation 2	0.7809	1.07	37.02
Formulation 3	0.8342	1.024	22.75

4.1.7 Significant Findings

The tensile and compressive strength of rigid polyurethane foams were found to be increased with increase in the MDI content. The highest values were obtained for the formulation 3 with MDI : Polyol ratio equal to 3:1. SEM studies had also shown evidence for improved cell morphology and closed packing with increase in MDI content.

4.2 Function of Silicon oil on the Castor Oil based RPUFs

RPUFs are usually prepared by physical blowing agents who provide the necessary gas expansion to produce foams by evaporation [109]. This work report the effect of different formulations of surfactant (Silicon oil) on the rigid polyurethane foams based on castor oil. The reaction is catalyzed by Cobalt octoate and Methylene chloride is used as a blowing agent. The samples were formed by varying the surfactant ratios. The surfactant “Silicon Oil” was incorporated in the ratio 3, 6 and 9 % by weight. The surfactant formulations used in this study are reported in Table 3.4. Results and discussion of effect of different formulations of surfactant on the properties of rigid polyurethane foam is given here.

4.2.1 Mechanical Properties

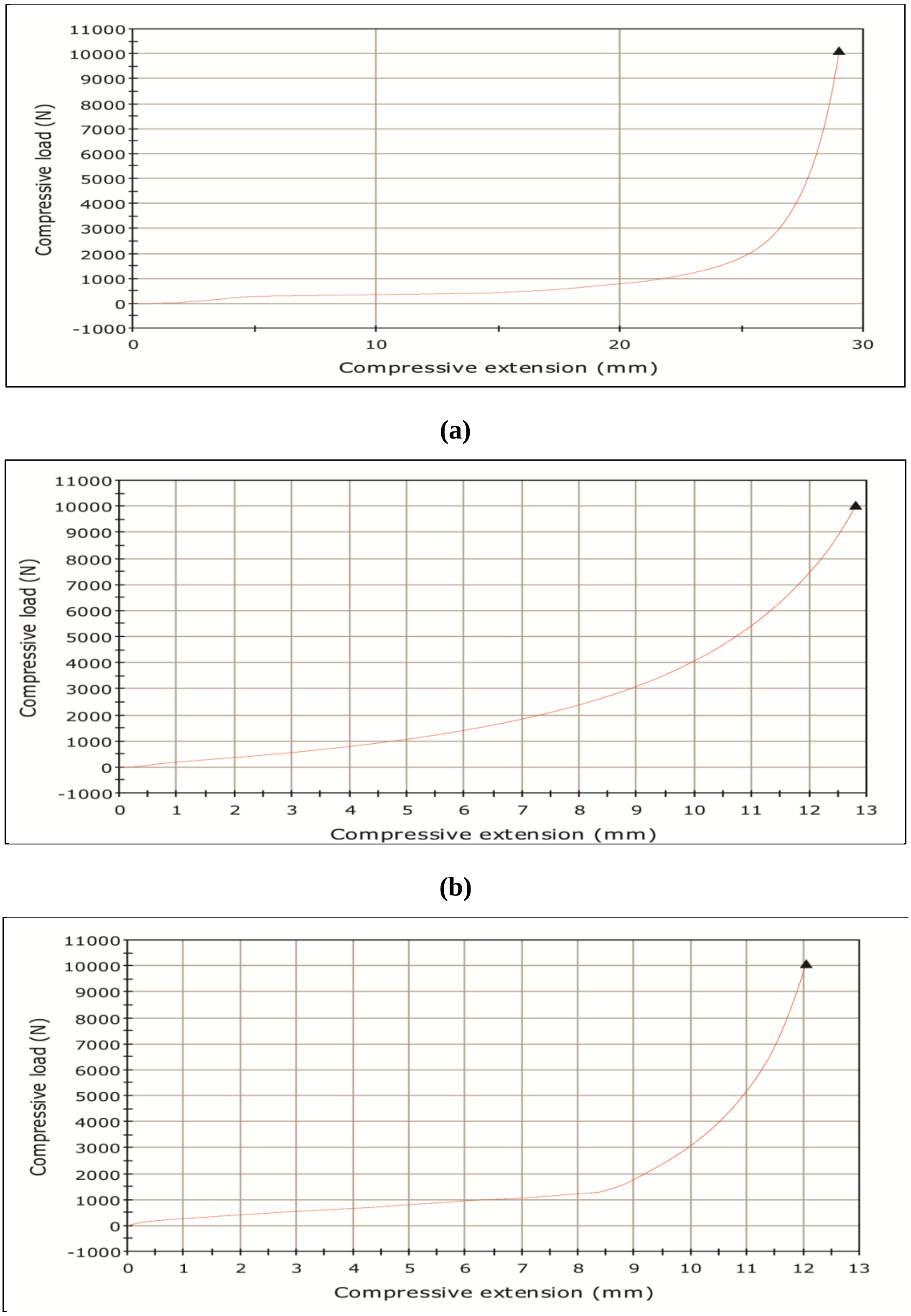
Standard procedure was followed to study the mechanical properties of the resulted RPUFs. Compressive and flexural properties of the resulted foams were measured using Instron (model No.: 3369) universal testing machine as per ASTM D 695 and ASTM D 790 methods respectively. The maximum compressive load (kgf) and flexure extension at maximum flexure load (mm) for different surfactant formulations are as given in Table: 4.2.2. The maximum flexure load is found to be increased with increase in the surfactant content for formulation 2, but it further decreased with the addition of more surfactant. The values of maximum compressive load showed the similar trend although the difference in values is not much significant. This clearly signifies the effect of silicon oil (surfactant) on the mechanical properties of the foam.

Table 4.2.1: Mechanical Properties of Castor Oil Based Rigid Polyurethane Foams

S No.	Maximum Compressive Load (kgf)	Flexure Extension at Maximum Flexure Load (mm)
Formulation 1	1023.26351	3.29994
Formulation 2	1027.66412	4.10000
Formulation 3	1021.81430	2.70831

4.2.1.1 Compressive Strength

The compressive strengths of the resulted rigid polyurethane samples were found good. The relationship between compressive load (kgf) and compressive extension (mm) for the castor oil based rigid polyurethane rigid foams is as shown in Figure 4.2.1 (a) to (c). It is seen that compressive strength was increased with increase in silicon oil content in formulation 1 to formulation 2 and then decreased with further addition of oil. It is seen from Figure 4.2.1 (a), for formulation 1 (Silicon oil=3% by weight) for a maximum compressive load of 1023.26351 kgf, an extension up to 26 to 29 mm is there. Similarly, for formulation 2 (Silicon Oil=6% by weight), for maximum compressive load of 1027.66412 kgf, an extension of 12-13 mm and for formulation 3 (Silicon Oil=9% by weight), for a maximum compressive load of 1021.81430 kgf, an extension of 12 mm has been observed. Thus, it is very clear that with increase in Silicon oil content in polyurethane foams, the load bearing capacity i.e. stiffness was increased and the extension was reduced.



(a)

(b)

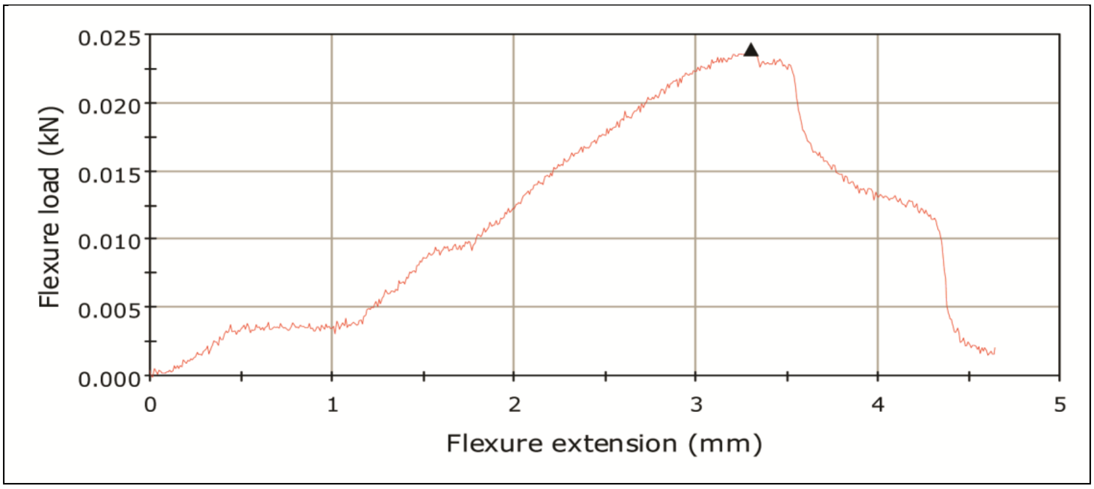
(c)

Figure 4.2.1: Relationship between Compressive Load and Compressive Extension for (a) Formulation 1 (b) Formulation 2 and (c) Formulation 3

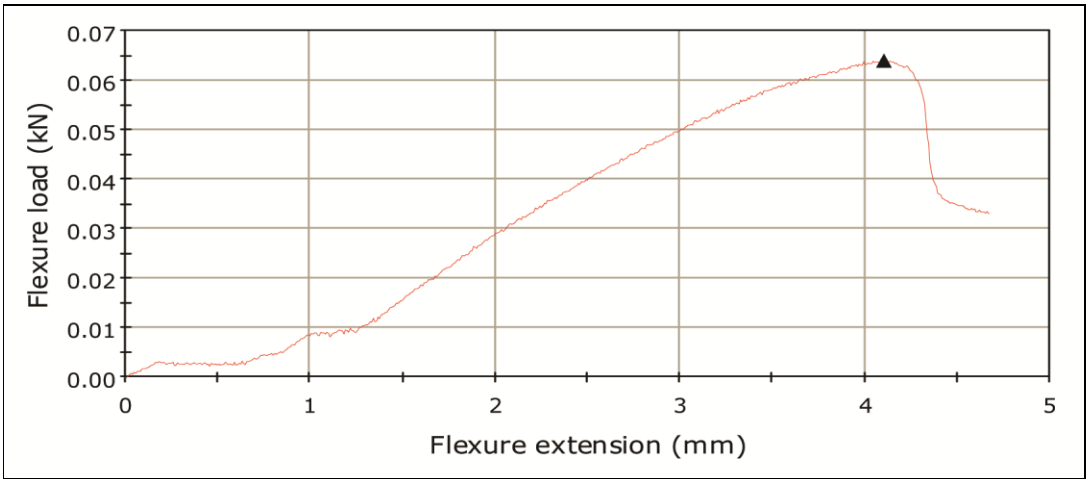
The increase in compression strength is favored by the decreased foam density (reported in subsequent section). The fact is that, with increased content of silicon oil, a more dense and closely packed structure is obtained as reported by Lim *et* al., 2008 [11] and Krupers *et* al, 1998 [110]. Due to rigid crosslinks within the foam structure, elastic recovery (that is more common in case of flexible foams) is restricted thus making foams rigid and stiff. This result is verified by the theory of rubber elasticity according to which, stiffness of the polymer get increased by the increase in cross linking. The efficiency of the blowing agent is also reportedly enhanced with the addition of surfactant, as it supports the formation of nuclei and boos the foam stability. Restricted airflow in closely packed foam results in a higher compressive load bearing capacity. With further increase in silicon oil content, i.e. in case of formulation 3, the heterogeneity of the system increases which resulted in decrease in compressive strength.

4.2.1.2 Flexural Strength

Standard method (ASTM D 790) was used in determining flexural properties of resulted RPUFs. The relationship between flexure load (kN) and flexure extension (mm) for the castor oil based rigid polyurethane rigid foams is as shown in Figure 4.2.2 (a) to (c). Initial linear portion of three curves is due to linear elastic deformation of the cell structures. As the cells get ruptured because of stretching, the slope of the load-deflection curve varies significantly and leads to deformation of foam and ultimately its failure at maximum load. It was found that flexure stress at maximum flexure load (MPa) for formulation 1 was 7.17901, which further increased more than three times for formulation 2 with a value of 23.99906.



(a)



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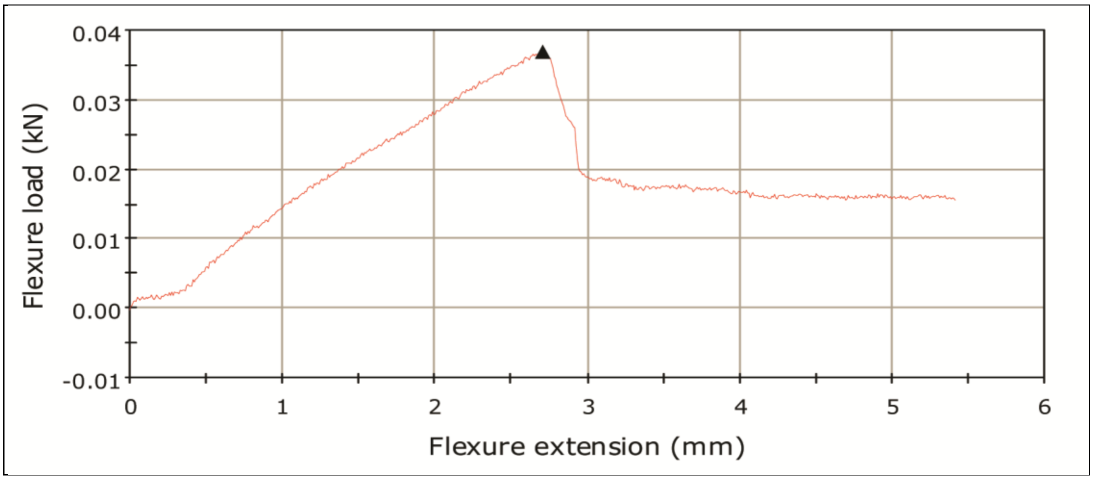


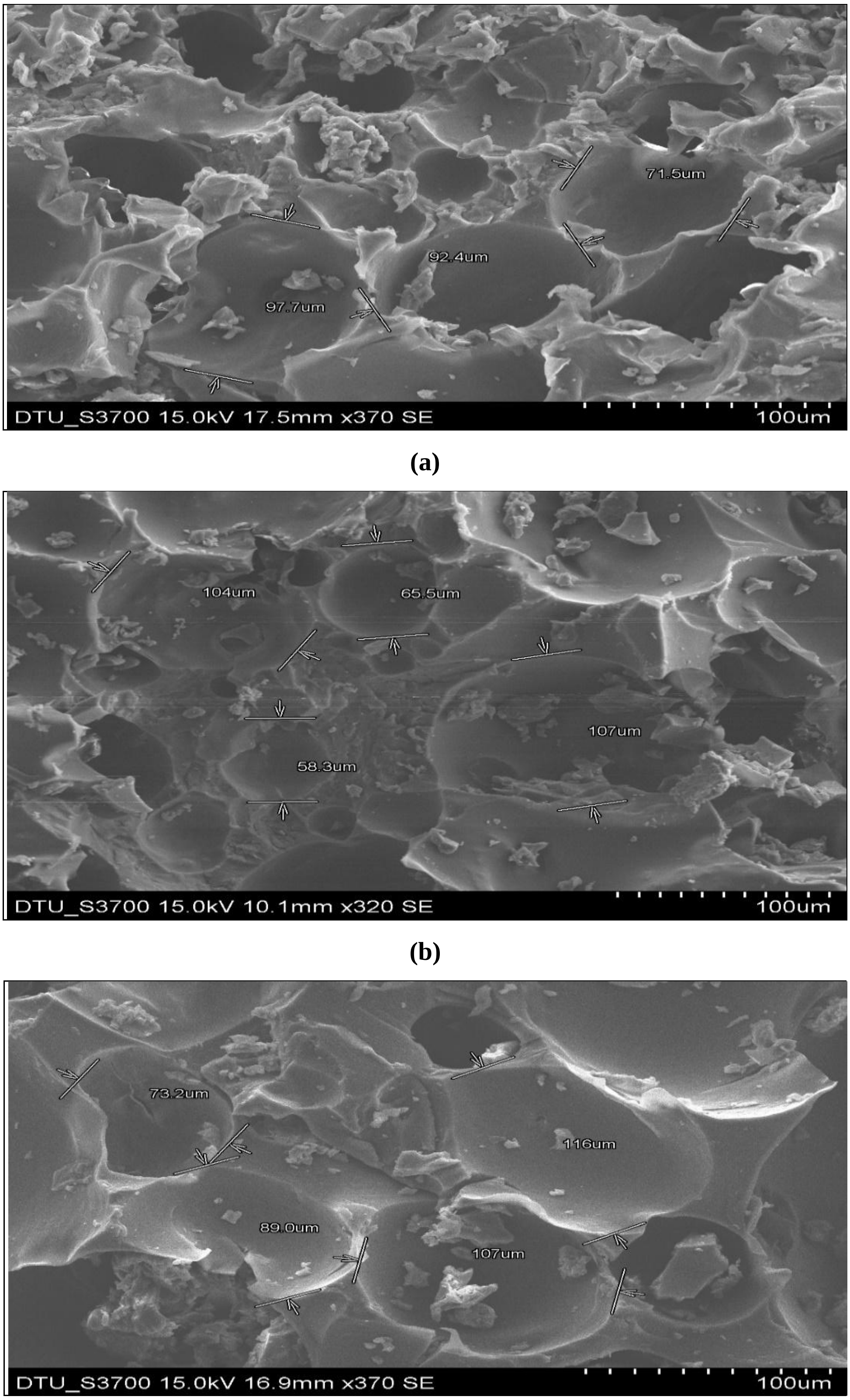
(c)

Figure 4.2.2: Relationship between Flexure Load and Flexure Extension for (a) Formulation 1 (b) Formulation 2 and (c) Formulation 3

The reason for this increase in flexural strength of the rigid polyurethane foam based on castor oil is due to the denser and closely packed structure. For formulation 3, i.e. for 9% surfactant, flexure stress at maximum flexure load (MPa) is found to be 6.15424. The observed decrease is due to increase in the heterogeneity of the system. In particular, two phenomena can explain the foam failure during flexural i.e. 1) Cell stretching in the tension side, which starts multiple cracks at the edge of specimen and 2) coalesce into a dominant crack leading to foam failure. Failure mode of the RPUF under study shows that the stretching phenomenon is dominant cause of foam failure in this study.

4.2.2 SEM Analysis

The cell structures of the samples were characterized with a Hitachi S3700 SEM (Scanning Electron Microscope) using an acceleration of 15 kV. Figure 4.2.3 (a) to (c) show the scanning electron micrographs of the castor oil based rigid polyurethane foams with different surfactant contents. As seen in Figure 4.2.3 (a), for the formulation 1, i.e. for Silicon Oil content = 3%, the average pore size equal to 87.2 µm and it subsequently get reduced for formulation 2. For formulation 2 (6% Silicon Oil) the average pore size is reduced to 83.7 µm. And, with further increase in Silicon oil content, i.e. for formulation 3, average pore size was observed to be 96.3 µm as shown in Figure 4.2.3 (c). Thus, there is nearly 9.5 % reduction in pore size when Silicon oil content is increased from 3 to 6%. With further increasing the amount of silicon oil, the average pore size is increased. The reduced pore size, as in case of formulation 2 indicated that the 3-D structure of foam was more packed and consequently resulted in increased density and increased mechanical properties.



(a)

(b)

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Figure 4.2.3: SEM of Castor Oil Based Rigid Polyurethane Foams for (a) Formulation 1 (b) Formulation 2 and (c) Formulation 3

The fact is that surfactants stabilize the foam cells structure to prevent collapse and sub-surface voids in the polyurethane foaming process. Bubble generation and cell stabilization is significantly influenced by the silicone surfactant.

Surfactants with more silicone content offer lower surface tension and number of air bubbles during mixing increases that act as the starting point for cell growth in foam. As a result, the cured PUF having higher silicone surfactant content exhibit a smaller bubble size. Also, silicone surfactant reduces the cell window drainage rate significantly due to the surface tension gradient along the cell window.

4.2.3 Density

Mechanical and thermal properties of closed cell foams are much dependent on its density [80,111]. With increasing surfactant concentration, foam density first increases and then decreases. The density values of all samples obtained from different formulations of surfactant are given in the Table 4.2.3. Formulation 2 has more density than the formulation 1 and 3. With high silicon oil concentration, density is found to be reduced. It is due to decrease efficiency of blowing agent with much increased surfactant concentrations. Similar results were obtained by Krupers *et* al., 1998 [110] who reported the increase in average foam height and decrease in density decreases with addition of fluoro surfactant.

Table 4.2.3: Density of Rigid Polyurethane Foam in Different Formulations

Formulation	Density (g/mm^3)
Formulation 1	6.0×10^4
Formulation 2	7.9×10^4
Formulation 3	6.2×10^4

4.2.4 Significant Findings

Rigid polyurethane foams are produced by reacting modified castor oil and MDI with varying Silicon oil concentrations. Silicon oil was found to have significant effect on the mechanical properties of the foam. The silicon oil acts as a surfactant which reduces the diffusion across the interfaces by lowering the surface tension, emulsifies the incompatibility among formulation ingredients, promote bubble generation during mixing, regulates the foam structure and the cell size. A minimum amount of surfactant is essential for satisfactory foam, below which there are chances of occurrence of structural defects such as splitting, collapsing or densification. Above that level, a restriction in airflow may happen due to the over stabilization of the cell windows, thus leading to shrinkage of foam and affects the mechanical properties of the foam.

CHAPTER 5

REINFORCEMENT OF GLASS FIBERS INTO RPUFs

Rigid polyurethane foam (RPUF) is a well-known contender for several light weight engineering and industrial applications. Because of their closed cell structures, they offer low thermal conductivity along with less moisture permeability. These properties of RPUF makes it a very attractive choice as a core material to be used in sandwiched construction panels, thermal insulation of refrigerated vehicles, in ship-building, in false-roofing etc. [112]. Inspite of wide applications, RPUFs suffer from major drawbacks such as lack of mechanical strength and thermal stability [6]. RPUF, due to its unique properties of low permeability, low thermal conductivity and light weight and a very good processing flexibility show the possibility to be used as matrix materials for high strength polymeric composite in combination with different reinforcing materials i.e. both fibers and particulates. Recent literature studies reported an innovation in the field of resin impregnated fabric bandages that were designed by the knitted fiberglass fabric soaked with a polyurethane resin [113]. Glass fibers are among the most functional industrial reinforcing agents known today because of their greater surface area to weight ratio [114] and reasonable cost with respect to the advantages offered by them. Their principal advantages are their enhanced insulating properties along with high tensile strength and chemical resistance. Following the present scenario of light weight polymeric composite materials, the present studies has been carried out with an aim to reinforce the cellulosic polyurethane material to produce a new composite material with an added advantage of high mechanical strength along with the retention of unique properties of

RPUF. Cell morphology, density, water absorption, and mechanical properties of prepared glass fibre reinforced RPUFs have been tested and reported in comparison with that of neat RPUF. The basic formulations for the preparation of glass fiber reinforced RPUFs are as given in Table 3.5. Results and discussion of reinforcement of glass fibers into RPUFs is given here.

5.1 Density

Density is a vital indicator of foam performance in terms of mechanical properties of closed cell foams [80,111]. Density was determined as per ASTM D 1622 with sample size of 30 x 30 x 30 mm (width x thickness x length). Five samples were tested for density and an average value was reported. It was observed that the insertion of glass fibre (GF) enhances foam density as shown in Figure 5.1. The rigid polyurethane foam without glass fibre (RPUF) posed a smaller cell density with large pore size as compared to that of RPUGF. Probably, the density increased due to cross linkage of foam cells [115]. Highly dense foams are expected to be more rigid which in turn exhibit higher mechanical strength.

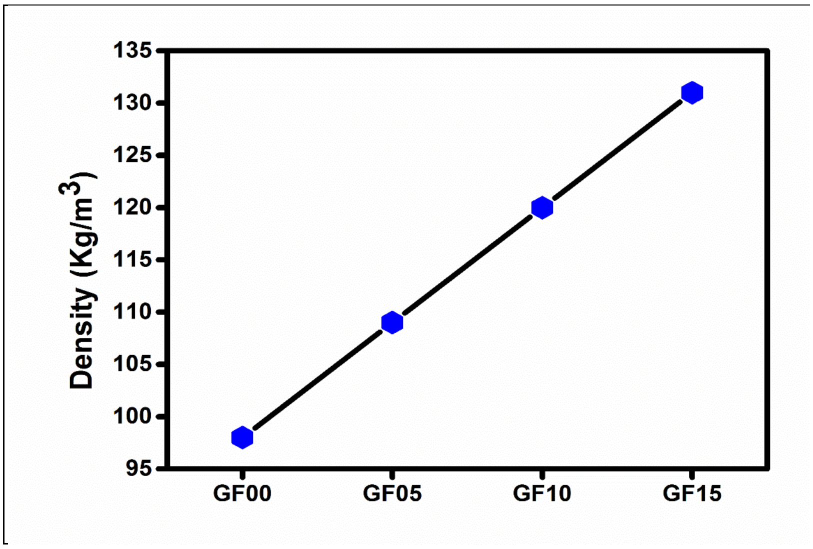
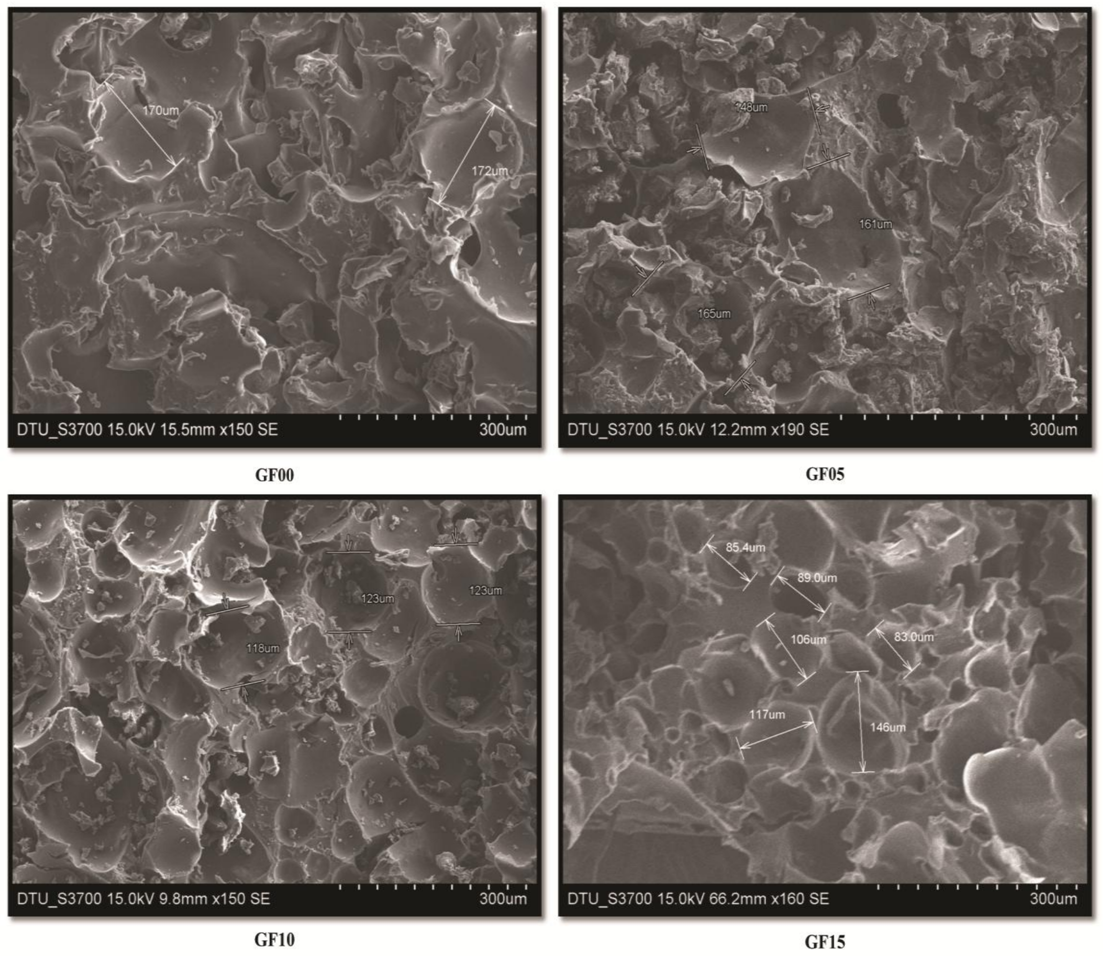


Figure 5.1: Density of RPUGF vs Glass Fiber Quantity

5.2 SEM Analysis

The cell structures of the resulted rigid polyurethane foam with glass fibre (RPUGF) were analysed by using Hitachi S3700 SEM (Scanning Electron Microscope) using an accelerating voltage of 15 kV.



GF00 **GF05**

GF10 **GF15**

Figure 5.2: SEM of RPUGF vs Glass Fiber Quantity

Figure 5.2 shows the SEM morphology of the resulted reinforced and neat rigid polyurethane foam. It is clearly observed that the shape of the cells is nearly spherical. The cell growth is retarded due to the involvement of glass fibres in the rigid PU that is evident from small sized cell around the glass fibre. This result is quite identical to that was prior reported in literature [111] for the similar studies. RPUF (GF00) exhibited the average pore equal to 171 μm. RPUGF (GF05), (GF10), (GF15) presented the average pore size equal to 158 μm, 121 μm and 104 μm respectively. The graph of average cell size of RPUGF versus amount of glass fibre (GF00, GF05, GF10, and GF15) is as seen in Figure 5.3. It is clear from the Figure 5.2 and Figure 5.3 that the average cell size was decreased as the glass fibre content was increased. The reduced pore size indicated that 3-D structure of foam was more closely packed and consequently resulted in increased density and in turn, increased the mechanical strength, as reported in subsequent section.

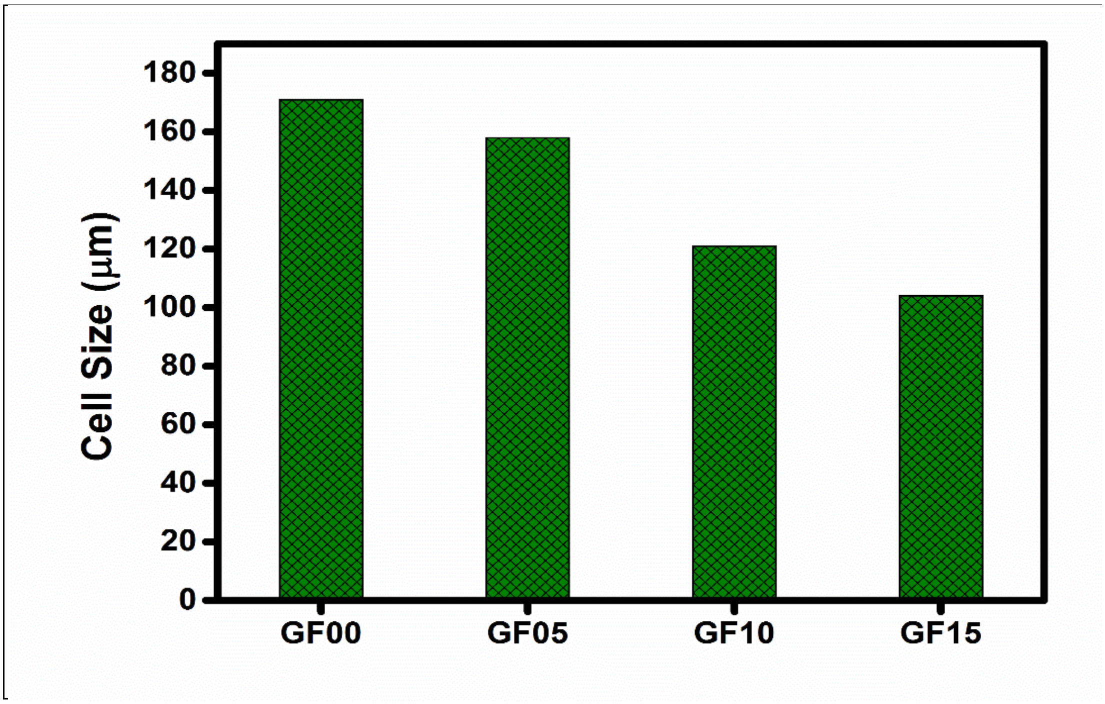


Figure 5.3: Cell Size of RPUGF vs Glass Fiber Quantity

5.3 Mechanical Properties

Mechanical properties of the prepared RPUFs were examined as per the ASTM procedures. Tensile, compressive, and flexural properties of the resulted foams were measured at room temperature using Instron (model No.: 3369) universal testing machine as per ASTM D-638, ASTM D- 695 and ADTM D 790 method respectively. Hardness was determined by using ASTM D 2240 method.

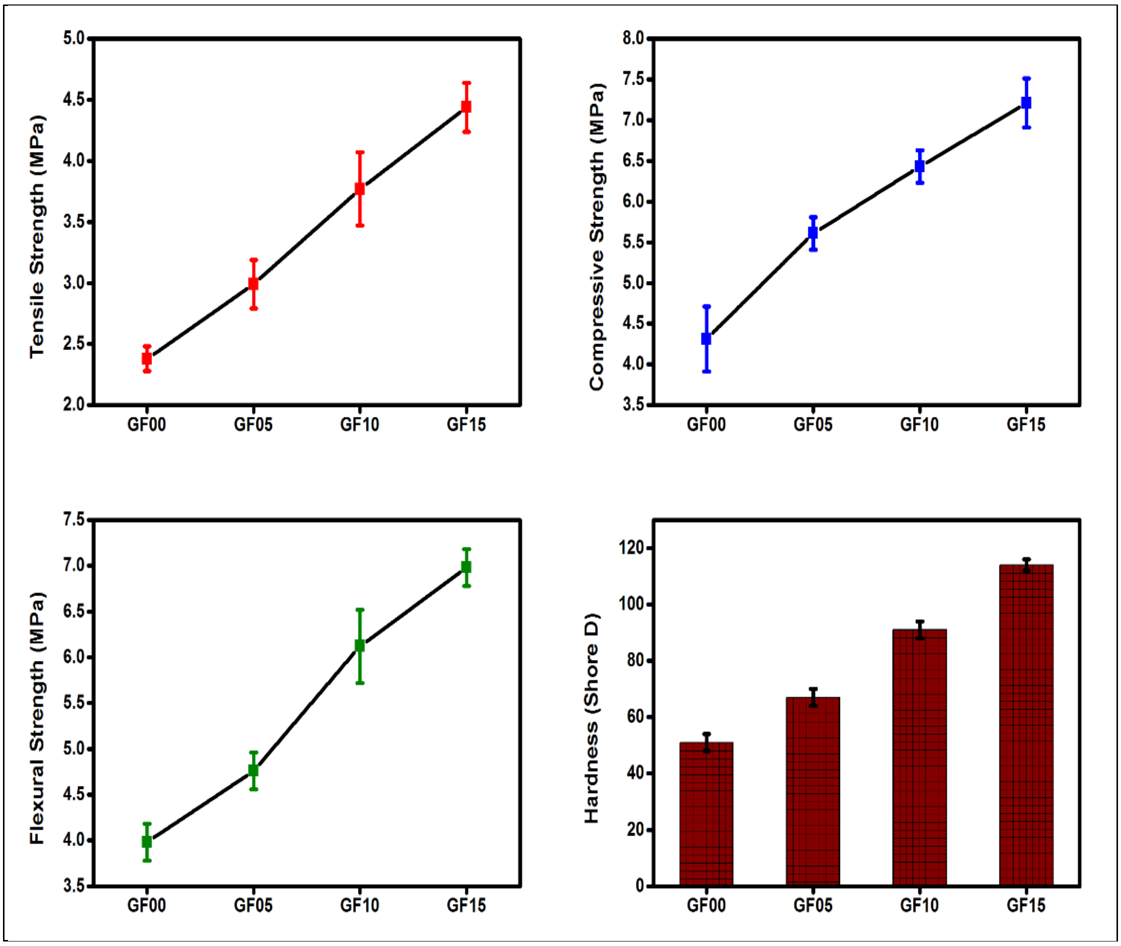


Figure 5.4: Mechanical Properties of RPUGF vs Glass Fiber Quantity

As expected, tensile strength (Figure 5.4), compressive strength (Figure 5.4), flexural strength (Figure 5.4) hardness (Figure 5.4) enhanced significantly and nearly linearly with the insertion of increased glass fibre content. RPUF (GF00) showed the average tensile strength, compressive strength, flexural strength and average hardness equal to 2.381 MPa, 4.312 MPa, 3.98 MPa and 51 (Shore D) respectively. RPUGF (GF05), (GF10), (GF15) showed the average tensile strength equal to 2.996 MPa, 3.776 MPa, 4.443 MPa respectively and average compressive strength 5.612 MPa, 6.432 MPa, 7.211 MPa respectively and average flexural strength 4.761 MPa, 6.120 MPa, 6.981 MPa respectively and average hardness 67, 91, 114 (Shore D) respectively. Linear (almost) increase of above said properties indicates that the dispersion of the glass fibres in the PU matrix was good with proper adhesion. SEM images (Figure 5.2) also indicated an average decrease in pore size with increase in glass fibres reinforcement and supported the idea of densely packed sturdy structure in contrast to that of neat RPUF, which in turn increases the mechanical properties in case of RPUGF.

5.4 Water Absorption

Results of the water absorption study of RPUF and RPUGF as shown in Figure 5.5.

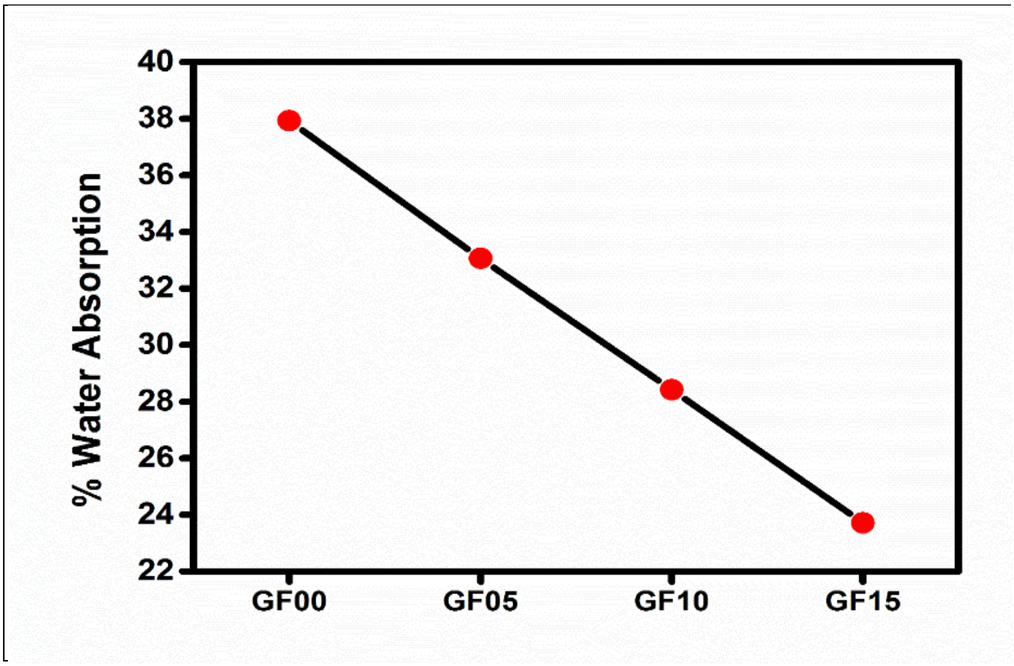


Figure 5.5: Water Absorption of RPUGF vs Glass Fiber Quantity

As evident from Figure 5.5, a decreasing trend in water absorption was observed with increased glass fiber insertion. RPUF (GF00) showed the average water absorption equal to 37.93% followed by 33.06%, 28.42% and 23.71% respectively for RPUGF (GF05), (GF10) and (GF15). The explanation is simple, as supported by SEM monographs i.e. Figure 5.2, with incorporation of glass fibre in RPUF, the pore size was decreased, and closely packed cell structure, do not allow the water absorption, as it was in case of simple RPUF.

5.5 Significant Findings

The higher values of hardness, tensile, flexural and compressive strength, with a relatively linearly increasing trend were observed for RPUGF (GF05, GF10, GF15) than RPUF (GF00). SEM studies had also revealed improved cell morphology with dense packing for RPUGF. The results for density measurement and water absorption studies supported the idea of more closely packed foam, when reinforced with glass fibre. The resulted castor oil based reinforced glass fibre rigid polyurethane foams, due to their high strength and load bearing capacity are suitable to be used as light weight moldable engineering material for various applications. These RPUGFs may be customized to prerequisite needs, by varying the amount of added reinforcement. In nutshell, being mechanically strong engineering material with desired characteristics, the resulted RPUGFs also offers an added advantage of being environment friendly, as it has been derived from a renewable plant source in contrast to the conventional RPUF. The material developed in the present research, is likely to be engaged in various construction application because of its sizes, shapes, and processing flexibility. Being a light weight, strong material with low thermal conductivity, it could be used as artificial roof or wall panels for various air conditioned assembles by designing it into various thickness.

CHAPTER 6

OPTIMIZATION

Rigid Polyurethanes Foams (RPUFs) can display quite different properties with extensive variety of applications as per the chemical reagent used in their synthesis. They are mostly made of unified networks of compact struts and cell walls intermingled by spaces with captured gas [66]. Processing limits that govern the inclusive properties of final product are needed to be optimized in order to improve price and dependability of the products. The processing limits of any product can be optimized using statisitical tools. It involves a strategic esperimentation in which the variables of interest are deviated over a definite range. Taguchi design of experiment is one of most common statistical approach. An orthogonal array is used to study the effects of experimental limits using a small number of trials. It is most practical way to investigate the influence of multiple factors on desired properties of the products and to to apply this to investigate the individual factor on the basis of properties. Processing limits for preparation of organoclay based PU nanocomposite have been successfully optimized using Taguchi method [80,138]. Continued developments in product value have become a requirement. Research on rigid polyurethane foam has been focused primarily on the optimization of the process limits to attain the better mechanical and surface properties.

In the present studies, RPUFs of the given formulations have been developed [Figure 6.1] and tested for its hardness, compressive, flexural, and tensile strength. The Taguchi method for the design of experiments was chosen as a tool for the optimization of the experiments, evaluation of the effects of various parameters and interpretation of the results. An effort has been carried out towards enlightening the mechanical and surface properties of rigid polyurethane foam by using Taguchi method. The effect of process limits such as polyol, fillers, surfactant, catalyst, blowing agent, antiflamming agent on tensile, compressive, and flexural strength as well as hardness (shore D) of rigid polyurethane foam has been extensively investigated.

Figure 6.1: Polyurethane Foam Samples of Different Formulatons

6.3 Taguchi Philosophy

Taguchi adopted an outstanding idea for quality control in the engineering industries. Taguchi is a standaradized tool to measure the best combination of inputs to obtain an optimized product or service. It is an appropriate procedure for designing and experimentation to inspect the processing variables. This is executed through design of experiments (DOE). Generally, it provide a method to identify the right ingredients that go together to make a high-quality product or service. DOE plays a very important role in optimization of product properties that reduces the number of trials and save energy, time and cost. Taguchi DOE helps to improve the process, yield, performance and quality of end product by optimizing the effects of control and noise factors on the product design [27,28,86]. The design variables and their selected level are given in Table 6.1. Taguchi tool to optimize the process limits has been explored extensively by the different researchers in the past [28]. Analysis of Variance (ANOVA) is performed to identify the important process variables. Best combination of process parameters are selected using S/N and ANOVA analyses. Each experiment had carried out three times under trial condition and the value of tensile strength, compressive strength, flexural strength, and hardness (shore D) for each run is measured. Tensile strength response characteristics are given in the Table 6.2, Compressive strength response characteristics are mentioned in the Table 6.3, Flexural strength response characteristics are tabulated in the Table 6.4 whereas Hardness (shore D) response characteristics in the Table 6.5.

Table 6.1: Selected Process Parameters and their Levels

Symbol	**Process Parameter**	**Unit**	**Level 1**	**Level 2**	**Level 3**
A	Filler	-	Flyash	$CaCO_3$	-
B	Polyol	-	2:1	3:1	4:1
C	Surfactant	-	1%	3%	5%
D	Catalyst	-	Cobalt Octoate	TEDA	DBTDL
E	Blowing Agent	-	5%	10%	15%
F	Antiflamming Agent	-	Melamine	TDCPP	TCP

Table 6.2: Experimental Trial Conditions and Results of Response Characteristics of Tensile Strength (MPa)

Exp. No.	**Input Parameters**						**Responses**			
							Raw Data Tensile Strength (MPa)			**S/N ratio (db)**
	A	**B**	**C**	**D**	**E**	**F**	**R_1**	**R_2**	**R_3**	
	Filler	**Polyol**	**Surfactant**	**Catalyst**	**Blowing Agent**	**Antiflamming Agent**				
1	1	1	1	1	1	1	2.01	1.78	1.79	5.35
2	1	1	2	2	2	2	6.46	6.59	6.98	16.48
3	1	1	3	3	3	3	2.71	3.32	2.99	9.47
4	1	2	1	1	2	2	3.77	3.88	3.74	11.58
5	1	2	2	2	3	3	5.93	5.86	5.98	15.45
6	1	2	3	3	1	1	1.38	1.32	1.22	2.29
7	1	3	1	2	1	3	1.94	2.13	2.46	6.63
8	1	3	2	3	2	1	2.89	3.08	3.08	9.58
9	1	3	3	1	3	2	2.58	2.56	2.62	8.25
10	2	1	1	3	3	2	2.85	3.32	3.19	9.83
11	2	1	2	1	1	3	1.94	2.02	1.87	5.76
12	2	1	3	2	2	1	1.99	2.31	2.33	6.82
13	2	2	1	2	3	1	2.77	3.23	3.44	9.85
14	2	2	2	3	1	2	2.89	2.93	2.66	9.00
15	2	2	3	1	2	3	1.39	1.45	1.23	2.59
16	2	3	1	3	2	3	1.97	1.93	1.88	5.69
17	2	3	2	1	3	1	2.18	2.43	2.76	7.69
18	2	3	3	2	1	2	1.88	1.72	1.76	5.02
Total							49.53	51.86	51.98	
Overall Mean							2.84			

R_1, R_2, R_3 Represent Tensile Strength response that performed in triplicate.

Table 6.3: Experimental Trial Conditions and Results of Response Characteristics of Compressive Strength (MPa)

Exp. No.	Input Parameters						Responses			
							Raw Data			S/N ratio (db)
							Compressive Strength (MPa)			
	A	**B**	**C**	**D**	**E**	**F**	**R_1**	**R_2**	**R_3**	
	Filler	**Polyol**	**Surfactant**	**Catalyst**	**Blowing Agent**	**Antiflamming Agent**				
1	1	1	1	1	1	1	1.66	1.58	1.54	4.04
2	1	1	2	2	2	2	7.85	7.46	7.93	17.78
3	1	1	3	3	3	3	3.67	3.66	3.89	11.45
4	1	2	1	1	2	2	4.10	4.27	3.90	12.22
5	1	2	2	2	3	3	5.93	5.84	5.79	15.34
6	1	2	3	3	1	1	1.24	1.34	1.09	1.63
7	1	3	1	2	1	3	2.21	2.23	2.42	7.17
8	1	3	2	3	2	1	2.61	2.23	2.47	7.68
9	1	3	3	1	3	2	2.52	2.33	2.21	7.39
10	2	1	1	3	3	2	2.96	2.57	2.69	8.72
11	2	1	2	1	1	3	1.59	1.27	1.33	2.78
12	2	1	3	2	2	1	1.73	1.68	1.73	4.67
13	2	2	1	2	3	1	2.82	2.77	2.92	9.05
14	2	2	2	3	1	2	2.49	2.14	2.24	7.15
15	2	2	3	1	2	3	1.22	1.30	1.34	2.16
16	2	3	1	3	2	3	1.90	1.15	1.99	3.69
17	2	3	2	1	3	1	1.58	1.47	1.56	3.73
18	2	3	3	2	1	2	1.61	1.57	1.51	3.86
Total							49.71	46.85	48.56	
Overall Mean							2.69			
R_1, R_2, R_3 Represent Compressive Strength response that performed in triplicate.										

Table 6.4: Experimental Trial Conditions and Results of Response Characteristics of Flexural Strength (mpa)

Exp. No.	Input Parameters						Responses			
							Raw Data			S/N ratio (db)
							Flexural Strength (MPa)			
	A	**B**	**C**	**D**	**E**	**F**	R_1	R_2	R_3	
	Filler	**Polyol**	**Surfactant**	**Catalyst**	**Blowing Agent**	**Antiflamming Agent**				
1	1	1	1	1	1	1	10.61	9.75	10.42	20.21
2	1	1	2	2	2	2	21.78	20.56	21.88	26.60
3	1	1	3	3	3	3	13.32	13.46	13.53	22.57
4	1	2	1	1	2	2	13.45	13.98	13.13	22.61
5	1	2	2	2	3	3	19.78	18.76	19.67	25.75
6	1	2	3	3	1	1	7.78	7.56	7.51	17.63
7	1	3	1	2	1	3	10.89	10.78	9.51	20.28
8	1	3	2	3	2	1	10.51	11.92	10.98	20.90
9	1	3	3	1	3	2	13.56	12.76	11.97	22.09
10	2	1	1	3	3	2	12.98	13.09	13.23	22.34
11	2	1	2	1	1	3	12.56	11.39	10.48	21.13
12	2	1	3	2	2	1	7.52	7.65	7.55	17.59
13	2	2	1	2	3	1	12.42	10.68	9.76	20.66
14	2	2	2	3	1	2	9.71	9.93	9.42	19.72
15	2	2	3	1	2	3	11.12	10.76	10.98	20.79
16	2	3	1	3	2	3	8.97	8.45	8.92	18.86
17	2	3	2	1	3	1	9.12	9.88	9.96	19.67
18	2	3	3	2	1	2	6.44	6.23	6.64	16.16
Total							212.52	207.59	205.54	
Overall Mean							11.59			
R_1, R_2, R_3 Represent Flexural Strength response that performed in triplicate.										

Table 6.5: Experimental Trial Conditions and Results of Response characteristics of Shore D Hardness

Exp. No.	Input Parameters						Responses			
							Raw Data			S/N ratio (db)
							Shore D Hardness			
	A	B	C	D	E	F	R_1	R_2	R_3	
	Filler	Polyol	Surfactant	Catalyst	Blowing Agent	Antiflamming Agent				
1	1	1	1	1	1	1	59	52	61	35.11
2	1	1	2	2	2	2	88	81	82	38.43
3	1	1	3	3	3	3	52	53	55	34.53
4	1	2	1	1	2	2	52	54	55	34.59
5	1	2	2	2	3	3	69	62	68	36.41
6	1	2	3	3	1	1	48	42	44	32.96
7	1	3	1	2	1	3	49	46	44	33.29
8	1	3	2	3	2	1	48	52	49	33.91
9	1	3	3	1	3	2	47	51	49	33.79
10	2	1	1	3	3	2	46	48	53	33.76
11	2	1	2	1	1	3	39	38	37	31.59
12	2	1	3	2	2	1	48	43	38	32.55
13	2	2	1	2	3	1	44	39	52	32.89
14	2	2	2	3	1	2	44	41	38	32.21
15	2	2	3	1	2	3	36	28	30	29.78
16	2	3	1	3	2	3	39	33	38	31.21
17	2	3	2	1	3	1	34	38	37	31.18
18	2	3	3	2	1	2	37	34	33	30.77
Total							879	835	863	
Overall Mean							47.72			
R_1, R_2, R_3 Represent Shore D Hardness response that performed in triplicate.										

6.2 Analysis and Discussion of Results

The experiments were planned by using the parametric approach of the Taguchi's L_{18} Orthogonal Array (OA). The response characteristics data are provided in Table 6.2 to Table 6.5. The standard procedure to analyze the data, as suggested by Taguchi, is employed. The average values and S/N ratio of the response characteristics for each parameter at different level are calculated from experimental data. The main effects of process parameters both for raw data and S/N ratio are plotted. The response curves (main effects) are used for examining the parametric effects on the response characteristics. The analysis of variance (ANOVA) of raw data and S/N ratio is performed to identify the significant parameters to quantify their effect on the response characteristics. The most favourable conditions (optimal setting) of process parameters in terms of mean response characteristics are established by analyzing response curves and the ANOVA tables.

Further, the effect of process parameters i.e. filler, polyol, surfactant, catalyst, blowing agent and antiflamming agent on the selected response characteristics (tensile strength, compressive strength, flexural strength and hardness) have been discussed. The average value of response characteristics and S/N ratio (dB) for each parameter at level one, two and three (L_1, L_2 and L_3) are calculated from Table 6.2 to Table 6.5.

6.2.1 Effect on Tensile Strength (TS)

The raw data for average values of tensile strength and S/N ratio for each parameter was analysed at three levels (L_1, L_2 and L_3). The results so obtained are presented in Tables 6.6 and 6.7 respectively. The response curves for individual effects of six process parameters for the average value of tensile strength and S/N ratio have been plotted as shown in Figure 6.2 to 6.7.

Table 6.6: Main Effects of Tensile Strength (Raw Data) at Various Levels

LEVEL	Filler	Polyol	Surfactant	Catalyst	Blowing Agent	Antiflamming Agent
L_1	3.37	3.14	2.67	2.33	1.98	2.33
L_2	2.31	3.05	3.81	3.65	3.16	3.47
L_3	*	2.33	2.04	2.53	3.37	2.72
L_2-L_1	-1.06	-0.08	1.14	1.32	1.18	1.13
L_3-L_2		-0.73	-1.77	-1.12	0.21	-0.74
DIFFERENCE	-1.06	-0.66	-2.90	-2.44	-0.97	-1.88
Where 1, 2 and 3 level of parameters is represented by L_1, L_2 and L_3 respectively. L_2-L_1 and L_3-L_2 represents average main effects especially when corresponding parameters changes from one level to other level such as from level 1 to level 2 and level 2 to level 3.						

Table 6.7: Main Effects of Tensile Strength (S/N Ratio) at Various Levels

LEVEL	Filler	Polyol	Surfactant	Catalyst	Blowing Agent	Antiflamming Agent
L_1	9.45	8.95	8.16	6.87	5.68	6.93
L_2	6.92	8.46	10.66	10.04	8.79	10.03
L_3	*	7.14	5.74	7.64	10.09	7.60
L_2-L_1	-2.54	-0.49	2.50	3.17	3.11	3.10
L_3-L_2	*	-1.32	-4.92	-2.40	1.30	-2.43
DIFFERENCE	-2.54	-0.82	-7.42	-5.57	-1.81	-5.53
Where 1, 2 and 3 level of parameters is represented by L_1, L_2 and L_3 respectively. L_2-L_1 and L_3-L_2 represents average main effects especially when corresponding parameters changes from one level to other level such as from level 1 to level 2 and level 2 to level 3.						

Figure 6.2 show that tensile strength is more in case of 1st filler (Flyash) than 2nd filler ($CaCO_3$) because of proper dispersion of flyash into rigid polyurethane foam. Fillers

play an important role in modifying the properties of various polymers. The effect of fillers on tensile strength of rigid polyurethane foam mainly depends on their concentration, size of the particles and shape as well as on the interaction of the particles with the matrix.

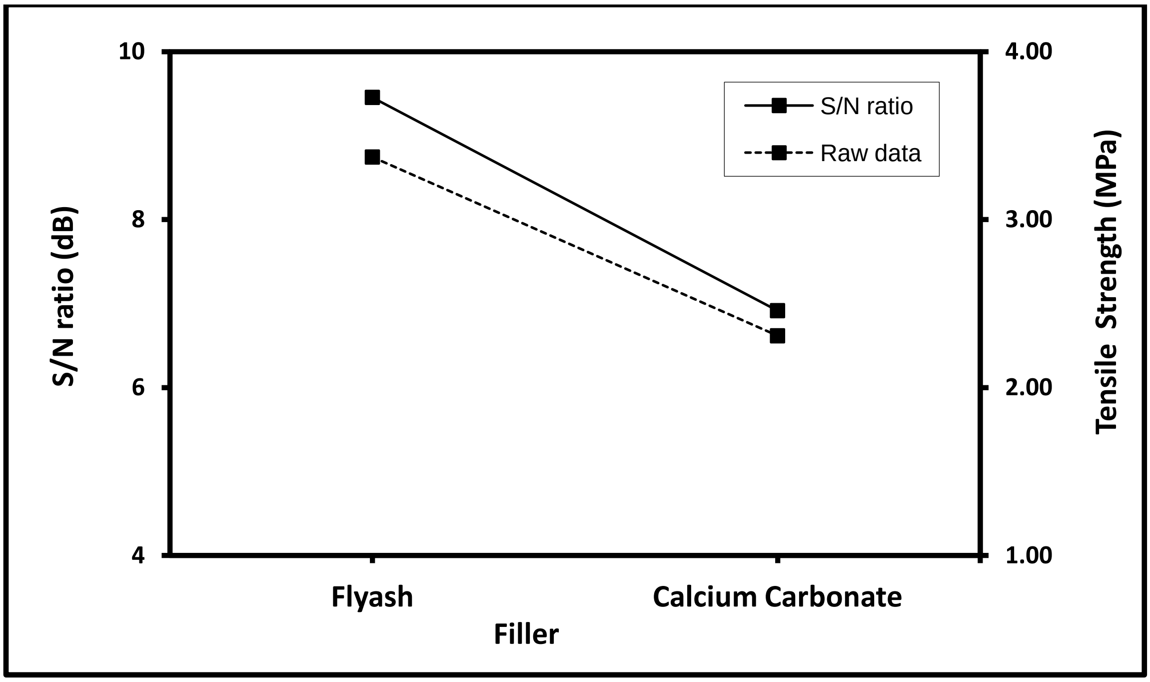


Figure 6.2: Effect of Filler on Tensile Strength and S/N Ratio

Figure 6.3 show that tensile strength is more in case of 1st polyol because of more number of hydroxyl group which causes more crosslinking. The network parmeters of the RPUFs mainly depend on the crosslinking density. Thus, most of the properties are expected to depend on the type of vegetable oil and hydroxyl group content of the polyols which is directly related to the crosslinking density of the polyurethanes [42]. Higher tensile strength performance was generally obtained with increasing cross linking density of polyurethane network.

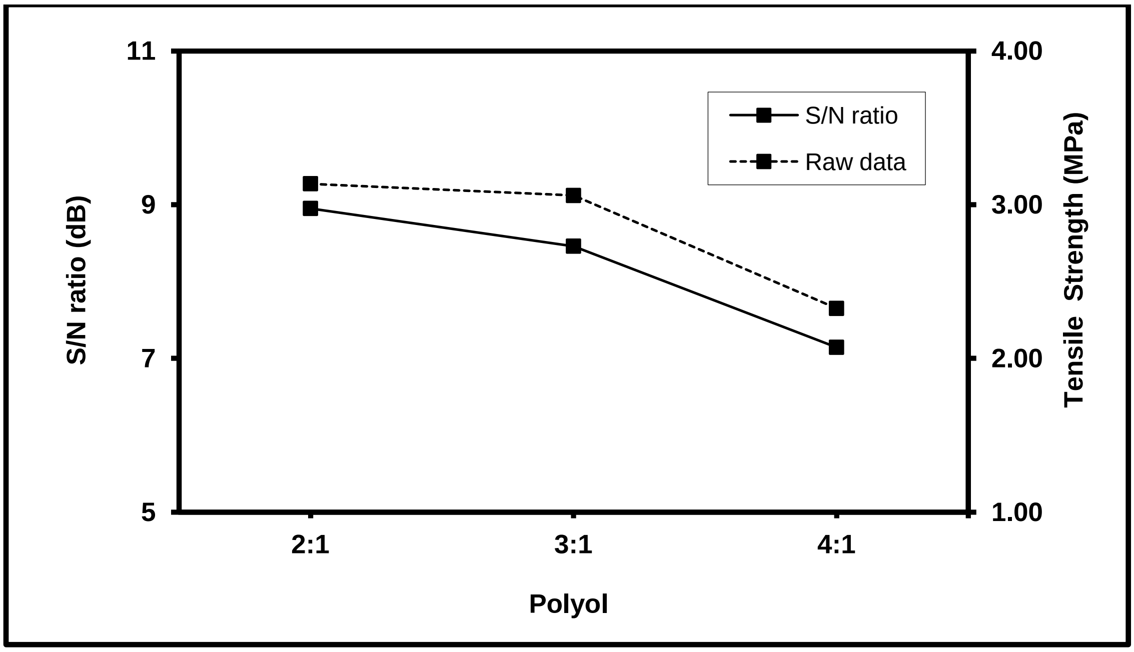


Figure 6.3: Effect of Polyol on Tensile Strength and S/N Ratio

Figure 6.4 show that tensile strength is more in case of 2nd surfactant because addition of 3 % concentration of surfactant depresses the pressure differences between bubbles of different sizes and enhance the stability of the bubbles significantly.

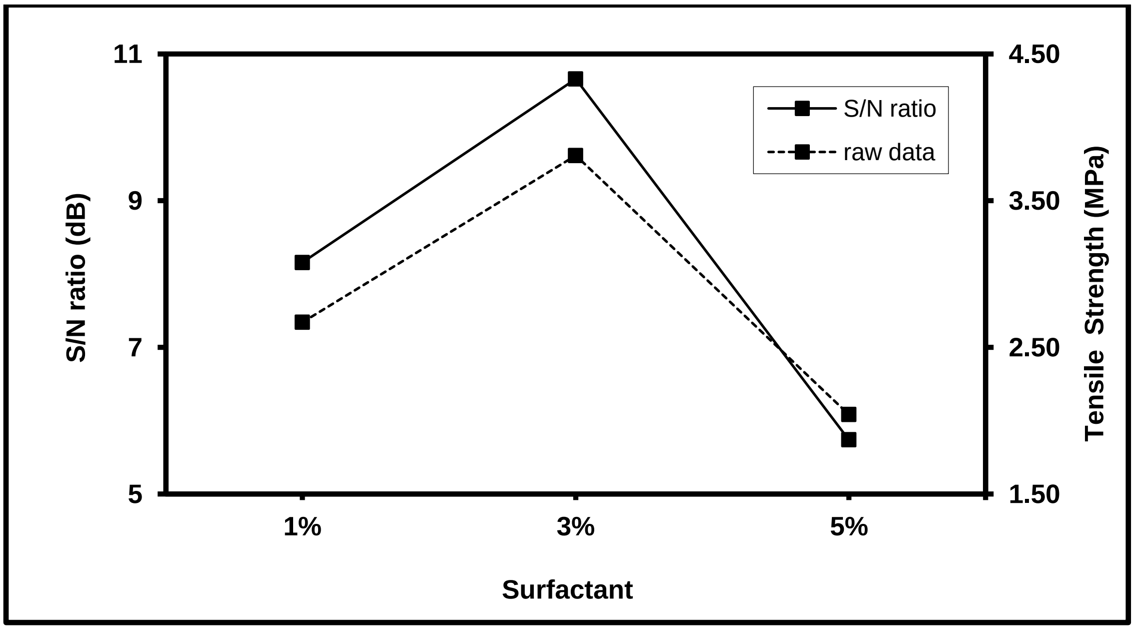


Figure 6.4: Effect of Surfactant on Tensile Strength and S/N Ratio

These air bubbles provide a site for initiation of foam cell growth. By reducing the surface tension of the polyols, surfactans can perform several useful functions in foam preparation. They can stabilize the initial liquid air dispersion by controlling the number of cells. As excessive amount of surfactant lead to collapse of the foam as the walls and ribs of the foam cells could not withstand the pressure of the gas.

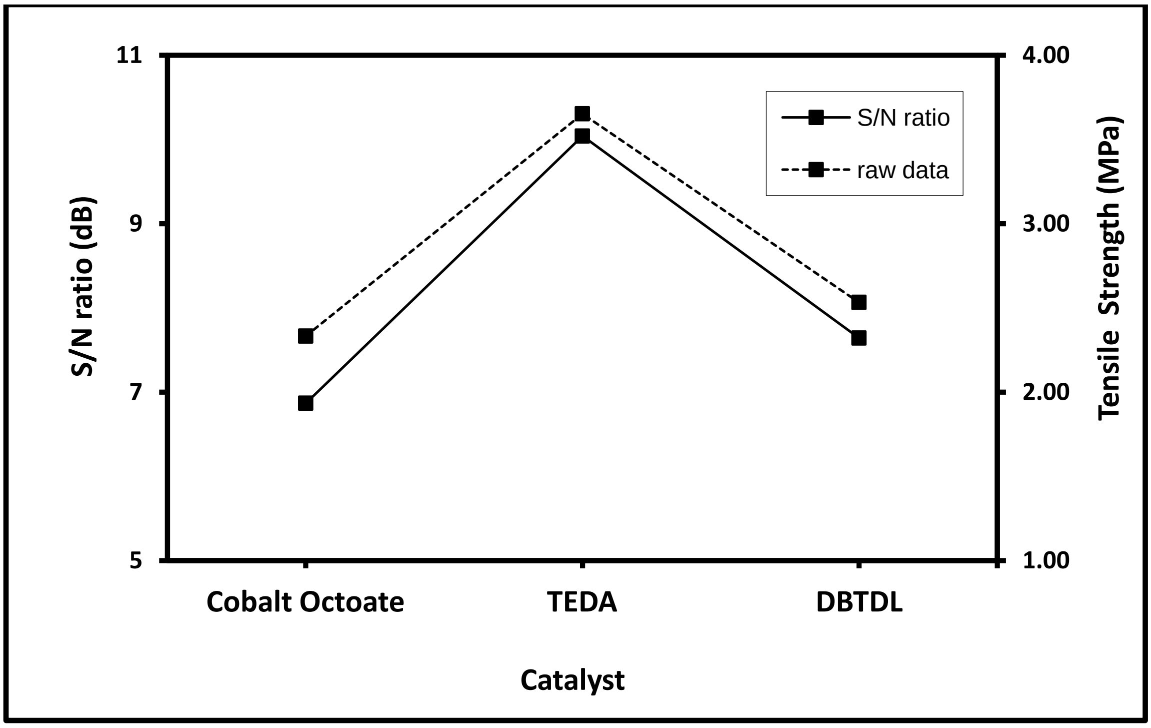


Figure 6.5: Effect of Catalyst on Tensile Strength and S/N Ratio

Figure 6.5 show that tensile strength is more in case of 2nd catalyst due to increased crosslinking. Amine catalysts have ability to control the blowing and gelling reaction that depends on its molecular structure as well as some other factors such as steric and electronic effects. Amine catalysts (TEDA) function by increasing the nucleophilicity of the diol component. They have non-sterically hindered nitrogen atom with a lone pair of electrons that has affinity to react with the C=N moiety of the isocyanate group.

Figure 6.6 show that tensile strength is more in case of 3rd blowing agent because increase in concentration of blowing agent results in smaller average cell size and increased in number of cells per unit volume. Physical blowing agents do not take part in foaming reaction, but they are highly volatile liquids that vapourise easily on reducing the pressure to make a cellular structure. Concentration of the blowing agents should be optimum to produce foam product. The rate of gelling and foaming reaction should also be matched to form desire foam.

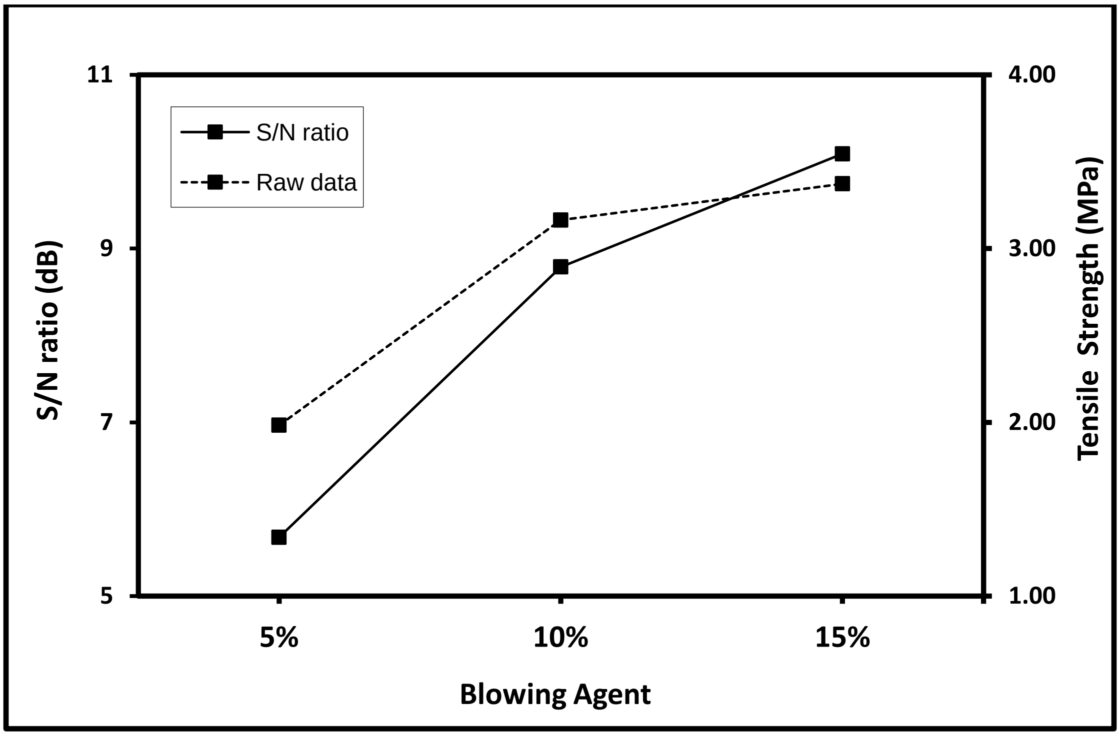


Figure 6.6: Effect of Blowing Agent on Tensile Strength and S/N Ratio

Figure 6.7 show that tensile strength is more in case of 2nd antiflamming agent. High value of tensile strength with Tris (1,3-dichloro-2-propylphosphate) (TDCPP) indicates that the dispersion of TDCPP in the PU matrix was good with proper adhesion. The decrease in tensile strength in case of 1st antiflamming agent is due to involvement of melamine in the polyurethane matrix that weakens the cellular structure. Higher particles size of the melamine results in collapsing of cellular structure during the formation of foam.

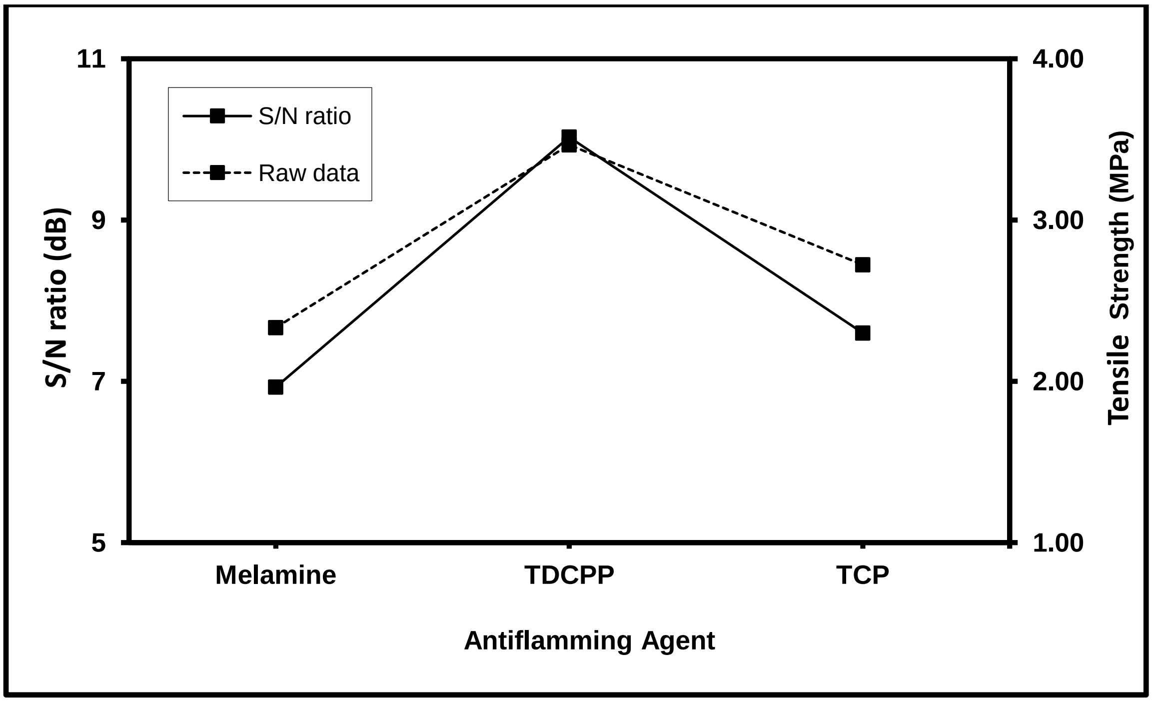


Figure 6.7: Effect of Antiflamming Agent on Tensile Strength and S/N Ratio

6.2.1.1 Selection of Optimal Levels

To determine which factors significantly affects the **response characteristics**, ANOVA has been performed. The pooled version of ANOVA for average values of **raw data** as well as **S/N ratio** is given in Tables 6.8 and 6.9 respectively. These Tables indicate that all the parameters significantly affect both the average values and the S/N ratio.

Table 6.8: ANOVA of Tensile Strength (Raw Data)

Source	**SS**	**DOF**	**V**	**F-Ratio**	**P %**	**SS'**
Filler	15.29	1	15.29	45.16	14.52	14.94
Polyol	7.22	2	3.61	10.67	6.86	6.54
Surfactant	28.81	2	14.40	45.16	27.36	28.13
Catalyst	18.21	2	9.11	26.91	17.30	17.54
Blowing Agent	9.63	2	4.82	14.23	9.14	8.95
Antiflamming Agent	11.92	2	5.96	17.62	11.32	11.25
Error	14.21	42	0.34		13.50	17.94
Total	105.29	53			100	105.29
Findings are significant at 95% level of confidence, SS is Sum of Squares, DOF is Degree of Freedom, V is Variance, F-ratio tabulated = 3.223 and P% is Percentage contribution.						

Table 6.9: ANOVA of Tensile Strength (S/N ratio)

Source	**SS**	**DOF**	**V**	**F-Ratio**	**P %**	**SS'**
Filler	29.01	1	29.01	34.16	11.91	28.16
Polyol	10.47	2	5.23	6.16	4.30	8.77
Surfactant	72.58	2	36.29	42.73	29.79	70.88
Catalyst	32.82	2	16.41	19.32	13.47	31.12
Blowing Agent	61.74	2	30.87	36.35	25.34	60.04
Antiflamming Agent	31.91	2	15.96	18.79	13.10	30.22
Error	5.10	6	0.85		2.09	14.44
Total	243.63	17	*		100	243.63
Findings are significant at 95% level of confidence, SS is Sum of Squares, DOF is Degree of Freedom, V is Variance, F-ratio tabulated = 3.223 and P% is Percentage contribution.						

6.2.1.2 Estimation of Optimum Performance Characteristics

The optimum value of tensile strength is predicted at the selected levels of significant parameters $A_1B_1C_2D_2E_3F_2$. The estimated mean of the response characteristic tensile strength is determined [106] as

$\mu_{TS} = \bar{A}_1 + \bar{B}_1 + \bar{C}_2 + \bar{D}_2 + \bar{E}_3 + \bar{F}_2 - 5 \times \bar{T}$

where

T : Overall mean of tensile strength = 2.84

A_1 : Average tensile strength at the 1st level of Filler = 3.37

B_1 : Average tensile strength at the 1st level of Polyol = 3.14

C_2 : Average tensile strength at the 2nd level of Surfactant = 3.81

D_2 : Average tensile strength at the 2nd level of Catalyst = 3.65

E_3 : Average tensile strength at the 3rd level of Blowing Agent = 3.37

F_2 : Average tensile strength at the 2nd level of Antiflamming Agent = 3.47

(Ref. to Table 6.6 and Figure 6.2 to 6.7)

Putting the values of different terms in the equation given above

$\mu_{TS} = 3.37 + 3.14 + 3.81 + 3.65 + 3.37 + 3.47 - 5 \times 2.84$

$\mu_{TS} = 6.61$

The 95% confidence interval of confirmation experiments (CI_{CE}) and of population (CI_{POP}) is calculated by using the following equations:

$$CI_{CE} = \sqrt{F_a\,(1, f_e\,)V_e\,[\,\frac{1}{n_{eff}} + \frac{1}{R}]}$$

$$CI_{POP} = \sqrt{\frac{F_a\,(1,f_e)V_e}{n_{eff}}}$$

Where $F_a(1, f_e)$: The ratio at the confidence level of (1-α) against DOF (Degree of freedom) 53 and error DOF $f_e = 42$,

N: Total number of results = 54 (Treatment = 18, Repetition = 3),

R: Sample size for confirmation experiments = 3,

V_e: Error variance = 0.34 (Ref. Table 6.8),

Fe (error DOF) = 42

$$N_{eff} = \frac{N}{1+[DOF\ associated\ in\ the\ estimate\ of\ mean\ response]}$$

$$N_{eff} = \frac{54}{1+11} = 4.5$$

$F_{0.05}(1, 42) = 3.223$ (tabulated F value),

So $CI_{CE} = \pm 2.82$, $CI_{POP} = \pm 1.78$

The predicted optimal range (for a confirmation runs of three experiments) is:

$\mu_{TS} - CI_{CE} < \mu_{TS} < \mu_{TS} + CI_{CE}$;

$3.79 < \mu_{TS} < 9.43$

The 95% confirmation interval of the predicted mean is as follows:

$\mu_{TS} - CI_{POP} < \mu_{TS} < \mu_{TS} + CI_{POP}$

$4.83 < \mu_{TS} < 8.39$

The optimal value of different process variables obtained for optimized tensile strength is as follows:

Filler (A, 1st level) = Flyash, Polyol (B, 1st level) = 2:1, Surfactant (C, 2nd level) = 3%, Catalyst (D, 2nd level) = TEDA, Blowing Agent (E, 3rd level) = 15 %, Antiflamming Agent (F, 2nd level) = TDCPP

6.2.1.3 Confirmation Experiment

Confirmation experiments were performed in triplicate at optimum setting of the process parameters for tensile strength. Filler is set at 1st level, polyol at 1st level, surfactant at 2nd level, catalyst at 2nd level, blowing agent at 3rd level and antiflamming agent at 2nd level. From the confirmation experiments the average tensile strength is found to be 5.24 MPa, which falls within the 95% confidence interval of the predicted optimum parameter.

6.2.2 Effect on Compressive Strength (CS)

The raw data for average values of compressive strength and S/N ratio for each parameter was analyzed at three levels (L_1, L_2 and L_3). The results so obtained are presented in Tables 6.10 and 6.11 respectively. The response curves for individual effects of six process parameters for the average value of compressive strength and S/N ratio have been plotted as shown in Figure 6.8 to 6.13.

Table 6.10: Main Effects of Compressive Strength (Raw Data) at Various Levels

LEVEL	Filler	Polyol	Surfactant	Catalyst	Blowing Agent	Antiflamming Agent
L_1	3.48	3.16	2.54	2.04	1.73	1.89
L_2	1.89	2.93	3.54	3.67	3.16	3.46
L_3	*	1.98	1.98	2.35	3.18	2.71
L_2-L_1	-1.59	-0.23	1.00	1.62	1.43	1.57
L_3-L_2		-0.95	-1.56	-1.31	0.02	-0.76
DIFFERENCE	-1.59	-0.73	-2.57	-2.94	-1.42	-2.33

Where 1, 2 and 3 level of parameters is represented by L_1, L_2 and L_3 respectively. L_2-L_1 and L_3-L_2 represents average main effects especially when corresponding parameters changes from one level to other level such as from level 1 to level 2 and level 2 to level 3.

Table 6.11: Main Effects of Compressive Strength (S/N Ratio) at Various Levels

LEVEL	Filler	Polyol	Surfactant	Catalyst	Blowing agent	Antiflamming Agent
L_1	9.41	8.24	7.48	5.39	4.44	5.13
L_2	5.09	7.93	9.08	9.65	8.03	9.52
L_3	*	5.59	5.20	6.72	9.28	7.10
L_2-L_1	-4.32	-0.31	1.59	4.26	3.59	4.38
L_3-L_2	*	-2.34	-3.88	-2.92	1.25	-2.42
DIFFERENCE	-4.32	-2.03	-5.47	-7.18	-2.35	-6.80

Where 1, 2 and 3 level of parameters is represented by L_1, L_2 and L_3 respectively. L_2-L_1 and L_3-L_2 represents average main effects especially when corresponding parameters changes from one level to other level such as from level 1 to level 2 and level 2 to level 3.

Figure 6.8 shows that compressive strength is more in case of 1st filler (Flyash) than 2nd filler ($CaCO_3$) because of proper dispersion of flyash into rigid polyurethane foam. Fillers play an important role in modifying the properties of various polymers.

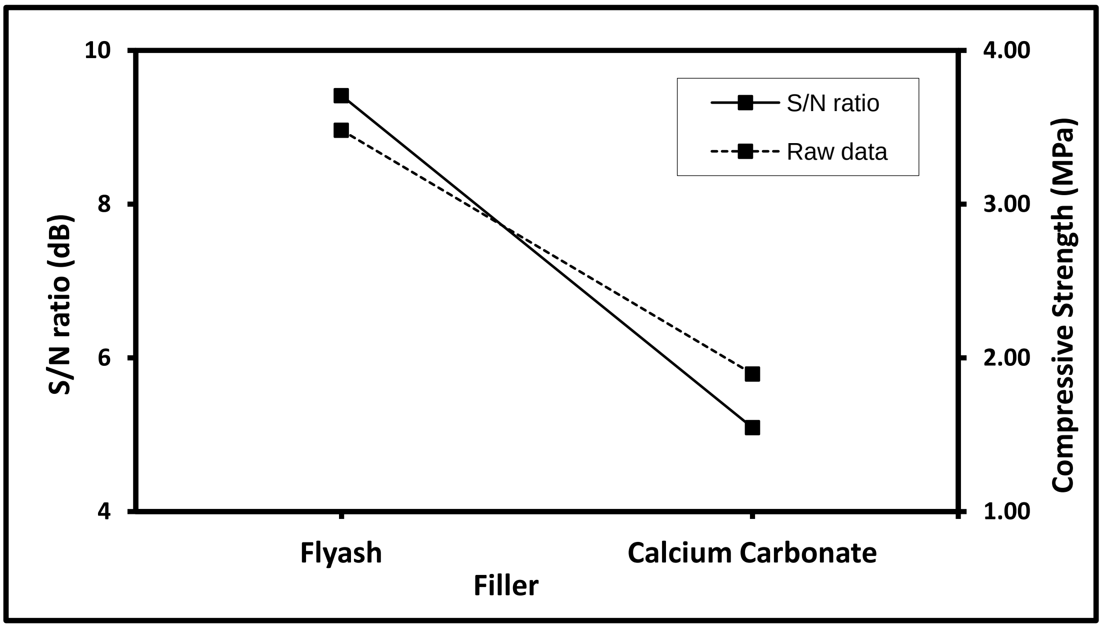


Figure 6.8: Effect of Filler on Compressive Strength and S/N Ratio

The effect of fillers on compressive strength of rigid polyurethane foam mainly depends on their concentration, size of the particles and shape as well as on the interaction of the particles with the matrix.

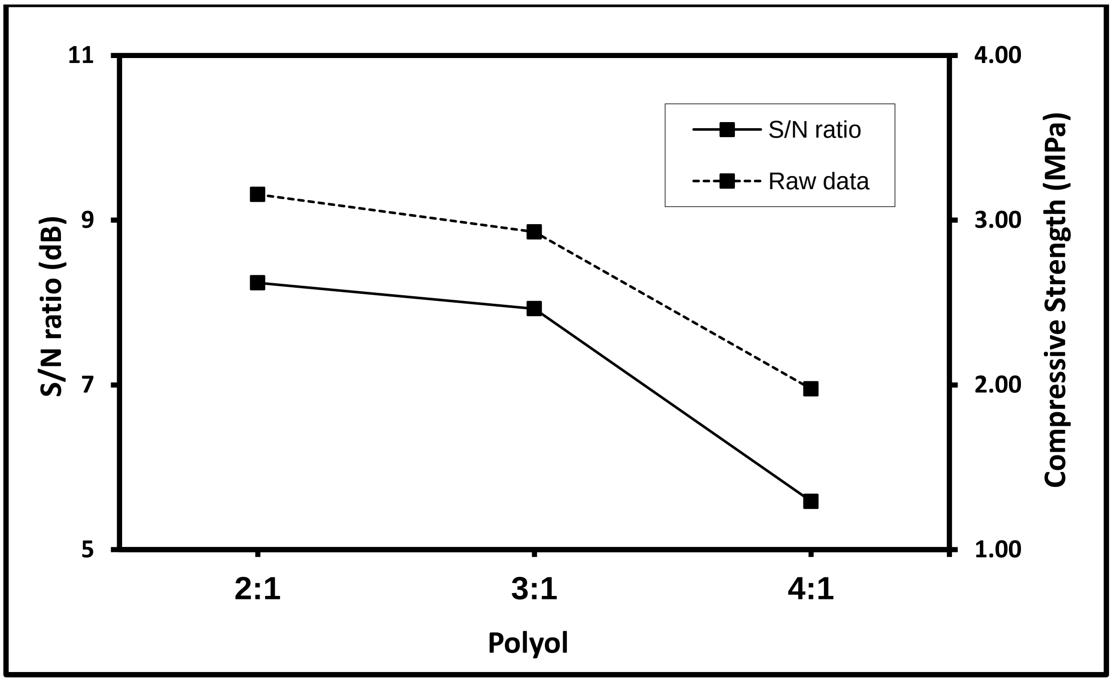


Figure 6.9: Effect of Polyol on Compressive Strength and S/N Ratio

Figure 6.9 shows that compressive strength is more in case of 1st polyol because of more number of hydroxyl group which causes more crosslinking. The network parmeters of the RPUFs mainly depend on the crosslinking density. Thus, most of the properties are expected to depend on the type of vegetable oil and hydroxyl group content of the polyols which is directly related to the crosslinking density of the polyurethanes [42]. Higher compressive strength performance was generally obtained with increasing cross linking density of polyurethane network.

Figure 6.10 shows that compressive strength is more in case of 2nd surfactant because addition of 3 % concentration of surfactant depresses the pressure differences between bubbles of different sizes and enhance the stability of the bubbles significantly. These air bubbles provide a site for initiation of foam cell growth. By reducing the surface tension of the polyols, surfactans can perform several useful functions in foam preparation. They can stabilize the initial liquid air dispersion by controlling the number of cells. As excessive amount of surfactant lead to collapse of the foam as the walls and ribs of the foam cells could not withstand the pressure of the gas.

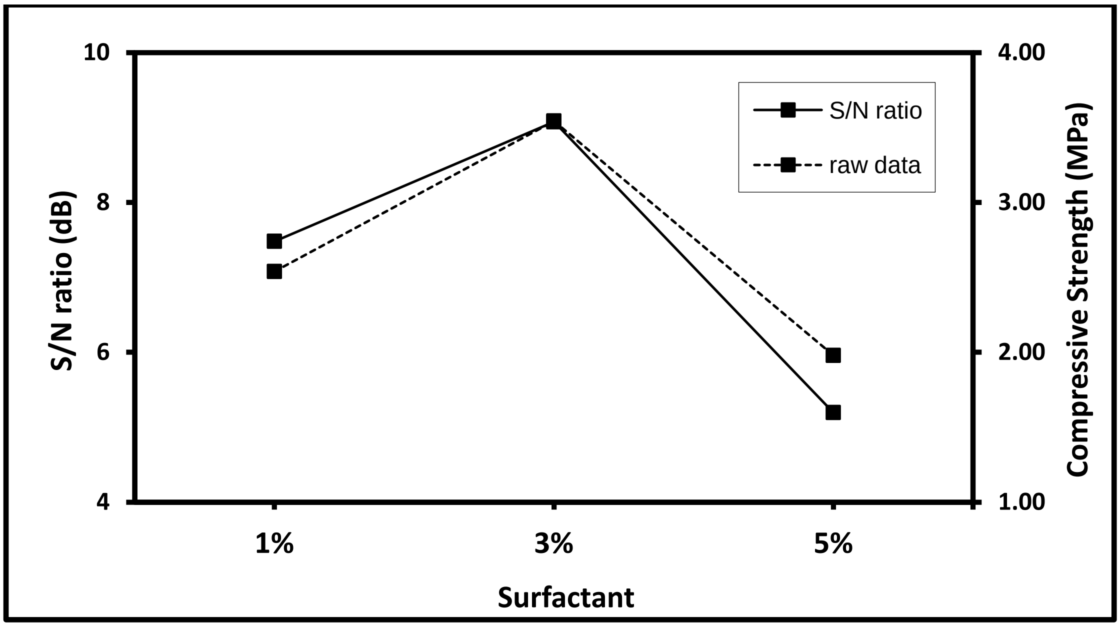


Figure 6.10: Effect of Surfactant on Compressive Strength and S/N Ratio

Figure 6.11 shows that compressive strength is more in case of 2nd catalyst due to increased crosslinking. Amine catalysts have ability to control the blowing and gelling reaction that depends on its molecular structure as well as some other factors such as steric and electronic effects. Amine catalysts (TEDA) function by increasing the nucleophilicity of the diol component. They have non-sterically hindered nitrogen atom with a lone pair of electrons that has affinity to react with the C=N moiety of the isocyanate group.

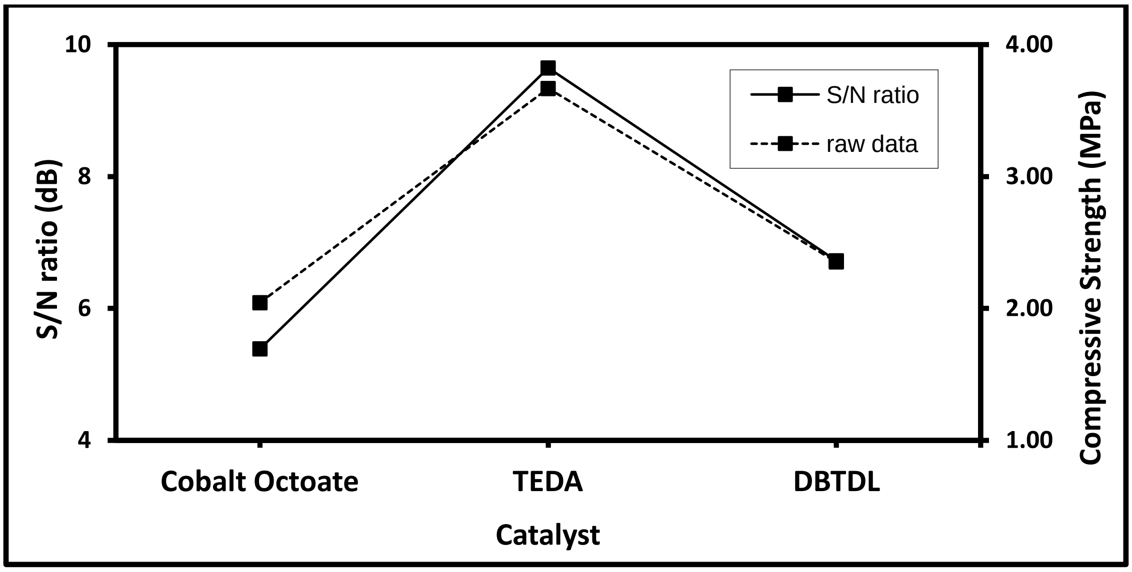


Figure 6.11: Effect of Catalyst on Compressive Strength and S/N Ratio

Figure 6.12 shows that compressive strength is more in case of 3rd blowing agent because increase in concentration of blowing agent results in smaller average cell size and increased in number of cells per unit volume.

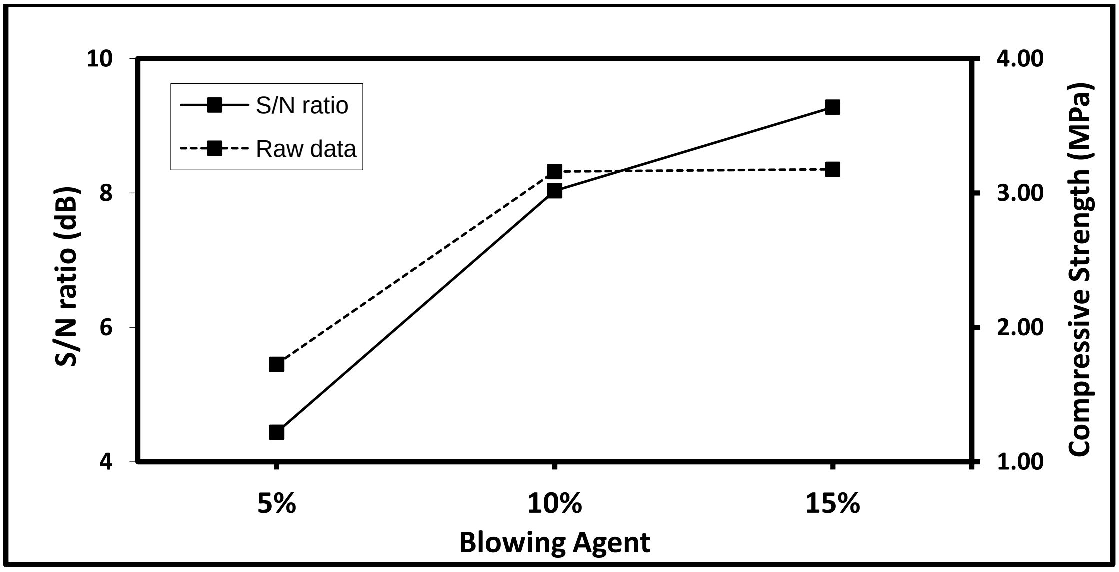


Figure 6.12: Effect of Blowing Agent on Compressive Strength and S/N Ratio

Physical blowing agents do not take part in foaming reaction, but they are highly volatile liquids that vapourise easily on reducing the pressure to make a cellular structure. Concentration of the blowing agents should be optimum to produce foam product. The rate of gelling and foaming reaction should also be matched to form desire foam.

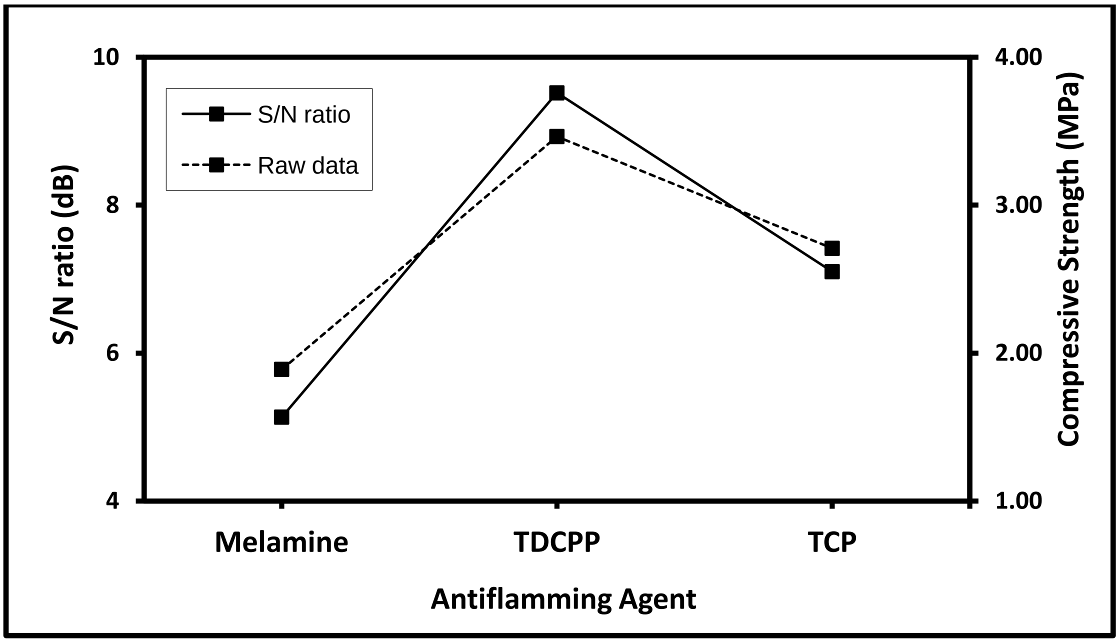


Figure 6.13: Effect of Antiflamming Agent on Compressive Strength and S/N Ratio

Figure 6.13 show that compressive strength is more in case of 3rd antiflamming agent. High value of compressive strength with Tris (1,3-dichloro-2-propylphosphate) (TDCPP) indicates that the dispersion of TDCPP in the PU matrix was good with proper adhesion. The decrease in compressive strength in case of 1st antiflamming agent is due to involvement of melamine in the polyurethane matrix that weakens the cellular structure. Higher particles size of the melamine results in collapsing of cellular structure during the formation of foam.

6.2.2.1 Selection of Optimal Levels

To determine which factors significantly affects the response characteristics, ANOVA has been performed. The pooled version of ANOVA for average values of raw data as well as S/N ratio is given in Tables 6.12 and 6.13 respectively. These Tables indicate that all the parameters significantly affect both the average values and the S/N ratio.

Table 6.12: ANOVA of Compressive Strength (Raw Data)

Source	**SS**	**DOF**	**V**	**F-Ratio**	**P %**	**SS'**
Filler	33.97	1	33.97	244.89	22.15	33.84
Polyol	14.12	2	7.06	50.90	9.21	13.84
Surfactant	22.63	2	11.31	244.89	14.75	22.35
Catalyst	26.76	2	13.38	96.46	17.45	26.46
Blowing Agent	27.74	2	13.87	99.99	18.09	27.46
Antiflamming Agent	22.33	2	11.16	80.47	14.56	22.05
Error	5.83	42	0.14		3.80	7.35
Total	153.38	53			100	153.35
Findings are significant at 95% level of confidence, SS is Sum of Squares, DOF is Degree of Freedom, V is Variance, F-ratio tabulated = 3.223 and P% is Percentage contribution.						

Table 6.13: ANOVA of Compressive Strength (S/N Ratio)

Source	**SS**	**DOF**	**V**	**F-Ratio**	**P %**	**SS'**
Filler	83.98	1	83.98	52.45	23.65	82.38
Polyol	25.24	2	12.62	7.88	7.11	22.04
Surfactant	45.64	2	22.82	14.25	12.85	42.44
Catalyst	56.95	2	28.48	17.78	16.04	53.75
Blowing Agent	75.80	2	37.90	23.67	21.35	72.60
Antiflamming Agent	57.87	2	28.94	18.07	16.30	54.67
Error	9.61	6	1.60		2.71	27.22
Total	355.09	17	*		100	355.1
Findings are significant at 95% level of confidence, SS is Sum of Squares, DOF is Degree of Freedom, V is Variance, F-ratio tabulated = 3.223 and P% is Percentage contribution.						

6.2.2.2 Estimation of Optimum Performance Characteristics

The optimum value of compressive strength is predicted at the selected levels of significant parameters $A_1B_1C_2D_2E_3F_2$. The estimated mean of the response characteristic compressive strength is determined [106] as

$\mu_{CS} = \bar{A}_1 + \bar{B}_1 + \bar{C}_2 + \bar{D}_2 + \bar{E}_3 + \bar{F}_2 - 5 \text{ x } \bar{T}$

where

T : Overall mean of compressive strength = 2.69

A_1 : Average compressive strength at the 1st level of Filler = 3.48

B_1 : Average compressive strength at the 1st level of Polyol = 3.16

C_2 : Average compressive strength at the 2nd level of Surfactant = 3.54

D_2 : Average compressive strength at the 2nd level of Catalyst = 3.67

E_3 : Average compressive strength at the 3rd level of Blowing Agent = 3.18

F_2 : Average compressive strength at the 2nd level of Antiflamming Agent = 2.71

(Ref. to Table 6.10 and Figure 6.8 to 6.13)

Putting the values of different terms in the equation given above

$\mu_{CS} = 3.48 + 3.16 + 3.54 + 3.67 + 3.18 + 2.71 - 5 \times 2.69$

$\mu_{CS} = 6.29$

The 95% confidence interval of confirmation experiments (CI_{CE}) and of population (CI_{POP}) is calculated by using the following equations:

$$CI_{CE} = \sqrt{F_a\,(1, f_e)V_e\left[\frac{1}{n_{eff}} + \frac{1}{R}\right]}$$

$$CI_{POP} = \sqrt{\frac{F_a\,(1, f_e)V_e}{n_{eff}}}$$

Where $F_a(1, f_e)$: The ratio at the confidence level of (1-α) against DOF 53 and error DOF $f_e = 42$,

N: Total number of results = 54 (Treatment = 18, Repetition = 3),

R: Sample size for confirmation experiments = 3,

V_e: Error variance = 0.14 (Ref. Table 6.12),

Fe (error DOF) = 42

$$N_{eff} = \frac{N}{1+[DOF\ associated\ in\ the\ estimate\ of\ mean\ response]}$$

$$N_{eff} = \frac{54}{1+11} = 4.5$$

$F_{0.05}\,(1, 42) = 3.223$ (tabulated F value), So $CI_{CE} = \pm 1.81$, $CI_{POP} = \pm 1.14$

The predicted optimal range (for a confirmation runs of three experiments) is:

$\mu_{CS} - CI_{CE} < \mu_{CS} < \mu_{CS} + CI_{CE;}$

$4.48 < \mu_{CS} < 8.10$

The 95% confirmation interval of the predicted mean is as follows:

$\mu_{CS} - CI_{POP} < \mu_{CS} < \mu_{CS} + CI_{POP}$

$5.15 < \mu_{CS} < 7.43$

The optimal value of different process variables obtained for optimized compressive strength is as follows:

Filler (A, 1st level) = Flyash, Polyol (B, 1st level) = 2:1, Surfactant (C, 2nd level) = 3%, Catalyst (D, 2nd level) = TEDA, Blowing Agent (E, 3rd level) = 15%, Antiflamming Agent (F, 2nd level) = TDCPP

6.2.2.3 Confirmation Experiment

Confirmation experiments were performed in triplicate at optimum setting of the process parameters for compressive strength. Filler is set at 1st level, polyol at 1st level, surfactant at 2nd level, catalyst at 2nd level, blowing agent at 3rd level and antiflamming agent at 2nd level. From the confirmation experiments the average compressive strength is found to be 6.37 MPa, which falls within the 95% confidence interval of the predicted optimum parameter.

6.2.3 Effect on Flexural Strength (FS)

The raw data for average values of Flexural strength and S/N ratio for each parameter was analysed at three levels (L_1, L_2 and L_3). The results so obtained are presented in Tables 6.14 and 6.15 respectively. The response curves for individual effects of six process parameters for the average value of flexural strength and S/N ratio have been plotted as shown in Figure 6.14 to 6.19.

Table 6.14: Main Effects of Flexural Strength (Raw Data) at Various Levels

LEVEL	Filler	Polyol	Surfactant	Catalyst	Blowing agent	Antiflamming Agent
L_1	13.33	12.88	11.17	11.44	9.31	9.53
L_2	9.85	12.02	13.79	12.69	12.23	12.82
L_3	*	9.86	9.80	10.63	13.22	12.41
L_2-L_1	-3.48	-0.85	2.63	1.26	2.92	3.29
L_3-L_2		-2.16	-4.00	-2.07	0.99	-0.41
DIFFERENCE	-3.48	-1.31	-6.62	-3.33	-1.93	-3.70
Where 1, 2 and 3 level of parameters is represented by L_1, L_2 and L_3 respectively. L_2-L_1 and L_3-L_2 represents average main effects especially when corresponding parameters changes from one level to other level such as from level 1 to level 2 and level 2 to level 3.						

Table 6.15: Main Effects of Flexural Strength (S/N ratio) at Various Levels

LEVEL	Filler	Polyol	Surfactant	Catalyst	Blowing Agent	Antiflamming Agent
L_1	22.07	21.74	20.83	21.08	19.19	19.44
L_2	19.66	21.19	22.29	21.17	21.22	21.59
L_3	*	19.66	19.47	20.34	22.18	21.56
L_2-L_1	-2.41	-0.54	1.47	0.09	2.04	2.14
L_3-L_2	22.07	21.74	20.83	21.08	19.19	19.44
DIFFERENCE	-2.41	-0.99	-4.29	-0.93	-1.08	-2.17
Where 1, 2 and 3 level of parameters is represented by L_1, L_2 and L_3 respectively. L_2-L_1 and L_3-L_2 represents average main effects especially when corresponding parameters changes from one level to other level such as from level 1 to level 2 and level 2 to level 3.						

Figure 6.14 shows that flexural strength is more in case of 1st filler (Flyash) than 2nd filler ($CaCO_3$) because of proper dispersion of flyash into rigid polyurethane foam. Fillers play an important role in modifying the properties of various polymers. The effect of fillers on flexural strength of rigid polyurethane foam mainly depends on their concentration, size of the particles and shape as well as on the interaction of the particles with the matrix.

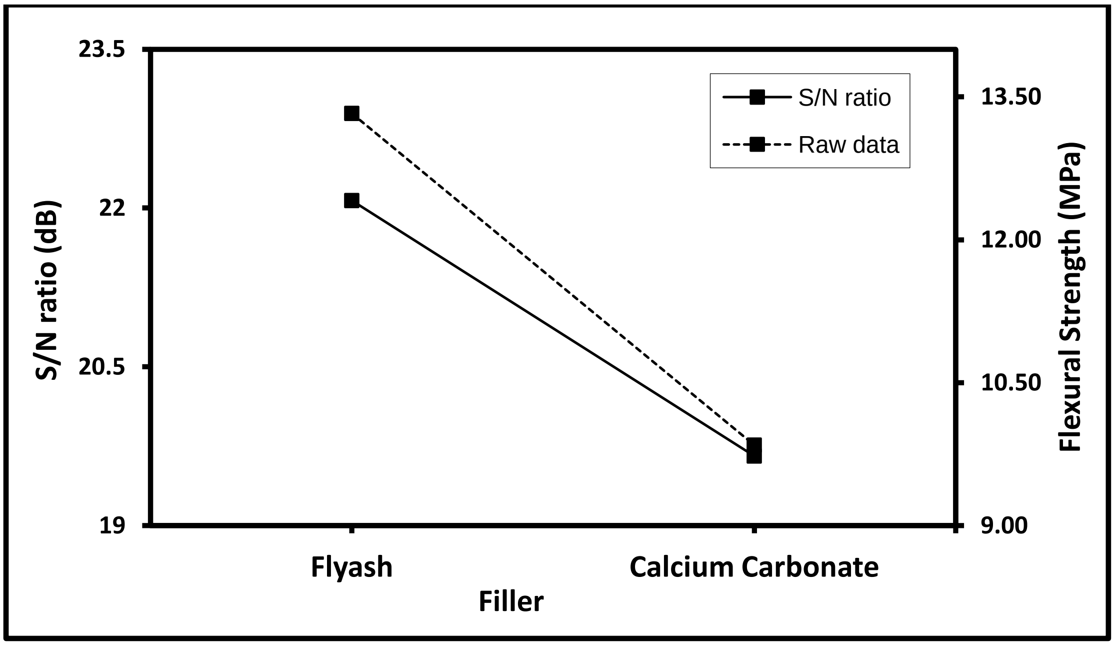


Figure 6.14: Effect of Filler on Flexural Strength and S/N Ratio

Figure 6.15 shows that flexural strength is more in case of 1st polyol because of more number of hydroxyl group which causes more crosslinking. The network parmeters of the RPUFs mainly depend on the crosslinking density. Thus, most of the properties are expected to depend on the type of vegetable oil and hydroxyl group content of the polyols which is directly related to the crosslinking density of the polyurethanes [42]. Higher flexural strength performance was generally obtained with increasing cross linking density of polyurethane network.

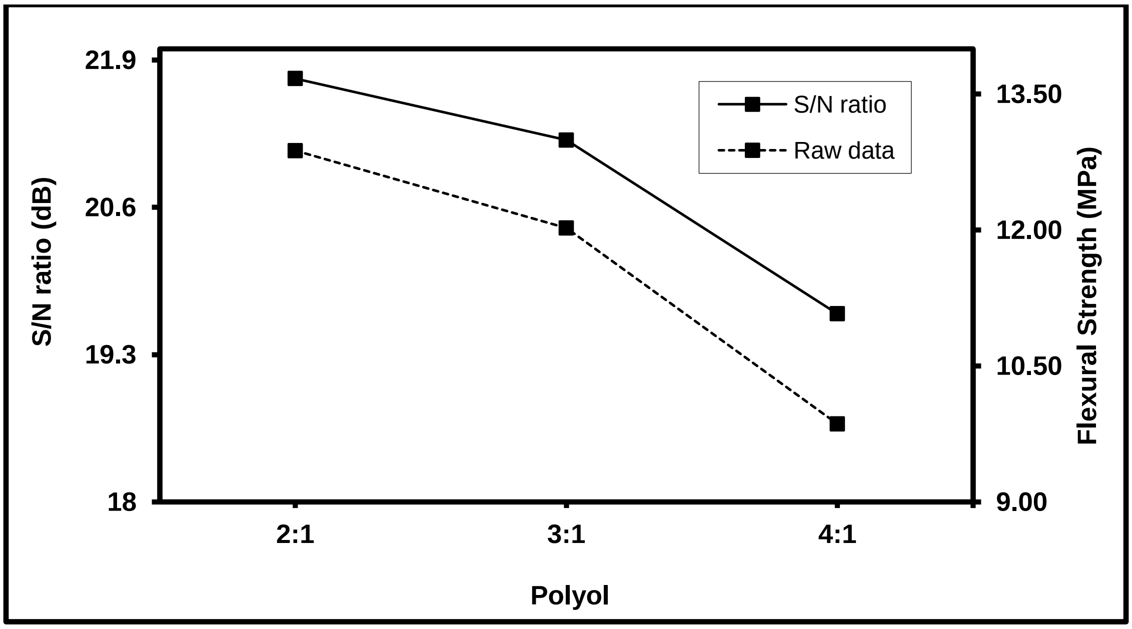


Figure 6.15: Effect of Polyol on Flexural Strength and S/N Ratio

Figure 6.16 shows that flexural strength is more in case of 2nd surfactant because addition of 3 % concentration of surfactant depresses the pressure differences between bubbles of different sizes and enhance the stability of the bubbles significantly.

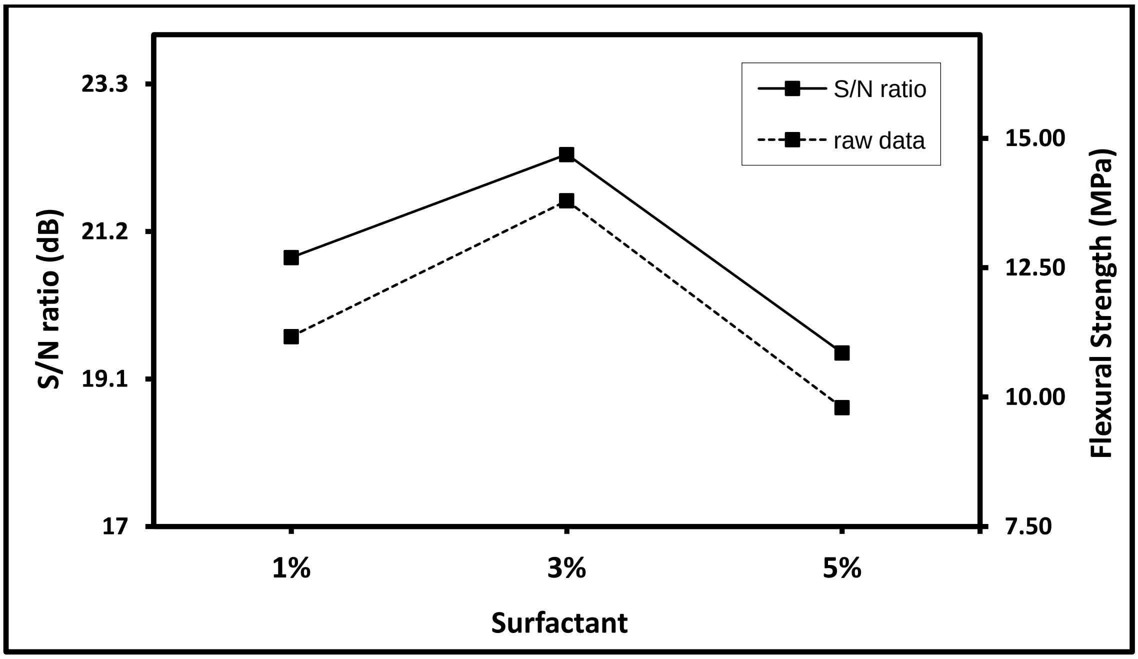


Figure 6.16: Effect of Surfactant on Flexural Strength and S/N Ratio

These air bubbles provide a site for initiation of foam cell growth. By reducing the surface tension of the polyols, surfactans can perform several useful functions in foam preparation. They can stabilize the initial liquid air dispersion by controlling the number of cells. As excessive amount of surfactant lead to collapse of the foam as the walls and ribs of the foam cells could not withstand the pressure of the gas.

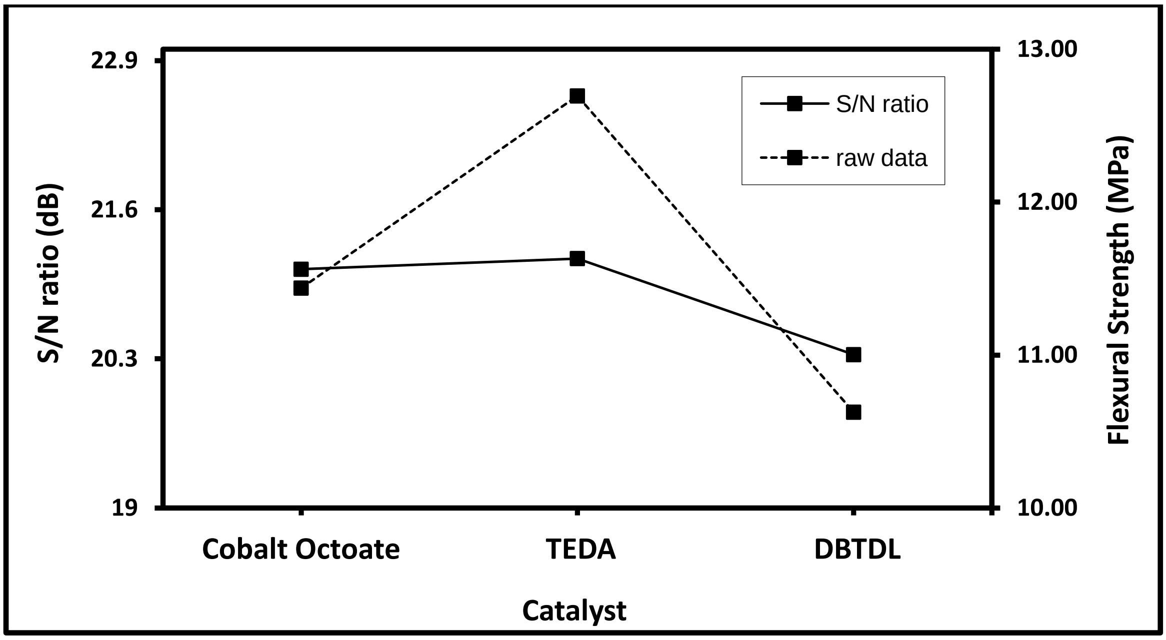


Figure 6.17: Effect of Catalyst on Flexural Strength and S/N Ratio

Figure 6.17 shows that flexural strength is more in case of 2nd catalyst due to increase in crosslinking. Amine catalysts have ability to control the blowing and gelling reaction that depends on its molecular structure as well as some other factors such as steric and electronic effects. Amine catalysts (TEDA) function by increasing the nucleophilicity of the diol component. They have non-sterically hindered nitrogen atom with a lone pair of electrons that has affinity to react with the C=N moiety of the isocyanate group.

Figure 6.18 shows that flexural strength is more in case of 3rd blowing agent because increase in concentration of blowing agent results in smaller average cell size and increased in number of cells per unit volume. Physical blowing agents do not take part in foaming reaction, but they are highly volatile liquids that vapourise easily on reducing the pressure to make a cellular structure. Concentration of the blowing agents should be optimum to produce foam product. The rate of gelling and foaming reaction should also be matched to form desire foam.

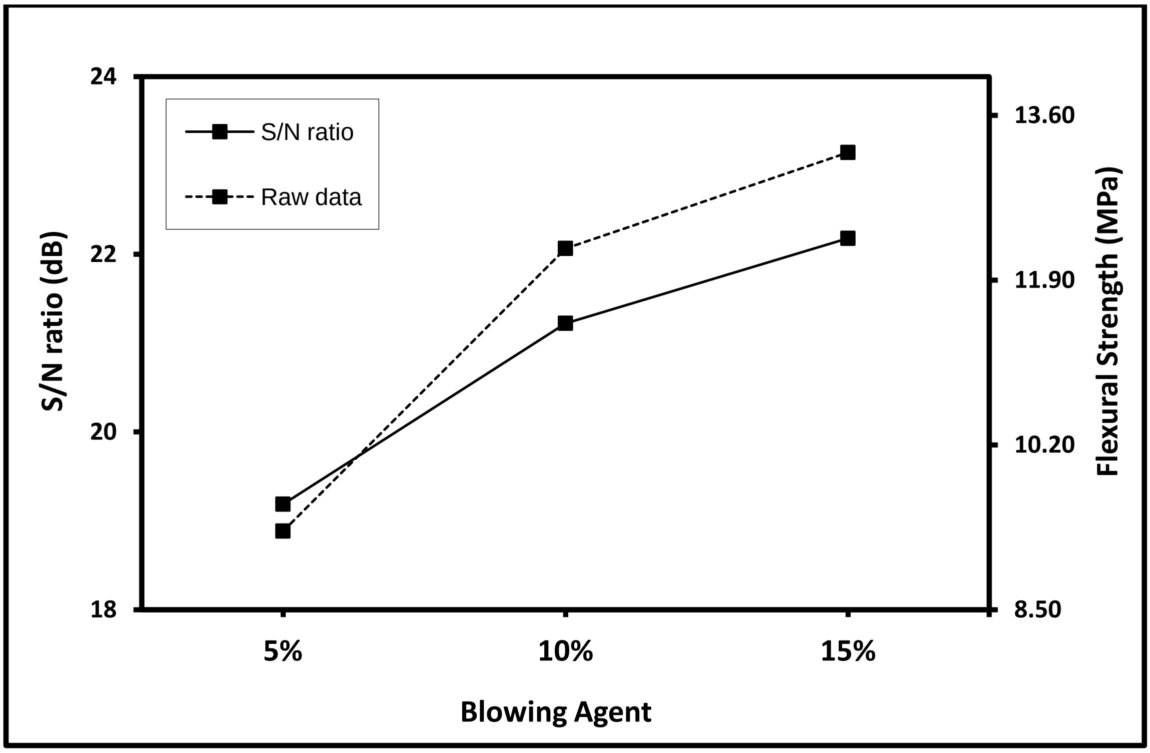


Figure 6.18: Effect of Blowing Agent on Flexural Strength and S/N Ratio

Figure 6.19 show that flexural strength is more in case of 2nd antiflamming agent. High value of flexural strength with Tris (1,3-dichloro-2-propylphosphate) (TDCPP) indicates that the dispersion of TDCPP in the PU matrix was good with proper adhesion. The decrease in tensile strength in case of 1st antiflamming agent is due to involvement of melamine in the polyurethane matrix that weakens the cellular structure. Higher particles size of the melamine results in collapsing of cellular structure during the formation of foam.

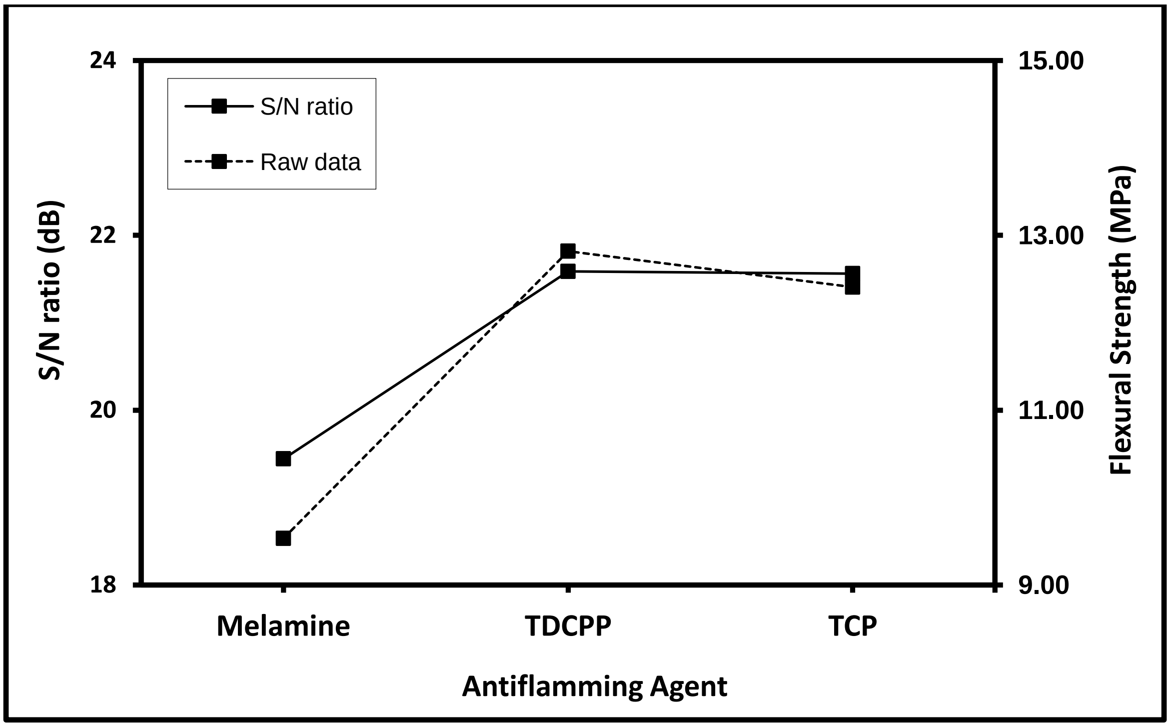


Figure 6.19: Effect of Antiflamming Agent on Flexural Strength and S/N Ratio

6.2.3.1 Selection of optimal levels

To determine which factors significantly affects the response characteristics, ANOVA has been performed. The pooled version of ANOVA for average values of raw data as well as S/N ratio is given in Tables 6.11 and 6.12 respectively. These Tables indicate that all the parameters significantly affect both the average values and the S/N ratio.

Table 6.16: ANOVA of Flexural Strength (Raw Data)

Source	SS	DOF	V	F-Ratio	P %	SS'
Filler	163.53	1	163.53	58.11	21.77	160.71
Polyol	86.95	2	43.47	15.45	11.57	81.32
Surfactant	148.53	2	74.26	58.11	19.77	142.90
Catalyst	39.10	2	19.55	6.95	5.20	33.47
Blowing Agent	79.61	2	39.81	14.15	10.60	73.99
Antiflamming Agent	115.42	2	57.71	20.51	15.36	109.80
Error	118.18	42	2.81		15.73	149.14
Total	751.32	53			100	751.33
Findings are significant at 95% level of confidence, SS is Sum of Squares, DOF is Degree of Freedom, V is Variance, F-ratio tabulated = 3.223 and P% is Percentage contribution.						

Table 6.17: ANOVA of Flexural Strength (S/N ratio)

Source	SS	DOF	V	F-Ratio	P %	SS'
Filler	26.19	1	26.19	34.52	22.32	25.43
Polyol	13.91	2	6.96	9.17	11.86	12.40
Surfactant	23.94	2	11.97	15.77	20.40	22.42
Catalyst	2.53	2	1.27	1.67	2.16	*
Blowing Agent	28.02	2	14.01	18.47	23.88	26.51
Antiflamming Agent	18.18	2	9.09	11.98	15.49	16.66
Error	4.55	6	0.76		3.88	13.91
Total	117.32	17	*		100	117.33
Findings are significant at 95% level of confidence, SS is Sum of Squares, DOF is Degree of Freedom, V is Variance, F-ratio tabulated = 3.223 and P% is Percentage contribution.						

6.2.3.2 Estimation of Optimum Performance Characteristics

The optimum value of flexural strength (FS) is predicted at the selected levels of significant parameters $A_1B_1C_2E_3F_2$. The estimated mean of the response characteristic flexural strength is determined [106] as

$\mu_{FS} = \bar{A}_1 + \bar{B}_1 + \bar{C}_2 + \bar{E}_3 + \bar{F}_2 - 4 \times \bar{T}$

where

T : Overall mean of flexural strength = 11.5

A_1 : Average flexural strength at the 1st level of Filler = 13.33

B_1 : Average flexural strength at the 1st level of Polyol = 12.88

C_2 : Average flexural strength at the 2nd level of Surfactant = 13.79

E_3 : Average flexural strength at the 3rd level of Blowing Agent = 13.22

F_2 : Average flexural strength at the 2nd level of Antiflamming Agent = 12.82

(Ref. to Table 6.14 and Figure 6.14 to 6.19)

Putting the values of different terms in the equation given above

$\mu_{FS} = 13.33 + 12.88 + 13.79 + 13.22 + 12.82 - 4 \times 11.59$

$\mu_{FS} = 19.68$

The 95% confidence interval of confirmation experiments (CI_{CE}) and of population (CI_{pop}) is calculated by using the following equations:

$$CI_{CE} = \sqrt{F_a\,(1, f_e)V_e\left[\frac{1}{n_{eff}} + \frac{1}{R}\right]}$$

$$CI_{POP} = \sqrt{\frac{F_a\,(1, f_e)V_e}{n_{eff}}}$$

Where $F_a(1, f_e)$: The ratio at the confidence level of (1-α) against DOF 53 and error DOF $f_e = 42$,

N: Total number of results = 54 (Treatment = 18, Repetition = 3), R: Sample size for confirmation experiments = 3,

V_e: Error variance = 2.81 (Ref. Table 6.16),

Fe (error DOF) = 42

$$N_{eff} = \frac{N}{1+[DOF\ associated\ in\ the\ estimate\ of\ mean\ response]}$$

$$N_{eff} = \frac{54}{1+11} = 4.5$$

$F_{0.05}$ (1, 42) = 3.2236 (tabulated F value),

So $CI_{CE} = \pm 8.09$, $CI_{POP} = \pm 5.12$

The predicted optimal range (for a confirmation runs of three experiments) is:

$\mu_{FS} - CI_{CE} < \mu_{FS} < \mu_{FS} + CI_{CE}$;

$3.5 < \mu_{FS} < 19.68$

The 95% confirmation interval of the predicted mean is as follows:

$\mu_{FS} - CI_{POP} < \mu_{FS} < \mu_{FS} + CI_{POP}$

$6.47 < \mu_{FS} < 16.71$

The optimal value of different process variables obtained for optimized flexural strength is as follows:

Filler (A, 1st level) = Flyash, Polyol (B, 1st level) = 2:1, Surfactant (C, 2nd level) = 3%, Blowing Agent (E, 3rd level) = 15%, Antiflamming Agent (F, 2nd level) = TDCPP

6.2.3.3 Confirmation Experiment

Confirmation experiments were performed in triplicate at optimum setting of the process parameters for flexural strength. Filler is set at 1st level, polyol at 1st level, surfactant at 2nd level, catalyst at 2nd level, blowing agent at 3rd level and antiflamming agent at 2nd level. From the confirmation experiments the average flexural strength is found to be 12.28 MPa, which falls within the 95% confidence interval of the predicted optimum parameter.

6.2.4 Effects on Hardness

The raw data for average values of hardness and S/N ratio for each parameter was analysed at three levels (L_1, L_2 and L_3). The results so obtained are presented in Tables 6.18 and 6.19 respectively. The response curves for individual effects of six process parameters for the average value of hardness and S/N ratio have been plotted as shown in Figure 6.20 to 6.25.

Table 6.18: Main Effects of Hardness (Raw Data) at Various Levels

LEVEL	Filler	Polyol	Surfactant	Catalyst	Blowing Agent	Antiflamming Agent
L_1	56.00	54.06	48.00	44.28	43.67	46.00
L_2	39.44	47	52.50	53.17	49.67	51.83
L_3	*	42.11	42.67	45.72	49.83	45.33
L_2-L_1	-16.56	-7.06	4.50	8.89	6.00	5.83
L_3-L_2		-4.89	-9.83	-7.44	0.17	-6.50
DIFFERENCE	-16.56	2.17	-14.33	-16.33	-5.83	-12.33

Where 1, 2 and 3 level of parameters is represented by L_1, L_2 and L_3 respectively. $L_2 - L_1$ and $L_3 - L_2$ represents average main effects especially when corresponding parameters changes from one level to other level such as from level 1 to level 2 and level 2 to level 3.

Table 6.19: Main Effects of Hardness (S/N ratio) at Various Levels

LEVEL	Filler	Polyol	Surfactant	Catalyst	Blowing Agent	Antiflamming Agent
L_1	34.78	34.33	33.47	32.67	32.65	33.10
L_2	31.77	33.14	33.95	34.06	33.41	33.92
L_3	*	32.36	32.40	33.10	33.76	32.80
L_2-L_1	-3.01	-1.19	0.48	1.39	0.76	0.83
L_3-L_2	*	-0.78	-1.56	-0.96	0.35	-1.12
DIFFERENCE	-3.01	0.41	-2.04	-2.34	-0.41	-1.95
Where 1, 2 and 3 level of parameters is represented by L_1, L_2 and L_3 respectively. L_2-L_1 and L_3-L_2 represents average main effects especially when corresponding parameters changes from one level to other level such as from level 1 to level 2 and level 2 to level 3.						

Figure 6.20 showss that hardness is more in case of 1st filler (Flyash) than 2nd filler ($CaCO_3$) because of proper dispersion of flyash into rigid polyurethane foam.

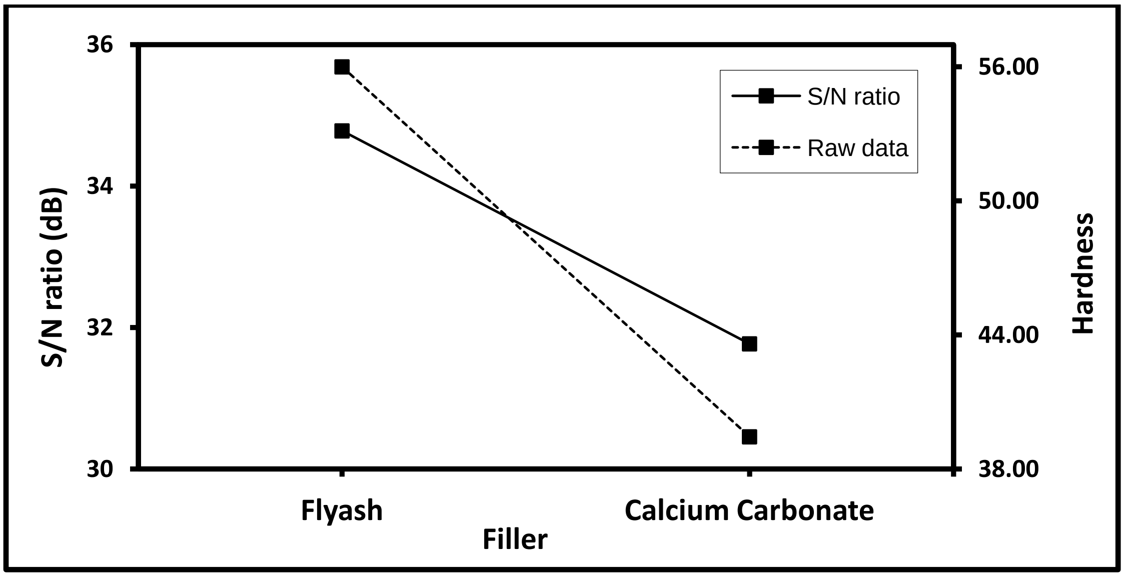


Figure 6.20: Effect of Filler on Hardness and S/N Ratio

Fillers play an important role in modifying the properties of various polymers. The effect of fillers on hardness of rigid polyurethane foam mainly depends on their concentration, size of the particles and shape as well as on the interaction of the particles with the matrix.

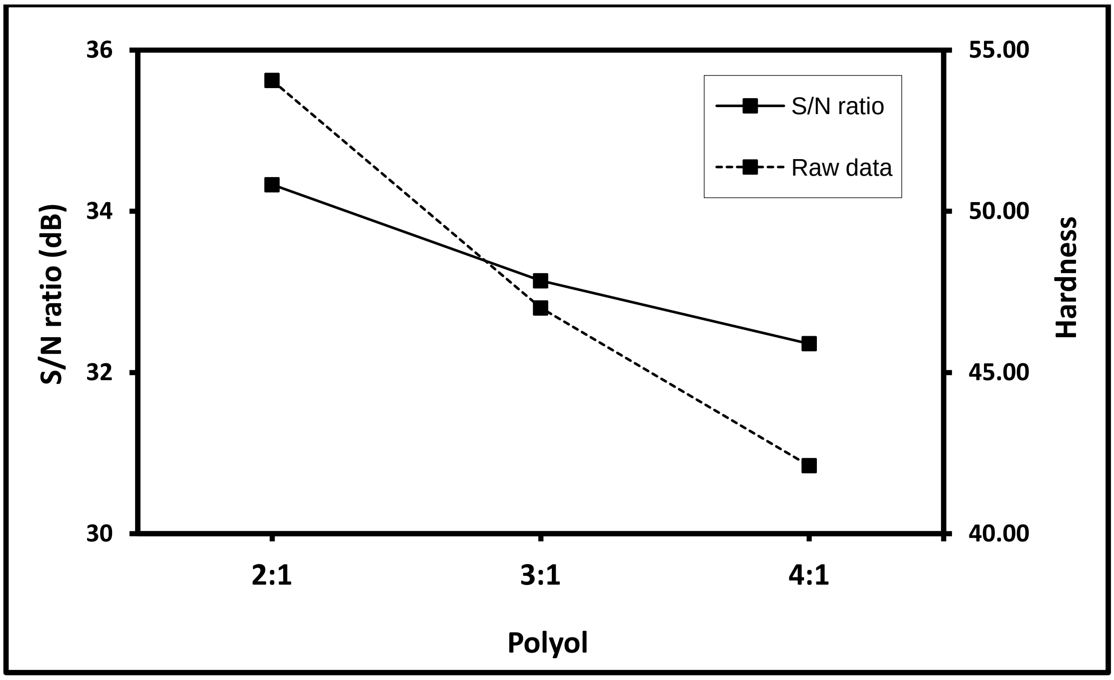


Figure 6.21: Effect of Polyol on Hardness and S/N Ratio

Figure 6.21 shows that hardness is more in case of 1st polyol because of more number of hydroxyl group which causes more crosslinking. The network parmeters of the RPUFs mainly depend on the crosslinking density. Thus, most of the properties are expected to depend on the type of vegetable oil and hydroxyl group content of the polyols which is directly related to the crosslinking density of the polyurethanes [42]. Higher hardness performance was generally obtained with increasing cross linking density of polyurethane network.

Figure 6.22 shows that hardness is more in case of 2nd surfactant because addition of 3 % concentration of surfactant depresses the pressure differences between bubbles of different sizes and enhance the stability of the bubbles significantly. These air bubbles provide a site for initiation of foam cell growth. By reducing the surface tension of the polyols, surfactans can perform several useful functions in foam preparation. They can stabilize the initial liquid air dispersion by controlling the number of cells. As excessive amount of surfactant lead to collapse of the foam as the walls and ribs of the foam cells could not withstand the pressure of the gas.

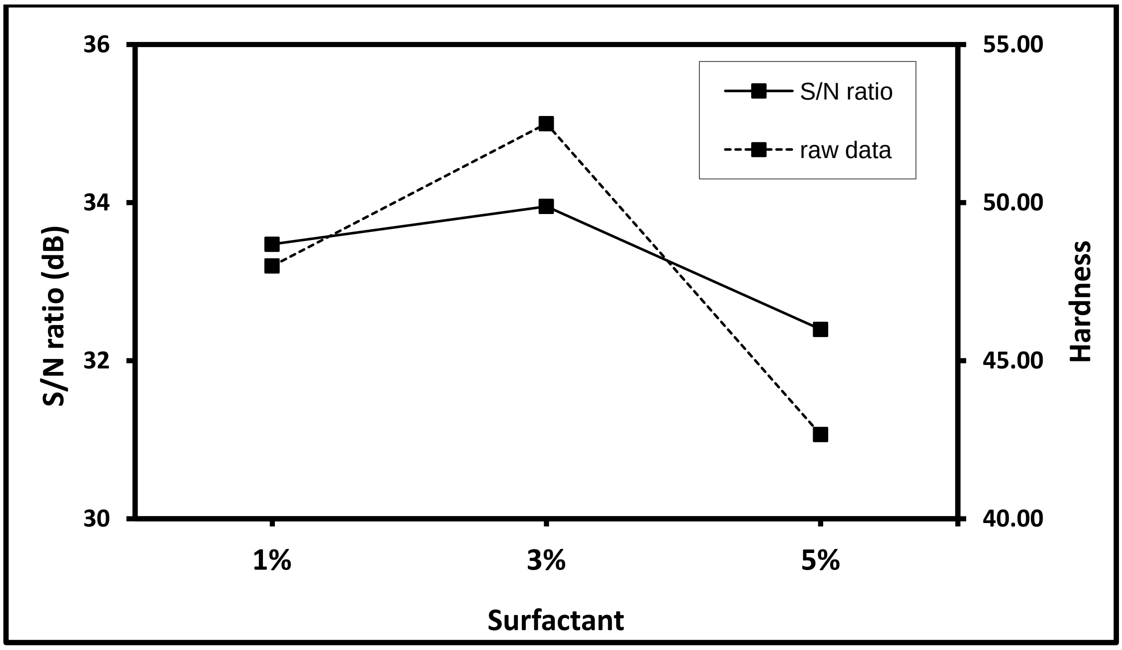


Figure 6.22: Effect of Surfactant on Hardness and S/N Ratio

Figure 6.23 shows that hardness is more in case of 2nd catalyst due to increase in crosslinking. Amine catalysts have ability to control the blowing and gelling reaction that depends on its molecular structure as well as some other factors such as steric and electronic effects. Amine catalysts (TEDA) function by increasing the nucleophilicity of the diol component. They have non-sterically hindered nitrogen atom with a lone pair of electrons that has affinity to react with the C=N moiety of the isocyanate group.

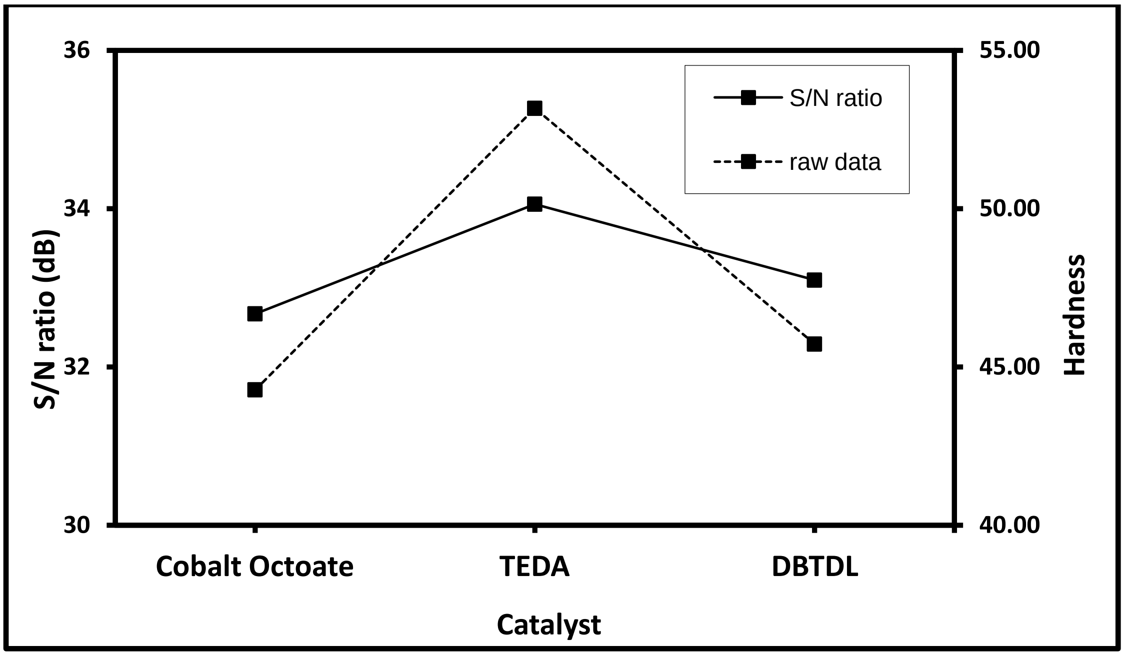


Figure 6.23: Effect of Catalyst on Hardness and S/N Ratio

Figure 6.24 shows that hardness is more in case of 3rd blowing agent because increase in concentration of blowing agent results in smaller average cell size and increased in number of cells per unit volume.

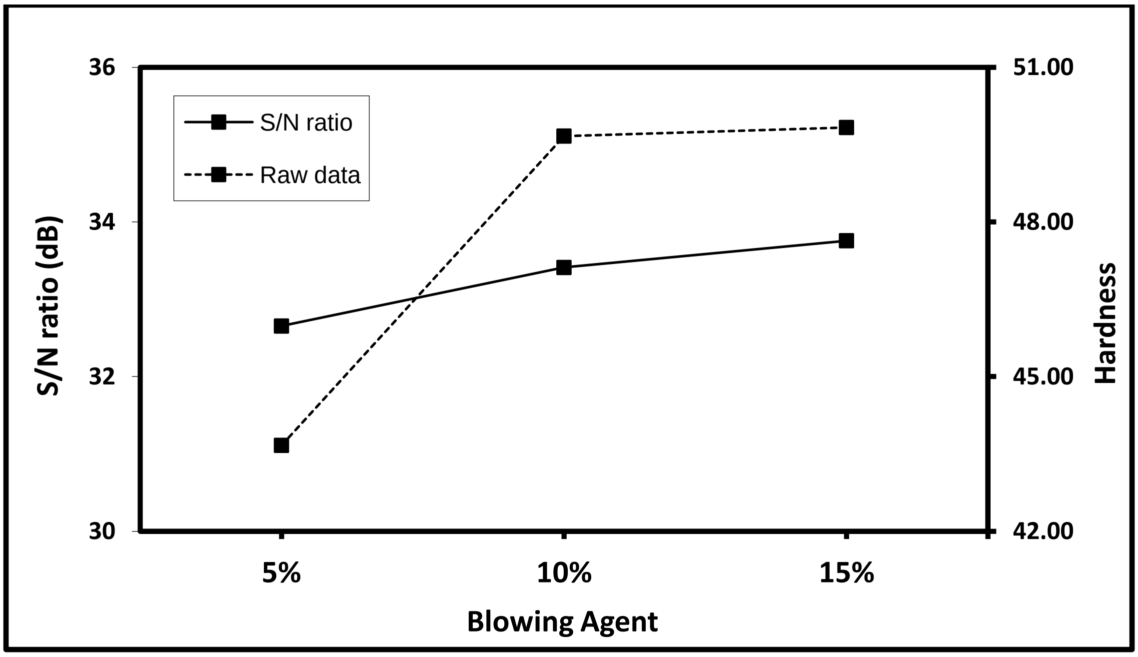


Figure 6.24: Effect of Blowing Agent on Hardness and S/N Ratio

Physical blowing agents do not take part in foaming reaction, but they are highly volatile liquids that vapourise easily on reducing the pressure to make a cellular structure. Concentration of the blowing agents should be optimum to produce foam product. The rate of gelling and foaming reaction should also be matched to form desire foam.

Figure 6.25 show that hardness is more in case of 2nd antiflamming agent. High value of hardness with Tris (1,3-dichloro-2-propylphosphate) (TDCPP) indicates that the dispersion of TDCPP in the PU matrix was good with proper adhesion. The decrease in hardness in case of 1st and 3rd antiflamming agents are due to involvement of melamine and TCP in the polyurethane matrix that weakens the cellular structure.

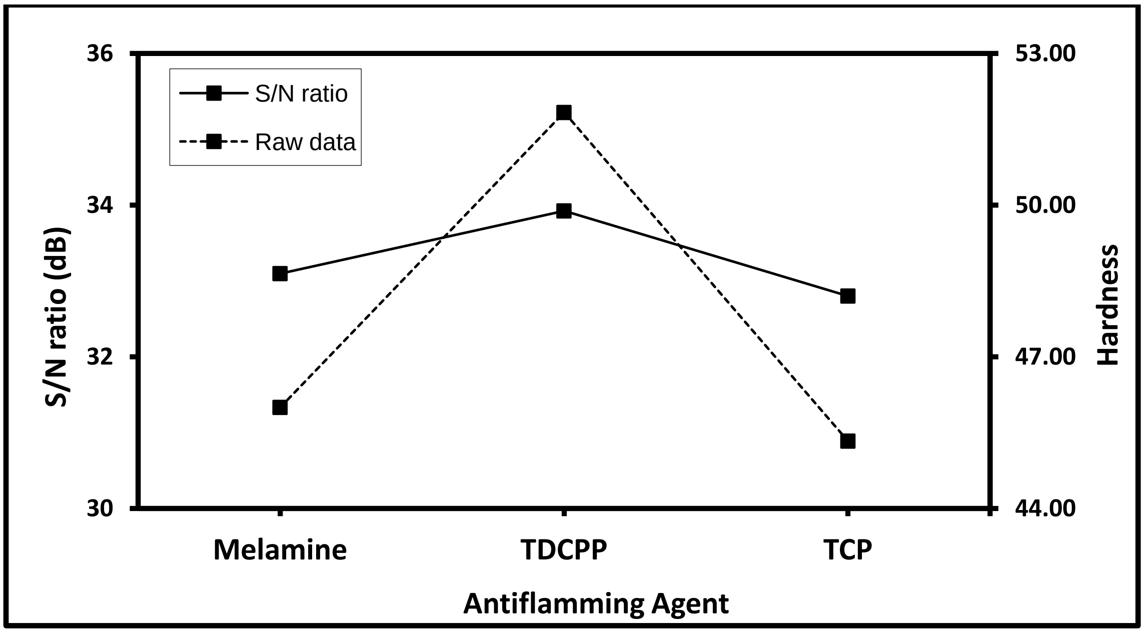


Figure 6.25: Effect of Antiflamming Agent on Hardness and S/N ratio

6.2.4.1 Selection of Optimal Levels

To determine which factors significantly affects the response characteristics, ANOVA has been performed. The pooled version of ANOVA for average values of raw data as well as S/N ratio is given in Tables 6.20 and 6.21 respectively. These Tables indicate that all the parameters significantly affect both the average values and the S/N ratio.

Table 6.20: ANOVA of Hardness (Raw Data)

Source	SS	DOF	V	F-Ratio	P %	SS'
Filler	3700.17	1	3700.17	207.57	43.83	3682.34
Polyol	1298.11	2	649.06	36.41	15.38	1262.46
Surfactant	872.33	2	436.17	207.56	10.33	836.68
Catalyst	819.11	2	409.55	22.97	9.70	783.46
Blowing Agent	544.06	2	272.02	15.26	6.44	508.40
Antiflamming Agent	460.33	2	230.16	12.91	5.45	424.68
Error	748.72	42	17.83		8.87	944.82
Total	8442.83	53			100	8442.84
Findings are significant at 95% level of confidence, SS is Sum of Squares, DOF is Degree of Freedom, V is Variance, F-ratio tabulated = 3.223 and P% is Percentage contribution.						

Table 6.21: ANOVA of Hardness (S/N ratio)

Source	SS	DOF	V	F-Ratio	P %	SS'
Filler	40.75	1	40.75	139.02	53.70	40.46
Polyol	11.82	2	5.91	20.16	15.58	11.23
Surfactant	7.63	2	3.82	13.01	10.06	7.05
Catalyst	6.04	2	3.02	10.30	7.96	5.45
Blowing Agent	3.82	2	1.91	6.52	5.04	3.24
Antiflamming Agent	4.06	2	2.03	6.93	5.35	3.48
Error	1.76	6	0.29		2.32	4.98
Total	75.88	17	*		100	75.89
Findings are significant at 95% level of confidence, SS is Sum of Squares, DOF is Degree of Freedom, V is Variance, F-ratio tabulated = 3.223 and P% is Percentage contribution.						

6.2.4.2 Estimation of Optimum Performance Characteristics

The optimum value of hardness is predicted at the selected levels of significant parameters $A_1B_1C_2D_2E_3F_2$. The estimated mean of the response characteristic Hardness is determined [106] as

$\mu_{Hardness} = \bar{A}_1 + \bar{B}_1 + \bar{C}_2 + \bar{D}_2 + \bar{E}_3 + \bar{F}_2 - 5 \times \bar{T}$

where

T : Overall mean of hardness = 47.72

A_1 : Average hardness at the 1st level of Filler = 56.00

B_1 : Average hardness at the 1st level of Polyol = 54.06

C_2 : Average hardness at the 2nd level of Surfactant = 52.50

D_2 : Average hardness at the 2nd level of Catalyst = 53.17

E_3 : Average hardness at the 3rd level of Blowing Agent = 49.83

F_2 : Average hardness at the 2nd level of Antiflamming Agent = 51.83

(Ref. to Table 6.18 and Figure 6.20 to 6.25)

Putting the values of different terms in the equation given above

$\mu_{Hardness} = 56 + 54.06 + 52.50 + 53.17 + 49.83 + 51.83 - 5 \times 47.72$

$\mu_{Hardness} = 78.79$

The 95% confidence interval of confirmation experiments (CI_{CE}) and of population (CI_{POP}) is calculated by using the following equations:

$$CI_{CE} = \sqrt{F_a\,(1, f_e)V_e\left[\frac{1}{n_{eff}} + \frac{1}{R}\right]}$$

$$CI_{POP} = \sqrt{\frac{F_a\,(1, f_e)V_e}{n_{eff}}}$$

Where $F_a(1, f_e)$: The ratio at the confidence level of (1-α) against DOF 53 and error DOF $f_e = 42$, N: Total number of results = 54 (Treatment = 18, Repetition = 3),

R: Sample size for confirmation experiments = 3,

V_e: Error variance = 17.83 (Ref. Table 6.20),

Fe (error DOF) = 42

$N_{eff} = \frac{N}{1+[DOF\ associated\ in\ the\ estimate\ of\ mean\ response]}$

$N_{eff} = \frac{54}{1+11} = 4.5$

$F_{0.05}$ (1, 42) = 3.2236 (tabulated F value),

So $CI_{CE} = \pm\ 20.39$, $CI_{POP} = \pm\ 12.90$

The predicted optimal range (for a confirmation runs of three experiments) is:

$\mu_{Hardness} - CI_{CE} < \mu_{Hardness} < \mu_{Hardness} + CI_{CE}$;

$58.4 < \mu_{Hardness} < 99.18$

The 95% confirmation interval of the predicted mean is as follows:

$\mu_{Hardness} - CI_{POP} < \mu_{Hardness} < \mu_{Hardness} + CI_{POP}$

$65.89 < \mu_{Hardness} < 91.69$

The optimal value of different process variables obtained for optimized hardness is as follows:

Filler (A, 1st level) = Flyash, Polyol (B, 1st level) = 2:1, Surfactant (C, 2nd level) = 3%, Catalyst (D, 2nd level) = TEDA, Blowing Agent (E, 3rd level) = 15%, Antiflamming Agent (F, 2nd level) = TDCPP

6.2.4.3 Confirmation Experiment

Confirmation experiments were performed in triplicate at optimum setting of the process parameters for hardness. Filler is set at 1st level, polyol at 1st level, surfactant at 2nd level, catalyst at 2nd level, blowing agent at 3rd level and antiflamming agent at

2nd level. From the confirmation experiments the average hardness (shore D) is found to be 72.43, which falls within the 95% confidence interval of the predicted optimum parameter.

CHAPTER 7

EFFECT OF DIFFERENT ANTI FLAMMING AGENTS ON RPUFS

The high combustibility of RPUF makes its use restricted in many important engineering applications. As per the experimental evidences, the pores of the foam entraps air which further aid in its combustion. This cellular material burns readily in the presence of oxygen and heat with a very high fire spread rate and a high smoke release rate [121–123]. The generation of poisonous smoke and reduction of oxygen concentration in the surroundings due to the combustion poses a threat to the human health and environment [124–126]. Due to fire threats of RPUFs, special fire protocols have to make compulsory by regulatory bodies for their use in furniture and buildings [127–129]. The development of the fire behaviour of the rigid polyurethane foams has presently been a significant issue of many studies among the researchers as it hinders its practical applications [130]. Hence, the improvement of flame retardancy of RPUFs is one of the areas of prime importance and has attracted the attention of many researchers. The use of fire retardants in RPUFs to decrease its combustibility and smoke production has become a vital parameter during the design and development of their products. RPUFs can be rendered fireproof by presenting flame retardants based on halogens, nitrogen, phosphorus, inorganic metal oxides and hydroxides [40]. Nitrogen and phosphorous based fire retardants are less poisonous and eco-friendly as they themselves and their gases or vapours products during combustion have low toxicity [131,132]. In contrast, another flame retardant melamine while combustion, grips the heat of the PU matrix and go through the advanced endothermic condensation with evolution of ammonia.

Polyurethane/phosphate combinations are reported to form intumescent flame retardant systems [133]. The growth of flame retardant materials in engineering and industrial applications is motivated by the increased consciousness towards the safety, among the consumers, and by the environment threats posed by the researchers [134,135]. The present studies report the effects of different anti-flaming agent's i.e. Melamine (2,4,6-Triamino-1,3,5-triazine), Tris(2-chloroethyl) phosphate (TCP) and Tris(1,3-dichloro-2-propylphosphate) (TDCPP) on the properties of RPUFs.

FTIR, XRD and TGA were performed to find out structure and thermal stability of resulted RPUFs. Fire behaviour of the resulted RPUFs was confirmed by UL-94 V test. The formulations of RPUFs incorporated with different anti-flamming agents is as given in Table 3.6.

7.1 Density

Foam density is a vital property which has significant effect on the surface and mechanical properties of RPUFs. The density of the resulted RPUFs samples was determined as per ASTM D 1622-03. The size of the specimen was taken as 30 x 30 x 30 mm^3 (length x width x thickness) and average result of four samples are reported. The density of all samples obtained from different formulations of flame retardants are as given in Table 7.2. It is found that density of RPUFs filled with melamine flame retardant decreases as compared to neat RPUFs. The reason for this is that there might be the formation of voids in cell structure, which affected the density of the foam significantly. This result is similar to that already reported in previous literature study [40]. Unlike to melamine, the density of RPUFs filled with TDCPP and TCP was found to be more than neat RPUFs which is due to the shrinkage in average cell size and the development of uniform cell structure, as also confirmed by SEM analysis.

Table 7.1 Density of RPUFs in different formulations

Formulation	**Density (kg/m^3)**
AF00	102
AF01	82
AF02	112
AF03	107

7.2 FTIR Analysis

A Fourier transform infrared (FTIR) spectrometer was employed to analyze the structure of modified polyols, MDI, and polyurethanes. On Nicolet 380 spectrometer, spectra were recorded in the range 400-4000 cm^{-1}. For analysis, powdered samples obtained by crushing the resulted foam were mixed with pure dried KBr to form transparent KBr pellets. Figure 7.1(a) shows the characteristic absorption peaks of polyols and MDI at 3402 cm^{-1} (O-H stretching frequency), 2925-2851 cm^{-1} (-CH_2 and -CH_3 stretching frequency) and 2268 cm^{-1} (-NCO stretching frequency). Figure 7.1(b) shows the FTIR of the RPUFs incorporated with antiflamming agents. It is evident from the Figure 7.1(a) and (b) that there is the disappearance of absorption peaks at 2268 cm^{-1} (-NCO stretching frequency) in RPUF (AF00), AF01, AF02 and AF03 which confirm that MDI is completely reacted with a polyol to form polyurethane.

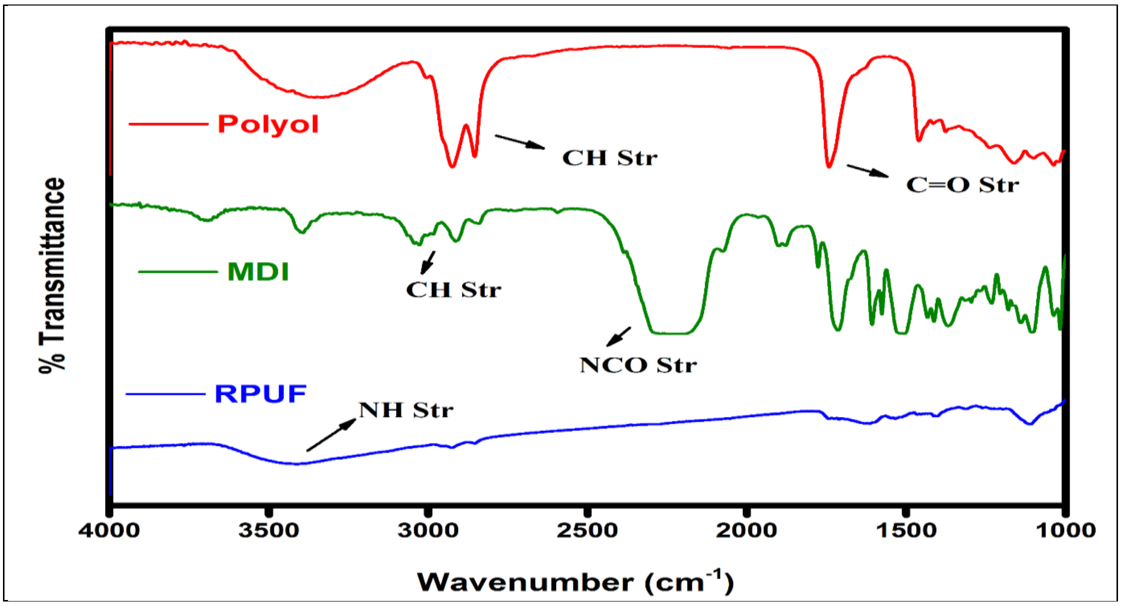


Figure 7.1(a): FTIR of Polyol, MDI, and Neat RPUF

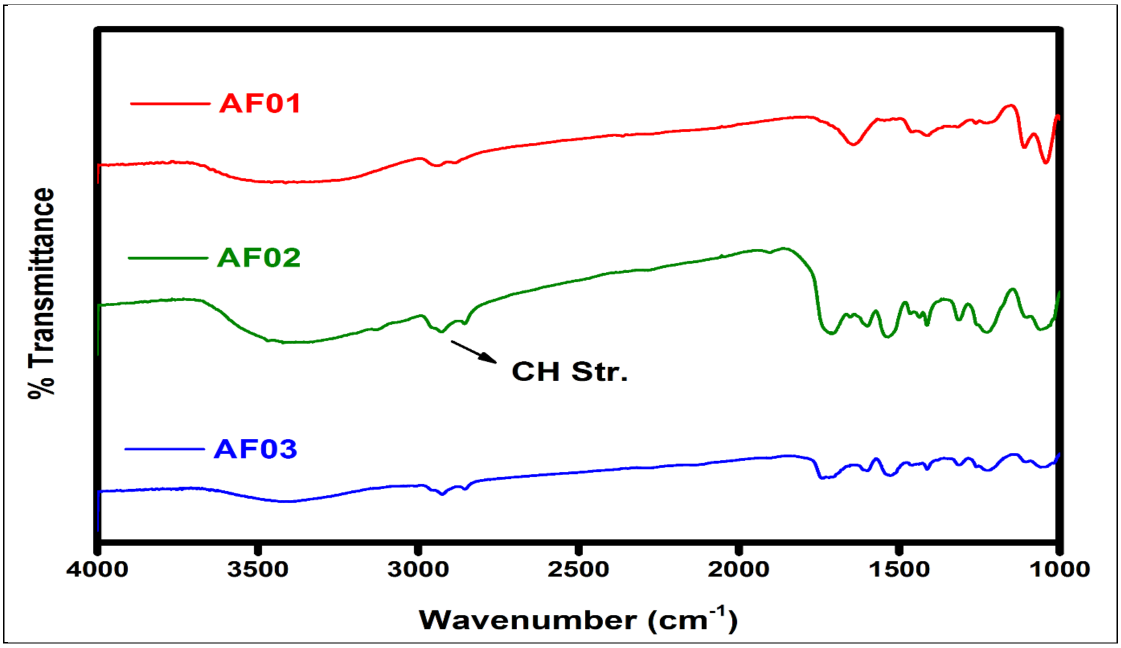


Figure 7.1(b): FTIR of Formulations AF01, AF02 and AF03

7.3 XRD Analysis

XRD patterns for Formulation AF00, AF01, AF02 and AF03 were obtained using BRUKER D8 ADVANCE diffractometer by employing CuKα (Kα –1.54056 Å) radiation. X- ray diffraction pattern of resulted RPUFs incorporated with anti-flaming agents are as shown in Figure 7.2. From the figure, it is evident that the RPUF exhibit amorphous structure, having broad amorphous peak at $2\theta = 20^{\circ}$. Foam samples incorporated with melamine shows slight shift towards crystalline behaviour due to its own crystalline structure.

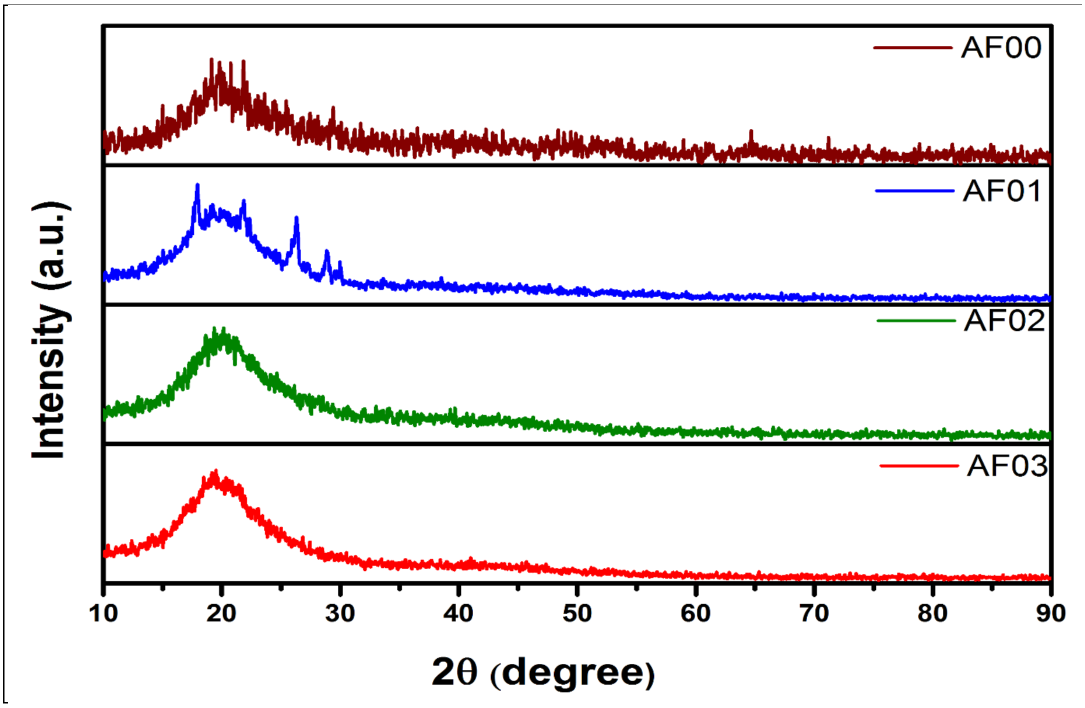


Figure 7.2: XRD Curve of AF00, AF01, AF02 and AF03

7.4 Thermogravimetric Analysis (TGA)

On Universal V4.5 A, TA instrument with a heating rate of 10 °C min^{-1} from 30 to 1000 °C under N_2 atmosphere, TGA of samples was carried out. Testing of all the samples was conducted with a gas flow rate of 30 mL min^{-1}. Continuously loss in mass was recorded as a function of time and temperature. Figure 7.3 shows the Thermogravimetric (TG) curves of the samples under investigation. The sample AF00 i.e. neat PU (without flame retardant) clearly exhibit three visible degradation stages. In the first stage between 80 and 140 °C, there is a loss of weight because of the evaporation of water from the sample. Second degradation step is visible in the 170 to 240 °C temperature ranges, which is, probably due to the cleavage of the urethane linkage. The third degradation step is due to decomposition of material occurring above 250 °C. Compared with the formulation AF00, the other formulations AF01 (Melamine), AF02 (TDCPP) and AF03 (TCP) have a significantly similar decomposing trend. PU foams incorporated with TDCPP shows higher thermal stability while PU foam with melamine composition shows least stability.

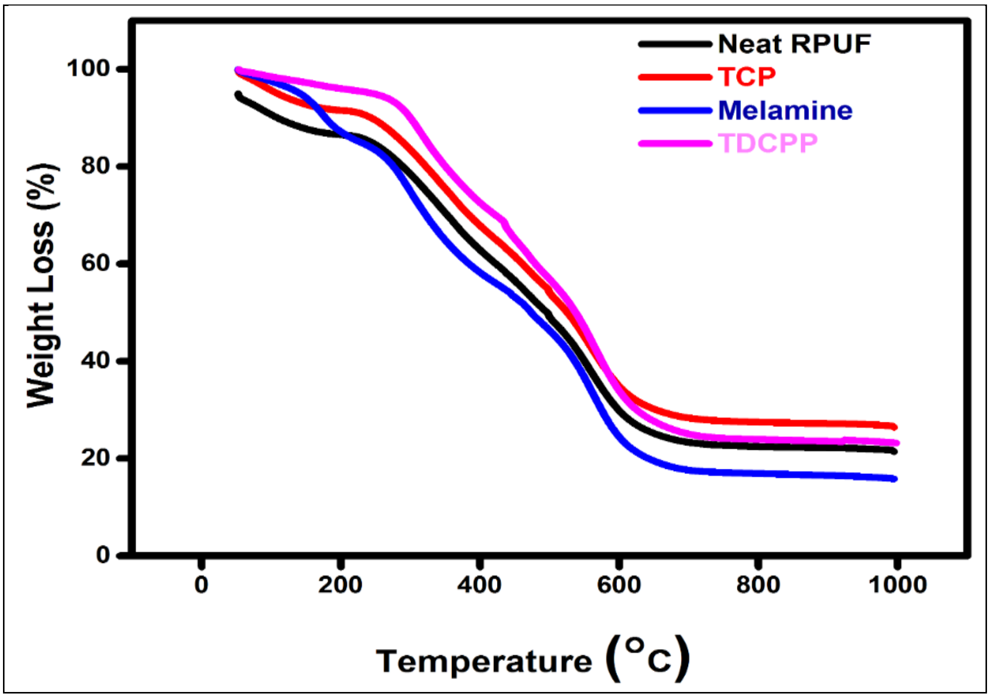


Figure 7.3: TGA Curves of the Samples AF00-AF03

7.5 Antiflammability

Flammability of the resulted RPUF samples was classified according to the UL-94 vertical burning standard test [136–138]. The flammability of RPUFs was tested as per the ASTM D 3014 standards. The specimens were mounted vertically on the stand and ignited with the help of a burner for 10 sec. As a standard procedure, a 3/4th inch high blue flame was used for heating at the bottom of the sample for exactly 10 sec and then withdrawn, and again applied for more 10 sec time. The time of glowing and flaming was noted as the sample was extinguished. To examine the ignitability of dripping material, a layer of cotton was placed beneath sample, during the test period. A record of time of burning, flame height and weight loss of the samples was accounted and reported in Table 7.3. From Table 7.3, it is clear that for the sample with formulation AF00, the recorded flame height travelled is more and for AF02 flame height was found to be least. With AF00 formulation extinguishing time is higher thus shows continuous burning. The reason may be the irregular and improperly disturbed cells in neat PU, with entrapped air, that supports prolong burning. As more is the extinguishing time, more is the recorded weight loss in the samples. Anti-flaming properties of RPUFs were found to be significantly enhanced by the incorporation of flame retardants due to better homogenization of foam structure as per the reported literature [15]. TDCPP incorporated foam samples i.e. formulation AF02 exhibited the best anti-flammable behaviour among the all three formulations.

Table 7.3: Flammability testing of RPUFs with different formulations

Formulation	Flame Height (mm)	Extinguishing Time (sec)	Loss of Weight (grams)	UL – 94 Ratings
AF00	35	Continuously Burn	5.2	No Ratings
AF01	28	82	3.1	V1
AF02	22	55	2.8	V1
AF03	25	62	2.9	V1

7.6 Mechanical Properties

Tensile, compressive and flexural properties of the resulted foams were measured using Instron (Model No.: 3369) universal testing machine as per ASTM D 638, ASTM D 695 and ASTM D 790, respectively. Hardness (Shore D) was determined by using ASTM D 2240 method. The results obtained are as shown in Figure 7.4. As evident from the figure, the neat RPUF (AF00) showed an average value of tensile, compressive and flexural strength and average hardness equal to 0.82 MPa, 6.87 MPa, 3.80 MPa and 45 (Shore D) respectively. RPUF (AF01), (AF02), (AF03) showed the average tensile strength equal to 0.69 MPa, 2.02 MPa, 1.10 MPa, respectively. The average compressive strength of RPUF (AF01), (AF02), (AF03) was recorded to be 7.24 MPa, 9.12 MPa, 7.42 MPa, respectively. The average flexural strength of RPUF (AF01), (AF02), (AF03) was observed to be 6.30 MPa, 12.02 MPa, 8.42 MPa, respectively and average hardness achieved was 48, 53, 48 (Shore D) respectively. Linear (almost) increase of above said properties (except tensile strength in case of formulation AF01) up to formulation AF02 indicates that the dispersion of antiflamming agents in the PU matrix was good enough, with proper adhesion. From AF02 to AF03 formulation, the observed mechanical properties were decreased. The decrease in tensile strength in case of the AF01 formulation is due to involvement of melamine in the polyurethane matrix that weakens the cellular structure. Higher particles size of the melamine results in collapsing of cellular structure during the formation of foam [138]. Significant enhancement in mechanical properties of final product is observed due to the homogenized dispersion of TDCPP into the polyol. Uniform cell morphology and small pore size of resulted RPUFs with formulation AF02 further support the enhancement in mechanical properties.

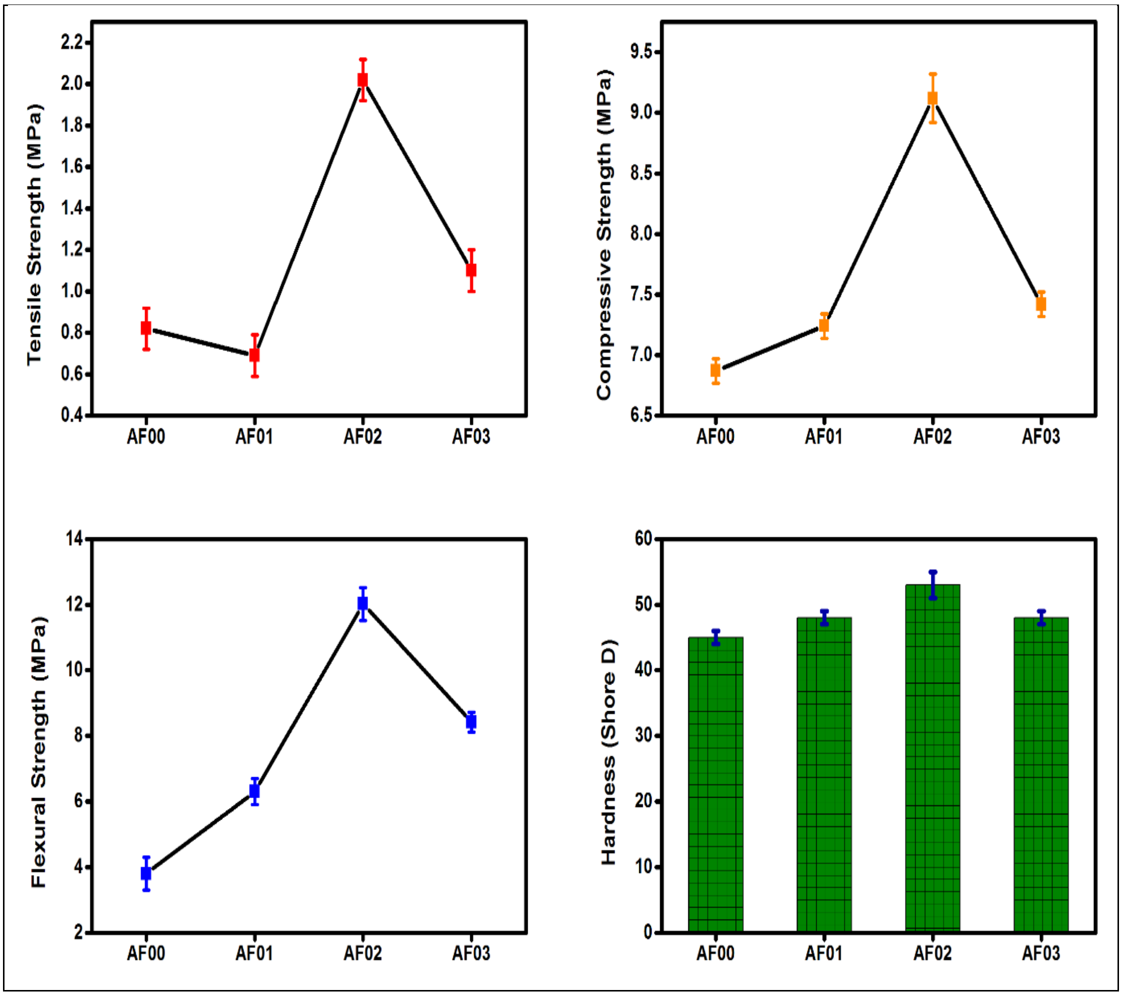
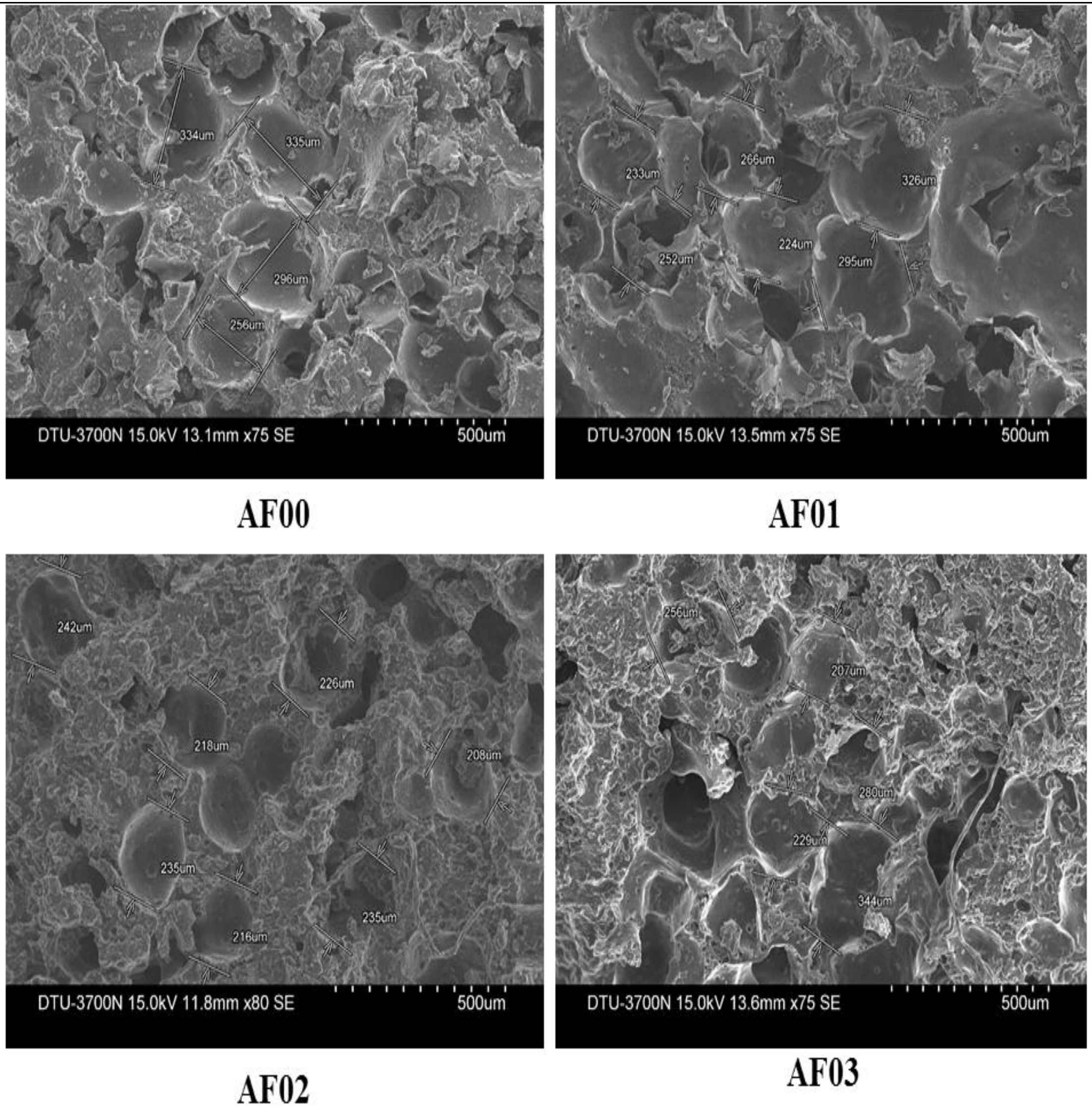


Figure 7.4 Mechanical Properties of Different Formulations of RPUFs

7.7 SEM Analysis

The morphologies of RPUFs coated with a gold layer were observed using scanning electron microscopy (SEM, Hitachi S3700) with an accelerating voltage of 15kV. Figure 7.5 shows the micrographs of the castor oil based rigid polyurethane foams with different formulations. It is clearly observed from Figure 7.5 that the shape of the cells is nearly spherical. For the formulations AF00, AF01, AF02 and AF03, the average pore size is equal to 305.25 µm, 266 µm, 225.71 µm and 263.2 µm, respectively. There is a significant reduction in pore size from AF00 to AF02 and then size increase occurs in formulation AF03. The reduced pore size for the formulation AF02 indicated that the 3D structure of the foam was more packed than AF00, AF01 and AF03. The further increase in pore size AF03 is may be due to collapsing of cells. A graph of cell size vs different formulations of RPUFs is as shown in Figure 7.6. The best results were obtained for mechanical properties for AF02 formulation i.e. RPUF incorporated with Tris (1,3-dichloro-2-propylphosphate) (TDCPP).



AF00 **AF01**

AF02 **AF03**

Figure 7.5: SEM of RPUFs with Formulation AF00, AF01, AF02 and AF03

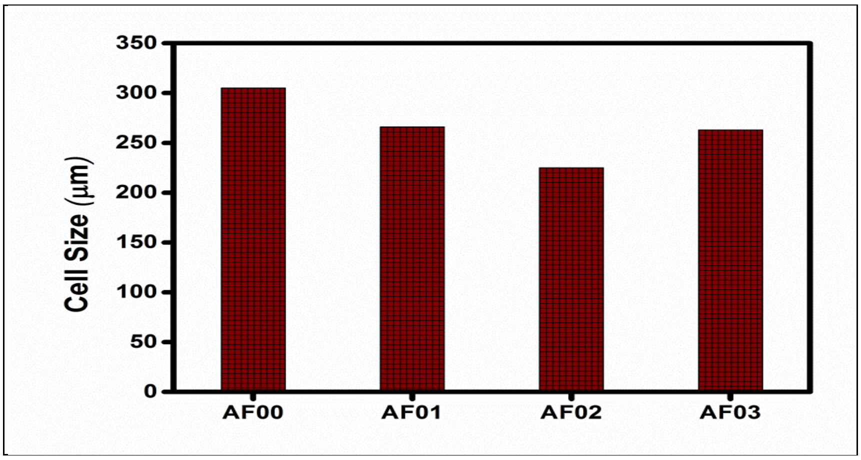


Figure 7.6: Cell Size of RPUFs with Formulation AF00, AF01, AF02 and AF03

7.8 Significant Findings

Combustion of RPUFs is characterized by the formation of dark smoke with the irritating smell, with release of toxic gases. Significant enhancement in the thermal and anti-flamming properties of RPUFs was observed with the addition of anti-flaming agents. RPUF incorporated with TDCPP was found to have exhibited best anti-flaming behaviour due to well homogenization of flame retardant into the polyol. Tensile, compressive & flexural strength and Hardness (Shore D) of RPUFs are found to be improved with TDCPP addition because of uniform cell structure and decreased in pore size of resulted RPUFs. Tensile strength was found to be poor with melamine based RPUFs as embedment of melamine in the polyurethane matrix weakens the structure due to the formation of inconsistent structure. The resulted foams incorporated with different antiflamming agents with their improved mechanical, thermal and anti-flammable properties are expected to be much suitable for the new generation anti-flammable lightweight materials for different engineering and industrial applications.

CHAPTER 8

CONCLUSIONS AND FUTURE PROSPECTS

8.1 Conclusions

In the past, usually petroleum polyols were used for polyurethane production. With the diminishing and non-renewable petroleum resource, vegetable oil based novel polyols have been explored for their potential of replacing the petroleum polyols. In the present research work, Rigid Polyurethane Foams (RPUFs) have been developed using castor oil based modified polyol. For the polyol synthesis, castor oil was modified with glycerol using transesterification process. The resulted RPUFs were explored to study the effect of varying MDI/Polyol ratios. Also the function of the surfactant used i.e. silicon oil on the properties of the RPUFs had been investicated. Mechanical properties were found to be enhanced with increase in the MDI content. SEM studies had also shown evidence for improved cell morphology and closed packing with increase in MDI content. As the silicon oil regulates the foam structure and has a significant affect on foam properties. The results indicated that, with the increase in content of silicon oil from 3 to 6%, i.e from formulation 1 to formulation 2, the compressive strength of the resulted foam was observed to be increased and then it decreased with further addition of silicon oil. The higher values of hardness, tensile, flexural and compressive strength, with a relatively linearly increasing trend were observed for RPUFs reinforced with glass fibers (RPUGF). SEM studies had also revealed improved cell morphology with dense packing for RPUGF. The results for density measurement and water absorption studies supported the idea of more closely packed foam structure, when reinforced with glass fibre. Different mechanical properties and hardness of various polyurethane formulations were optimized with the help of Taguchi's L_{18} Orthogonal Array (OA). From the Taguchi confirmation experiments the average tensile strength is found to be 5.24 MPa; average compressive strength equal to 6.37 MPa; average flexural strength is found to be 12.28 MPa and the average hardness (shore D) is found to be 72.43. All these values found comparable with experiment values. (falls within the 95% confidence confidence interval of the predicted optimum parameter. Addition of the anti-flamming agents in the resulted, optimized formulation of the RPUFs makes the studies complete. Combustion of RPUFs is characterized by the formation of dark smoke with irritating aroma, justifies the release of toxic gases like CO_2. Thermal and Anti-flaming properties of RPUFs were found to be significantly enhanced by incorporating TDCPP due to well homogenization of flame retardant materials and polyol. Compressive strength, flexural strength, and hardness (shore D) of RPUFs are found to be good with TDCPP because of uniform cell structure and decreased in pore size of resulted RPUFs. The tensile strength of the resulted foams samples was found to be good with TDCPP composition and poor with melamine composition. Significant findings of this research work are concluded below:

- A noticeable improvement in overall mechanical properties of the foam was observed with increase in MDI/Polyol ratio. Tensile stress varies from 0.12903 MPa to 0.35285 MPa on increasing MDI from formulation 1 to formulation 3, while maximum compressive load increases from 1030.185 Kgf to 1091.649 Kgf.
- A more denser and closely packed structure of RPUF was obtained by increasing the concentration of the surfactactant from 3% to 6%. It was found

that flexure stress at maximum flexure load (MPa) for formulation 1 (3% surfactant) was 7.179, which further increased more than three times for formulation 2 (6% surfactant) with a value of 23.999. The justification for this triple fold increase is the more packed structure of the foam. With further increase in surfactant concentration (i.e. 9%), for formulation 3, flexure stress at maximum flexure load (MPa) is found to be 6.154 due to increase in the heterogeneity of the system.

- Compressive strength was increased with increase in silicon oil content in formulation 1 to formulation 2 and then decreased with further addition of silicon oil.
- Insertion of glass fibers into rigid polyurethane enhances the density and mechanical properties of the foam.
- From the Taguchi confirmation experiments the average values of mechanical properties are found to be comparable with that of experimental values.
- PU foams incorporated with TDCPP shows higher thermal stability while PU foam with melamine composition shows least stability.

Castor oil based Rigid Polyurethane Foam (RPUF) due to its excellent mechanical properties and eco-friendly source shows an excellent prospect for the production of many industrial and engineering applications. In simple wodrs it can be said: “Future is of Polyurethane.”

8.2 Future Prospects

The agriculture based vegetable oils are available in abundance in the nature. The costly petrochemical based raw materials can be replaced partly (even fully) by these vegetable oil based raw materials. In the future studies, the formation of Non isocyanate polyuretnane (NIPU) that is now in the budding stage can be achieved on commercial scale, using these environment friendly resources i.e. vegetable oil. The properties of RPUFs can further be improved by the use of more reinforcing fillers. Though the one of the raw material source is renewable, the biodegradability of rigid polyurethane foams can be studied extensively in the nearby future.

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PUBLICATIONS (FROM THESIS WORK)

Publication in International Journals

1. **Mukesh Kumar** and Raminder Kaur, Function of Silicon oil in the Castor Oil Based Rigid Polyurethane Foams, **Journal of Polymer Engineering** 2013, 33(9), 875-880.
2. **Mukesh Kumar** and Raminder Kaur, Effect of Different Formulations of MDI on Rigid Polyurethane Foams based on Castor Oil, **International Journal of Scientific Research and Reviews** 2013, 2(1) Suppl., 29-42.
3. **Mukesh Kumar** and Raminder Kaur, Glass Fiber Reinforced Rigid Polyurethane Foam: Synthesis and Characterization **e-Polymers** 0(0), pp.-. Retrived 18 Sep. 2017, from doi: 10.1515/epoly-2017-0072.
4. **Mukesh Kumar** and Raminder Kaur, RPUF Incorporated with Different Flame Retardants: A Study of Anti-flammable, Thermal and Mechanical Behaviour **(communicated).**
5. Raminder Kaur, R.S. Walia, **Mukesh Kumar**, A Taguchi Approach for Investing the Mechanical Properties of Rigid Polyurethane Foam **(communicated).**

Conference Publications

1. **Mukesh Kumar** and Raminder Kaur, Function of Blowing agent in the Castor oil Based Rigid Polyurethane Foams, National Conference on Emerging Trends in Physics and Material Science organized by Department of Physics, Chaudhary Devi Lal, University, Sirsa, Haryana, India (March 19-20, 2016).
2. **Mukesh Kumar** and Raminder Kaur, Rigid polyurethane foam based on modified castor oil and reinforced with glass fiber: Mechanical characterization, National Conference on Emerging Trends in Physics and Material Science organized by Department of Physics, Chaudhary Devi Lal, University, Sirsa, Haryana, India (March 9-10, 2015).
3. **Mukesh Kumar** and Raminder Kaur, Development of rigid polyurethane foam from castor oil, National Conference on Emerging Trends in Chemical Science and Technology (ETCST-15) organized by Department of Chemistry, Chaudhary Devi Lal, University, Sirsa, Haryana, India (February 25, 2015).

4. **Mukesh Kumar** and Raminder Kaur, Preparation and Study of Structure and Mechanical Properties of Polyurethane Rigid foams Based on Castor Oil, International Conference on Recent Advances in Chemical Science organized by Department of Chemistry, Arya PG College, Panipat, Haryana, India (February 2013).

APPENDIX-I

AP-1 Determination of Acid Value of Vegetable oil

Apparatus/Reagent required: Conical flaks (250 ml capacity), Burette, Pipette, N/10 KOH, Neutral Ethyl Alcohol, Phenolphthalein indicator, Toluene, and Water bath.

Procedure:

Weight out accurately about 6-8 g of the oil under test into a conical flask and add 50 ml of neutral alcohol. Heat the flask over a water bath for about 30 minutes. Cool the flask and the contents to room temperature and add a few drops of phenolphthalein indicator. Titrate with the standard N/10 KOH solution until a faint permanent pink colour appears at the end point. Similarly, make a blank determination in the same manner as the sample was titrated. And alcoholic solution of KOH should be freshly prepared and should be standardized just before the test.

Acid value is calculated as:

$$\textbf{Acid value (mg KOH/g)} = (C - D) \times N\,(KOH) \times 56.1 / W$$

Where,

C is volume of KOH standard solution consumed in sample titration, ml;

D is volume of KOH standard solution consumed in blank titration, ml;

W is sample weight, gm;

N (normality) is equivalent concentration of KOH standard solution, mol/l.

AP-2 Determination of Hydroxyl Value of Vegetable Oil

Apparatus/Reagent required: Erlenmeyer flask (250 ml), Standard ground glass stoppered, condensers and Straight tube, Acetic anhydride, n-butyl alcohol, Ethyl alcohol, Phenolphthalein indicator, Potassium hydroxide and Pyridine.

Procedure:

Take one gram of the oil under test into conical flask (250 ml) and add 5.0 ml solution of pyridine acetic anhydride. After thoroughly mixing the contents, take another 5.0 ml solution of pyridine acetic anhydride into an empty flask for the reagent. Now insert the reflux condensers into the conical flasks. Heat the flask for one hour by using the steam bath. Add 10 ml of water through the condensers to the flasks. After heating, allow the flasks to cool to room temperature. Now add 25 ml of neutralized n-butyl alcohol to each flask. Add 1 ml of phenolphthalein indicator solution to each flask and titrate to a faint pink end point with 0.5 N alcoholic KOH solutions.

Hydroxyl value is calculated as:

$$\textbf{Hydroxyl value} = \frac{\mathbf{B + \left(\frac{SA}{C}\right) - V}}{\mathbf{S}}\ \mathbf{N\ X\ 56.1}$$

Where,

A = KOH solution required for titration of the acid value, ml,

B = KOH solution required for titration of the reagent blank, ml,

C = Sample used for the acid value, g,

V = KOH solution required for titration of the acetylated specimen, ml and

S = Sample used for acetylation, g.

AP-3 Determination of Viscosity of Oil

Apparatus used: Brookfield Viscometer

Figure AP-1: Brookfield viscometer

Procedure:

Sample was taken in a beaker. The temperature was maintained at 25 °C and set rpm at 20 with spindle no. 2. Beaker kept below viscometer and spindle deep in sample and starts viscometer rpm and takes viscometer reading in cp. The results are obtained directly on the digital screen.

AP-4 Determination of Specific Gravity

Details:

To find the specific gravity of a solid or liquid we must know its density in Kg/m^3 or in g/cm^3. Then this density is divided bythe density of pure water in the similar units. Formula used is

$$\mathbf{Specific\ gravity} = \frac{\mathbf{density\ of\ the\ object}}{\mathbf{density\ of\ water}}$$

Procedure:

Empty specific gravity bottle was weighed (Mc), specific gravity bottle poured with castor oil was weighed to get (Mo). The oil was then substituted with water of the same volume and reweighed to give Mw. The specific gravity was determined by using the formula given below:

$$\mathbf{Specific\ gravity} = \frac{\mathbf{Mo - Mc}}{\mathbf{Mw - Mc}}$$

AP-5 Determination of Percentage NCO

Apparatus/Reagent Required

Dibutyl amine solution, HCl, Water bath, Methanol, Bromo phenol blue (Indicator)

Procedure: Isocyanate liquid was mixed with solution of toluene and dibutylamine (DBA) and the reaction between DBA and isocyanates takes place and the excess is titrated with HCl solution. The % of NCO content is determined by using the formulation given below:

$\% \text{NCO} = [(B\text{-}S)\, N \times 4.202]/W$

Where,

B is HCl (ml) used for titration of the blank,

S is HCl (ml) used for titration of the sample,

N is the molarity of HCl solution and

W is the weight of the sample in grams.

APPENDIX-II

AP-2.1 FTIR Analysis

Fourier Transform Infra-Red spectroscopy has wide applicability in structure clarification which are either manufactured chemically or of natural origin. Now a day, FTIR spectroscopy is widely used for qualitative as well as quantitative analysis in almost all fields of science.

Figure AP-2.1: FTIR (Nicolet 380 spectrometer)

FTIR spectra were recorded in the range of 400–4000 cm^{-1}. This is the simplest technique to check the presence of functional group in a molecule. When IR radiation is passed through a sample, some radiation is absorbed by the sample and some passes through (is transmitted). The resulting signal at the detector is a spectrum representing a molecular fingerprint of the sample. The usefulness of infrared spectroscopy arises because different chemical structures produce different spectral fingerprints.

AP-2.2 Thermogravimetric Analysis (TGA)

This is the technique in which we observed changes in chemical and physical property of a material as a function of variation in temperature.

Figure AP-2.2: Thermogravimetric analysis (Universal V4.5A, TA Instruments)

TGA includes the study of polymeric products such as thermoplastic, elastomers, plastic film, thermosets as well as coatings. There will be no change observed in the mass of the sample when it is thermally stable over a range of temperature. The thermal degradation behaviour of the rigid polyurethane foam under a nitrogen atmosphere was studied by TGA (Universal V 4.5A, TA Instruments). The samples at a rate of 10 °C/min were heated from room temperature to 1000 °C. The weight of the sample is continuously recorded as the temperature is increased.

AP-2.3 XRD Analysis

Powder XRD outlines were obtained by means of D-8 Advance, Bruker diffraction, with monochromatic Cu K_α radiation (λ = 1.5418 $\mathring{A}$). XRD is one of the most potential characterization tool and a non-destructive method which has been used for crystallographic structure determination. It can provide information on unit cell dimensions and it is primarily used for phase identification of a crystalline material.

Figure AP-2.3: X-ray diffraction (D-8 Advance, Bruker)

AP-2.4 SEM Analysis

The cell structure of the samples was characterized with a Hitachi S3700 SEM (scanning electron microscope) using an acceleration of 15kV. Samples were cut into rectangular parts: 7 x 9 x 4 mm. SEM scans the sample by means of beam of electrons to produce pictures of sample. When electrons interact with atoms of the sample then they produces signals that gives information related to the surface topography and composition of the sample. To get SEM images, samples should be electrically conductive in nature.

Figure AP-2.4: Scanning electron microscopic (Hitachi S-3700N)

AP-2.5 Mechanical Testing

Mechanical testing of the vegetable oil based rigid polyurethane samples was done as per the standard procedures. Tensile, compressive, and flexural strength of the resulted foams was measured at room temperature using Instron (Model No. 3369) universal testing machine (UTM) as per ASTM D-638, ASTM D 695 and ASTM D 790 method respectively. Tensile property measures the material's ability to bear the force that tends to pull it apart and the extent of deformation before breaking. Tensile test is normally employed for quality control of the products and research and development purposes. It also measures indirectly the other related properties like the progress of physical and chemical changes taking place in the polymer. For example, polymer exposed to light may undergo de-polymerization and oxidation reaction which will be reflected in change in tensile properties. Compressive strength is the material’s ability to resist forces that tends to compress and this property is useful for quality control of the material and acceptance or rejection of the material/products manufactured. Unlike tensile and flexural properties, compressive properties find limited design applications. Generally, compressive strength at any point between 1 to 10% deformations of original length of specimen is considered. Flexural properties are largely specified properties for various products. Flexural strength is the material’s ability to withstand bending forces applied perpendicular to its longitudinal axis.

AP-2.6 Durometer (Shore) Hardness Test

Hardness is an important surface property. Resistance of a substance to indentation, penetration, scratches, and deformation is called hardness. It is usually expressed in number scale; so, it has no unit. This test is used as an indicator of surface durability. Durometer hardness test is depended on penetration of an indenter onto the exterior of the substance. A pressure foot, an indentor and an indicating device are major part of the tester. Spring loaded indentor protrudes through the hole in the base. The test samples are at least 3 mm thick. There are two types of durometers i.e. Shore A and Shore D which are most commonly used. For soft and harder materials, Shore A and Shore D are used respectively.

AP-2.7 UL-94 V Test

Underwriter’s laboratories developed the UL-94 Vertical flammability test to evaluate the physical characteristics and safety of different plastics when they are exposed to flame.

AP-2.7.1 Procedure

1) Before the test begins, plastic samples are placed vertically in the burn chamber. Each sample is 127 mm x 12.7 mm in dimension, with the same thickness as the final product that will be formed from the plastic.
2) Once the sample has been mounted, a carefully controlled flame is placed under the specimen for 10 seconds and then removed. Any residual flaming combustion of the plastic sample is observed and recorded.
3) When the plastic sample finally self-extinguishes, the controlled flame is instantly again applied for next 10 seconds and then detached. Again, the specimen's flaming combustion is recorded.
4) Lastly, a piece of dry surgical cotton is placed 12 inches below the combustion sample. If any drips fall onto the cotton and cause it to ignite, this detail is also recorded.

When all the flame test data has been gathered, it's used to group the tested material into one of three specific material classes given below in table 3.1.

Table AP-2.1: UL 94 -V Ratings

V-Zero Vertical Burn	Flaming stops within ten seconds after two applications of ten seconds each of a flame to a test bar. No burning trickles are permitted.
V-One Vertical Burn	Flaming stops within sixty seconds after two applications of ten seconds each of a flame to a test bar. No burning trickles are permitted.
V-Two Vertical Burn	Flaming stops within sixty seconds after two applications of ten seconds each of a flame to a test bar. Burning trickles are permitted.

CURRICULUM VITAE

MUKESH KUMAR

Chemistry Lecturer

Education Department, Haryana

Professional Experience & Qualifications

Dec. 2013 to Contd.	Chemistry Lecturer Education Department, Haryana
July 2012 to Contd.	Ph.D. from Delhi Technological University, Delhi (Pursuing)
November 2011	Qualified HTET Examination (Board of School Education Haryana)

Academic Qualifications

Examination	Institution	Board/University	Year	Percentage (%)
M.Sc. (Chemistry)	C.D.L.U., Sirsa	C.D.L.U.	2011	73.30
B.Sc. (Biotech.)	G.N.C., Sirsa	K.U.K.	2009	72.27
12th (Intermediate)	S.P.School, Sirsa	C.B.S.E.	2004	67.4
10th (Matriculation)	C.S.S.School, Sirsa	B.S.E.H.	2002	75.30

Awards

- ✓ Awarded by National Children's Science Congress organized by NCSTC for my project report titled "Present Situation of Cotton" (December 2000).
- ✓ Got 3rd Prize in Debate at College level (February 2008).
- ✓ Got 1st Prize in Debate at District level (September 2008).
- ✓ Got 2nd Prize in Debate at State level (September 2008).
- ✓ Got Roll of Honour & Gold Medal for N.S.S. Activities (Unit Leader, Best

Volunteer, Literacy, Blood Donation etc.) (Session 2008-09).

- Got Roll of Honour& Silver Medal for Cultural Activities (Session 2008-09).
- Got Best Student Award for my distinguished performance in Academic, N.S.S. and Cultural activities (Session 2008-09).

Personal Dossier

Discipline	Chemistry		
Positive Traits	Confident, Hardworking, Good Team Leader		
Area of Interest	Education/Teaching and Polymer Field		
Personal Details	Date of Birth	:	07-10-1986
	Sex	:	Male
	Marital Status	:	Married
	Nationality	:	Indian
	Blood Group	:	B^+
	Languages	:	English, Hindi & Punjabi