MAJOR PROJECT

"STUDIES ON THE EFFECT OF VARIOUS FILLERS ON THE PROPERTIES OF RIGID POLYURETHANE FOAM"

A MAJOR PROJECT REPORT SUBMITTED IN THE PARTIAL FULLFILLMENT OF THE REQUIREMENTS OF THE AWARD OF THE DEGREE OF

MASTER OF TECHNOLOGY
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POLYMER TECHNOLOGY

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CERTIFICATE

This is to certify that **Mr. Ashish Sharma,** Roll No.: 2K12/PTE/04 had carried out this project entitled "**Studies on the effect of various fillers on the properties of rigid polyurethane foam"** under my supervision and guidance. This project work had been conducted for the partial fulfillment for the award of the degree of M.Tech. in Polymer Technology in the Department of Applied Chemistry and Polymer Technology, Delhi Technological University, Delhi. To the best of my knowledge and belief, this is an indigenous work has not been submitted to any other university or institutions for the award of any degree or diploma.

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ABSTRACT

Polyurethane serves the mankind in its various roles such as flexible foam, rigid foam, elastomers, surface coatings and adhesives. PU foam is versatile material and can be produced with open cell structure to be more flexible or a close cell structure to be more rigid. Rigid polyurethane foams (RPUFs) are very popular and highly energy-efficient materials of polyurethane product and are good at both through its physical strength and mechanical properties. RPUFs have closed cell structure with low thermal conductivity, high compression strength, low density, high strength to weight ratio and low moisture permeability. Consequently, polyurethane rigid foams find such applications as insulations of refrigerators, freezers, piping, tanks, ship building and in the construction field as polymeric concrete and sealants.

As there is a growing worldwide interest in the development of vegetable oil based polyurethane because of being relatively inexpensive and a renewable resource, the present studies had been carried out on castor oil based rigid polyurethane foams. In the present project rigid polyurethane foams have been prepared from modified castor oil and 4, 4-diphenylmethane diisocyanate. The studies had been conducted for the effect of addition of various fillers on the castor oil based rigid polyurethane foam. The fillers used for this purpose the fillers were flyash, glass fibre, mica, talc and calcium carbonate. The formation of RPUF was confirmed by FTIR studies .The resulted RPUFs had been characterized for their mechanical properties suchtensile, flexural and compressive strength. It had been found that by the addition of the filler such as mica, calcium carbonate and glass fibre the mechanical properties of the rigid polyurethane got improved. The addition of glass fibre resulted in many folds increase in the strength to the foam as compared to neat RPUs. The addition of the fly-ash as well as talc did not contributed much toward the strength. The SEM analysis of the resulted castor oil based rigid polyurethane foam showed the decrease in pore size with addition of fillers. Thus overall density of the rigid PU material was found to be increased. As per the various test performed, the resulted filled RPUFS are found to be comparable to that of commercial material specially in the cases where mica and calcium carbonate are used as fillers. The retardence in the properties of flyash and talc filled RPUFs is due to hollowness of fly-ash particles and weak interfacial contact between resin & fly-ash. The glass fibre filled RPUF even showed better properties as compared to neat RPUF, thus acted more or less acted as a reinforcing agent.

Key Words: Rigid polyurethane foam, Castor oil, Glycerol, 4, 4-Diphenylmethane diisocyanates (MDI), Mica, Talc, Glass Fibre, Calcium Carbonate, Fly-ash, FTIR, SEM, Mechanical properties.

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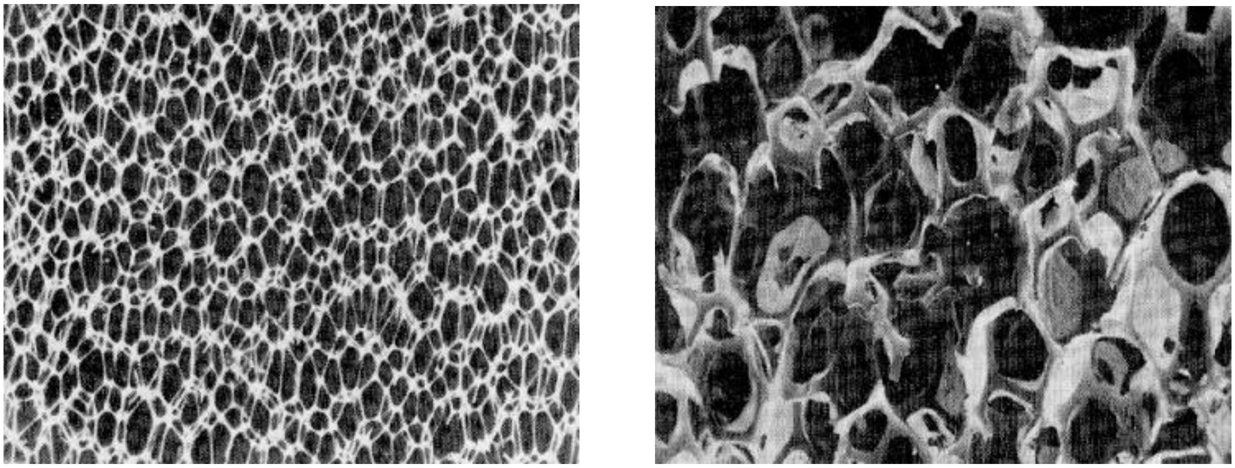
CHAPTER-1

INTRODUCTION

1.1 Introduction

With a global market of approximately six million tonnes per annum, the polyurethane industry covers a diverse business area with its multitude of applications. PU serves the mankind in its various roles such as flexible foam, rigid foam, elastomers, surface coatings and adhesives. Polyurethane foams are some of the most versatile of the foamed plastics systems available and their production has increased markedly in recent years. They can be fabricated in flexible, semi-flexible or rigid form by the reacting polyol and isocyanate with suitable catalyst and other additives. The broad spectrum of properties is achieved by the appropriate selection of polyols and additives. PUFs have a remarkably broad range of applications including thermal insulation, cushioning, buoyancy, energy absorption, packaging etc. Their low density also allows the design of light, rigid components such as aircraft-interior panels, structural shapes, impact-limiters and crash-pads, composite foam cores, mold-patterns and plugs, sports-equipment core material, and composite tooling [1, 2, 3, 4].

Foams are cushiony materials formed by the creation of gas bubbles in a base material such as natural rubber, synthetic rubber or other elastomeric materials. Polymer foams are made up of a solid and gas phase mixed together. This generally happens by combining the two phases too fast for the system to respond in a smooth fashion. In polymeric foam the gas phase is generally dispersed in the solid phase. The dispersed phase of the foam is usually called the internal phase (air or gas), whereas the other continuous phase or the external phase is made up of polymeric material. The solid part forms the matrix and the gas is being entrapped within the solid part. The resulting foam thus obtained has a polymer matrix with either air bubbles or air tunnels incorporated in it, which thus forms either closed-cell or open-cell structure (Figure 1.1). Open cell structure foam contains pores, which are connected to each other to form an interconnected appearance. Flexible PU foam is found on having open-cells cellular structure. It is usually consists of a minimum of two phases which is a solid polymer matrix and a gaseous phase derived from carbon dioxide (CO2) [5]. Closed cell structures do not have a network of connected cells. Normally this kind of foam has higher compressive strength due to its structure. This kind of foam has a higher dimensional stability, absorbs less moisture and has higher strength when compared to open-cell foam. Its structure makes it have a harder surface feel and makes it better at absorbing impacts. Closed–cell foams are generally rigid. Higher molecular weight polyols (molecular weights from 2,000 to 10,000) are used to make flexible polyurethane foams, while lower molecular weight polyols make more rigid products.



a) b)

Figure: 1.1 Structure of Polymeric Foam a) Closed Cell b) Opened Cell

Polyols are usually developed to have the necessary reactivity with the isocyanate to produce polyurethanes with specific properties. If polyols are of higher functionality, i.e. contain more hydroxyl groups per molecule, tougher products may be obtained i.e. rigid foam will result. Polymeric foams may be flexible, semi-flexible (or semi-rigid) and rigid, depending on chemical composition and the rigidity of the resin used as a matrix and the type of cross linking that exists between the molecules. Flexible foams have a glass transition temperature (Tg) below room temperature, whereas rigid foams have one above room temperature. Khemani, 1997 and Kumar and Kaur, 2013 reviewed the background and history of urethane foams and elaborates on their potential future utility [6, 7, 8].

1.2 Rigid Polyurethane Foam

Rigid polyurethane foams are derived from highly functional starting materials; therefore, they are densely cross-linked and have high strength. RPUFs have closed cell structure with low thermal conductivity, high compression strength, high strength to weight ratio and low moisture permeability. Additionally, Rigid polyurethane foam has a number of advantages such as (1) It can be produced in a wide range of densities, (2) It adheres to various facings without the use of adhesives and (3) It can also be produced in complex cavities.

Rigid polyurethane foams (RPUFs) are very popular and highly energy-efficient materials of polyurethane product and are good at both through its physical strength and mechanical properties. As rigid polyurethane foam is currently one of the best thermal insulating materials available. As a result, thermal insulation is a key feature of almost all its applications. Consequently, polyurethane rigid foams find such applications as insulations of refrigerators, freezers, piping, tanks, ships and buildings. Rigid, or cross-linked, polyurethane foams are used to produce insulation in the form of boards or laminate. Laminates are used extensively in the commercial roofing industry. Buildings are often sprayed with polyurethane foam. When sandwiched between metal, paper, plastics or wood, polyurethane rigid foam plays an important role in the construction industry (as polymeric concrete and sealants). Such composites can replace conventional structures of brick, concrete, wood or metal, particularly when these later materials are used in combination with other insulating materials such as polystyrene foam, glass fibre or mineral wool. Technically advanced wood composites can be produced for use in load-bearing applications and wood construction boards for flooring and roofing.

Polymer foams are produced by a number of different ways like through slab-stock by pouring, extrusion and different forms of moulding. RPUFs can be produced without difficulty using one-shot technique either on large factory installed machines or alternatively on small portable equipment. In most system reaction is rather slower than with the flexible foam and conditions of manufacture rather less critical. In addition to one-shot process, quasi-prepolymer system is used commercially with rigid polyether foams. The quasi-prepolymer is commonly produced using excess TDI rather than diphenylmethane di-isocynate. Since the former isocynate is light in colour and latter dark, quasi-prepolymer foams are usually lighter in colour. The quasi-prepolymer system is also more tolerant to variation in processing conditions and often carefully control of the process can be tolerated.

By suitable choice of ingredients, the properties of RPUF can be tailored to particular requirements through variation of molecular and phase structure. As density determines the mechanical property level of rigid polyurethane foams, density can be adjusted via the content of physical blowing agent and water in the PU system. Based upon the density, rigid polyurethane foams can be employed in various applications as given in Table 1.1.

Table 1.1: Density Based Applications of Rigid Polyurethane Foam [9]

Density range g/cm^3	Typical applications
0.016-0.027	In-situ packaging, flower arrangements
0.027-0.096	In-situ insulation of (refigerators, deep freezers, cold stores, ships), chair shells
0.098-0.16	Decorative mouldings eg: wood beams
0.16-0.48	Picture frames, imitation wood
0.48-0.96	Structural plastics mouldings eg: furniture, car body parts, brush handles and gun stocks
1.2	As above

1.3Chemistry of the Polyurethane Reaction

Polyurethanes are the compounds which have repeated urethane (-NH-COO-) unit in their structure. These polymers are formed through step-growth polymerization reaction. In this process, a monomer containing polyisocyanates reacts with another monomer containing polyols. At least two isocyanate functional groups reacts with another monomer containing at least two hydroxyl groups in the presence of a catalyst and other additives. The generalized Polyurethane reaction is:

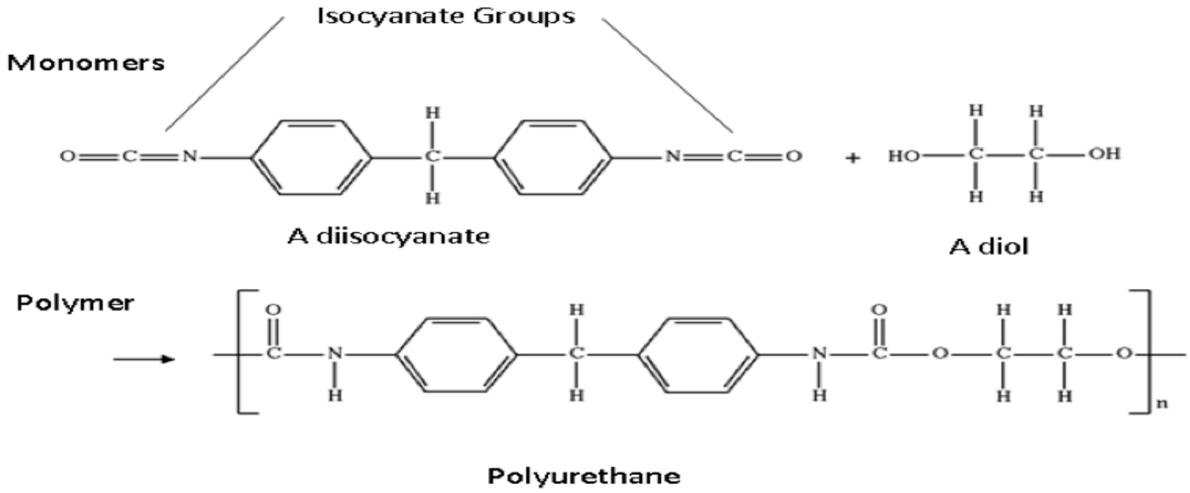


Figure 1.2: Generalized Polyurethane Reaction

The mixing of the two monomers will form a dimer, which again will continue to react with other monomers, dimers and oligomers and form long polyurethane chains. The positive charge due to oxygen's electro negativity on the hydrogen at the end of the diol attracts the nucleophile, which wants to bind to a nucleus. The oxygen then becomes more negative and reacts with a carbon on an isocyanate group. This leaves the nitrogen on the isocyanate group to be negative, which is highly unfavourable. The nitrogen will give off its negative charge to the hydrogen atom on the alcohol group, finally forming a urethane bond between the two monomer units, resulting in a urethane dimer. The dimer will have one end group that is isocyanate, while the other is an alcohol group. Each end can now react with other monomers and oligomers until polyurethane is formed. This is called a step growth reaction. The choice of polyol, especially the number of reactive hydroxyl groups per polyol molecule and the size and flexibility of its molecular structure, ultimately control the degree of cross-linking between molecules. This has an important effect on the mechanical properties of the polymer. Chemical compounds with isocyanate groups (NCO-) as functional groups are known as isocyanates. di- and polyfunctional isocyanates are commonly used to make polyurethanes. Among those isocyanates, toluene diisocyanate (TDI), 4,4'-diphenylmethane diisocyanate (MDI), hexamethylene diisocyanate (HDI), and isophorone diisocyanate (IPDI) are commonly used. In the formation of polyurethane foams, the most commonly used type of catalyst are the tertiary amines. The gas that is used in the foam is due to presence of blowing agent, and it can be either chemical or physical. Chemical blowing agents are chemicals that take part in are action or decompose, giving off chemicals in the process. Physical blowing agents are gases that do not react chemically in the foaming process and are therefore inert to the polymer forming the matrix. The commonly used blowing process in PUFs is the physical blowing process in which a low-boiling liquid e.g CFCs, pentane etc, incorporated in the reaction mix is vaporized due to the heat of the reaction. Generally surfactants (non-ionic) are used in the foam manufacturing because they provide stabilization to the cell walls which in turn make foam structure stable.

1.4 Fillers

Thermosetting resins are usually induced with fillers or fibrous reinforcements to enhance both properties and thermal and dimensional stability. Traditionally, most filler were considered as additives because their major contribution is in lowering the cost of materials by replacing the most expensive polymer. Depending on the type of filler, other polymer properties could be affected; for example, melt viscosity could be significantly increased through the incorporation of fibrous materials. On the other hand, mold shrinkage and thermal expansion would be reduced, a common effect of most inorganic fillers [10, 11].

The term reinforcing filler has been invented to describe discontinuous additives, the form, shape, and/or surface chemistry of which have been suitably modified with the objective of improving the mechanical properties of the polymer, particularly strength. Inorganic reinforcing fillers are stiffer than the matrix and deform less, causing an overall reduction in the matrix strain, especially in the vicinity of the particle as a result of the particle–matrix interface.

Reinforcing fillers are characterized by relatively high aspect ratio, the ratio of length over diameter for a fiber or the ratio of diameter over thickness for platelets and flakes. For spheres, which have minimal reinforcing capacity, the aspect ratio is unity. A useful parameter for characterizing the effectiveness of filler is the ratio of its surface area A to its volume V, which needs to be as high as possible for effective reinforcement.

In developing reinforcing fillers, the aims of process or material modifications are to increase the aspect ratio of the particles and to improve their compatibility and interfacial adhesion with the chemically dissimilar polymer matrix. Such modifications may not only enhance and optimize the primary function of the filler (in this case, its use as a mechanical property modifier) but also introduce or enhance additional functions. New functions attained by substitution or modification of existing fillers, thus broadening their range of applications. Commonly used fillers in industries are given in Table 1.2.

Table No 1.2: Commonly Used Fillers

Chemical Family	**Examples**
A) Inorganic	
Oxides	Glass fibers, MgO, SiO_2 , Sb_2O_3 , Al_2O_3
Hydroxides	$Al(OH)_3$ and $Mg(OH)_2$
Salts	$CaCO_3$, $BaSO_4$, $CaSO_4$, phosphates
Silicates	Talc, mica, kaolin, wollastonite
Metals	Boron and steel

B) Organics	
Carbon, graphite	Carbon fibers, graphite fibers and flakes
Natural polymers	Cellulose fibers, wood flour and fibers
Synthetic polymers	Polyamide, polyester, Aramid, PVA

The most commonly used particulate fillers are industrial minerals, such as talc, calcium carbonate, mica, kaolin, wollastonite, feldspar, and aluminum hydroxide. The most commonly used fibrous fillers are glass fibers and, recently, a variety of natural fibers. Carbon black has long been considered a nanofiller. More recent additions, rapidly moving to commercial markets, are nanoclays such as montmorillonite and hydrotalcite, a variety of oxides, and nanofibers such as single- or multiple-wall carbon nanotubes. Graphene sheets and halloysite nanotubes are potential additives in advanced nanocomposites; the first are single layers of carbon atoms tightly packed in a honeycomb structure [12], whereas the second are naturally occurring nanotubes produced by surface weathering of aluminosilicate minerals [13]. A more convenient scheme, first proposed by Mascia [14] for plastic additives, is to classify fillers according to their specific function, such as their ability to modify mechanical, electrical, or thermal properties, flame retardancy, processing characteristics, solvent permeability, or simply formulation costs. Fillers, however, are multifunctional and classified according to five primary functions, as follows:

- . Mechanical property modifiers (and further subdivision according to aspect ratio);
- . Fire retardants;
- . Electrical and magnetic property modifiers;
- . Surface property modifiers;
- . Processing aids.

Additional functions may include degradability enhancement, barrier characteristics, anti-aging characteristics, bioactivity, radiation absorption, warpage minimization, and so on.

Global demand for fillers/reinforcing fillers including calcium carbonate, aluminium trihydrate, talc, kaolin, mica, wollastonite, glass fiber, aramid fiber, carbon fiber, and carbon black for the plastics industry has been estimated to be about 15 million tons [15]. Primary end-use markets are building/construction and transportation, followed by appliances and consumer products;

furniture, industrial/ machinery, electrical/electronics, and packaging comprise smaller market segments. Various types of fillers used for reinforcement purposes are listed below:

Glass Fiber

GLASS FIBERS [Figure 1.3] are among the most versatile reinforcing industrial materials known today. Glass fibers are made of silicon oxide with addition of small amounts of other oxides. Glass fibers fall into two categories, low-cost general-purpose fibers and premium special-purpose fibers. Over 90% of all glass fibers are general- purpose products. These fibers are known by the designation E-glass and are subject to ASTM specifications [16]. The remaining glass fibers are premium special-purpose products. Typical properties of Glass Fibers are as given in Table 1.3.

Table 1.3: Properties of Glass Fibers [19]

Property	**Glass Fiber**
Density (gm/cc)	2.55
Elongation at break (%)	4.8
Tensile Strength(MPa)	2000
Young’s Modulus (GPa)	80

Glass fibers are characteristic for their high strength, good temperature and corrosion resistance and low price. The use of fiber composites based on glass fibers is wide spread in the industry when low cost and good performances are needed. Reinforcement of polymer matrix with glass fiber leads to general improvement of mechanical properties. They exhibit useful bulk properties such as hardness, transparency, resistance to chemical attack, stability, and inertness, as well as desirable fiber properties such as strength, flexibility, and stiffness [17]. Glass fibers are used in the manufacture of structural composites, printed circuit boards and a wide range of special-purpose products [18]. Their principal advantages are the relationship between their low cost, high tensile strength, high chemical resistance, and insulating properties. The disadvantages are low tensile modulus, relatively high specific gravity, sensitivity to abrasion during handling, low fatigue resistance, and high hardness. Application of glass fiber composite materials depends on proper utilization of glass composition, size chemistry, fiber orientation, and fiber volume in the appropriate matrix for desired mechanical, electrical, thermal, and other properties.

GFRP are finding increasing use as primary load bearing structures and also in a wide range of high technology engineering applications. Among the different applications one of particular interest is that for pipe systems of chemical plants. The advantages of replacing metal pipes with composites pipes are lower weight, increased resistance to aggressive fluid, easiness to build complex shapes. The advantage of the easy building of complex shapes, at low production numbers, is related to the possibility to build on demand using cheap techniques such as hand lay-up. Currently glass fibers only are used as reinforcement for these applications.

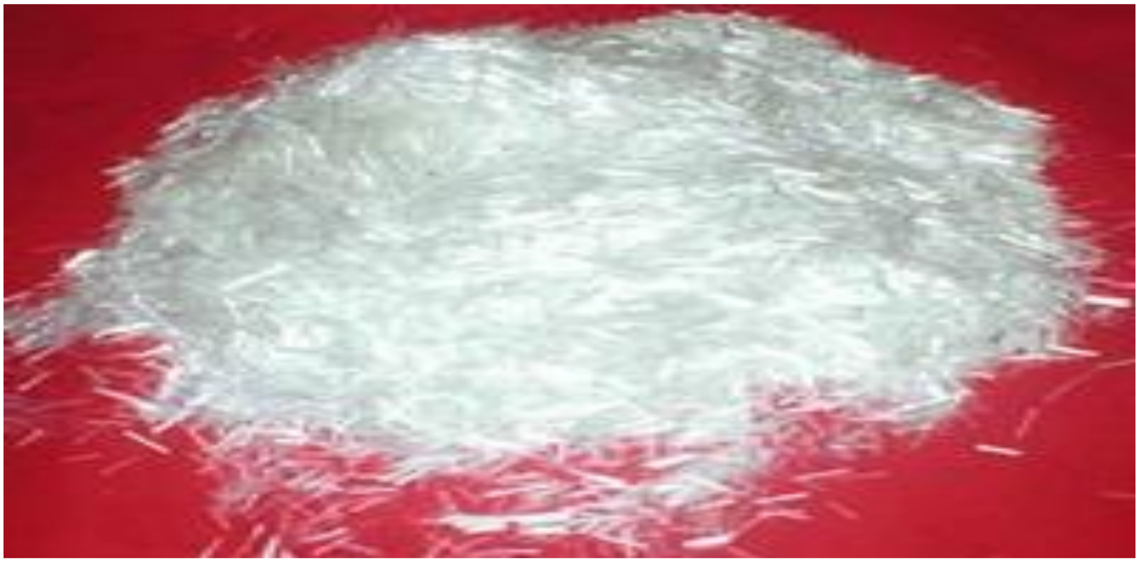


Figure 1.3: Chopped Glass Fiber as Filler

Fly ash

The Fly- Ash [Figure 1.4] is the main bi-product of the power plants and coal burning industries. The major waste management options currently used for fly ash are disposal in land fill or ash lagoons. Significant negative environmental impacts are associated with both of these methods [20]. Approximately 5% of fly ash is currently utilized as a partial replacement for cement in concrete, as a substitute raw material in cement manufacture and as a fill material in general and structural civil engineering applications [21]. The constituents of flyash particles, as obtained from coal are silica (59.5%), Alumina (20.3%), FeO /$Fe2O3$ (6.5%), remaining being FeO, MgO and unburnt coal etc. Flyash depending upon the source of coal, contain different proportions of silica, alumina, oxides of iron, calcium, magnesium etc along with elements like carbon, Ti, Mg, etc. From decades, refined fly-ash had been reported to be used as filler in liquid-resin applications like vinyl plastisols and thermoset bulk and sheet molding compounds. The utilization of fly ash as filler material in polymer composites is considered important from both economic and commercial point of view Fly ash is used as reinforcing filler in polyurethane foam to develop composites.

Figure 1.4: Fly-Ash Powder as Filler

Mica

Mica [Figure 1.5] is a generic name given to a family of hydrous potassium aluminium silicates. Mica is not affected by fire, water, acid or alkali. Mica is useful particulate filler extensively used to enhance the performance of many polymeric materials. It surface resistance and arc resistance contributes towards its improvement in mechanical properties.. It is one of the most common filler to be used in industries, when the material with elasticity and tancity is required to act as a heat insulator. Mica is the material with contributes towards the ease of processing and reduction in cost. Mica has an outstanding mechanical, thermal, electrical and chemical properties rarely found in any other products. Mica [22] provides cost effective improvements in the critical properties for a wide range of thermoplastic and thermoset composites. Mica products come in a wide range of colors depending upon the source and impurities. Fine white grades are coated with metal oxides to produce colored pearlescent pigments for specially applications. Typical grades range from 5-500 μm, but are usually reported in mesh size. Surface –treated grades are also available. The most important markets for mica are joint cements, roofing’s, well drilling muds, paints, plastics and rubber. The main plastic applications of mica are in polyolefin, thermoplastic polyesters, structural foam, phenolics, epoxies, and thermoset polyesters. Because of a high aspect ratio mica imparts high stiffness, high heat deflection temperature, reduced warpage and shrinkage and dielectric strength. The HDT improvement of mica has expanded its use in auto part applications since many plastic parts must now pass through a paint bake oven. Mica is mainly used for adhesive and sealant.

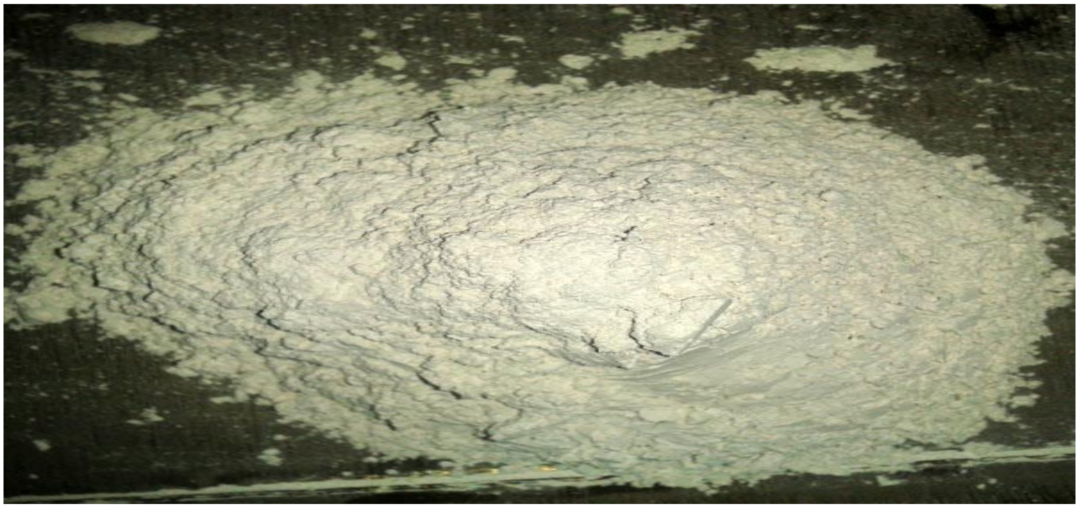


Figure 1.5: Mica Powder as Filler

Calcium Carbonate

Calcium carbonate [Figure 1.6] is the most abundant white mineral in the earth's crust; consequently, it is widely exploited around the world. Calcium carbonate is also known as marble, limestone, calcite, chalk, aragonite, and dolomite. It is the largest-volume mineral filler in the plastic, sealant, rubber, paper, coating, adhesive, textile and carpet backing industries. Its wide utility is due to its whiteness, low abrasion, ready availability, wide particle size range and low cost. Three major commercial grades of calcium carbonate dominate applications: coarse ground, fine ground, and precipitated. Most of the calcium carbonate used as filler is precipitated one, which is high purity whiting (99.75%), of regular shape and size and high degree of aggregation. As filler calcium carbonate has unique advantages as it is non-toxic, odourless, white, soft and easily mixed into formulations. It also has possible disadvantages such as chemical reaction with acid, little reinforcing action and moisture sensitivity. To improve impact strength of filled polymer calcium carbonate has been used with talc as mixed filler.

Figure 1.6: Calcium Carbonate Powder as Filler

Talc

Talc [Figure 1.7] is a white to pale green platy hydrated magnesium silicate. Talc is the softest filler and has slippery texture. The major market for talc is ceramics, paint, paper, plastics, cosmetics and roofing materials. Due to its plate like form or high aspect ratio, talc is considered as reinforcing filler in many plastic applications. Composites filled with plate like talc always exhibit a higher stiffness and creep resistance. But a high loading of talc impact strength is reduced. This effect can be minimized through proper selection of talc particle size and size distribution, surface treatment of talc and resin formulation. Talc is also utilized as medium filler of average whiteness in plastics where improvement in electrical insulation, heat and moisture resistance, chemical inertness and good machinability of molding is required. Often talc will be classified by its origin, since quality greatly differs with source. Talc's hydrophobic surface allows excellent dispersion and wet-out in polymers. Most applications of talc are in automotive or appliance parts, where talc imparts increased stiffness and high temperature creep resistance. Generally loading levels are between 10 and 40 %.Paint is the major end-use market for talc as filler because talc is very soft and contributes minimum abrasion. Talc is used in both architectural and industrial coatings to reduce gloss.

Figure 1.7: Talc Powder as Filler

Moreover, the mechanical properties of the foam being also governed by the mechanical properties of the constitutive material, the reinforcement level of the foam depends on the interaction between the filler and the polymer matrix [23].In principle any material can be used as filler. However, some aspects must be considered when selecting the material for this purpose. These include: size [24], in that the particles must be small and able to easily disperse in the polymer matrix; chemical purity, to avoid undesired reactions; and abrasiveness, which can cause excessive deterioration to the mixing equipment and increase costs [25]. Table 1.4 gives the type of the filler used based on the required properties enhancement.

Table 1.4: Type of the Filler Used for Imparting Required Properties

Primary function	**Examples of fillers**	**Additional functions**	**Examples of fillers**
Modification of Mechanical Properties	High aspect ratio: glass fibers, mica, nanoclays, carbon nanotubes, carbon/graphite fibers, and aramid/synthetic/natural fibers Low aspect ratio: talc, CaCO3, kaolin, wood flour, wollastonite, and glass spheres.	Control of permeability	Reduced permeability: impermeable plate-like fillers: mica, talc, nanoclays, glass flakes

Enhancement oFfire Retardancy	Hydrated fillers: Al(OH)3 and Mg(OH)2	Bioactivity	Enhanced permeability: stress concentrators for inducing porosity: CaCO3 and dispersed polymers Bone regeneration: hydroxyapatite, tricalcium phosphate, and silicate glasses
Modification of Electrical and Magnetic properties	Conductive, nonconductive, and ferromagnetic: metals, carbon fiber, carbon black, and mica	Degradability	Organic fillers: starch and cellulosic fibers
Modification of Surface Properties	Antiblock, lubricating: silica, CaCO3, PTFE, MoS2, and graphite	Radiation absorption	Metal particles, lead oxide, and leaded glass
Enhancement of Processability	Thixotropic, antisag, thickeners, and acid scavengers: colloidal silica, bentonite, and hydrotalcite	Improved dimensional stability Modification of optical properties Control of damping	Isotropic shrinkage and reduced warpage: particulate fillers, glass beads, and mica. Nucleators, clarifiers, and iridescent pigments: fine particulates and mica/pigment hybrids. Flake fillers, glass, and BaSO4

1.5 Polyurethanes from Castor Oil

The synthesis of vegetable oil based polymeric materials with excellent physical and chemical properties has drawn great interest in the recent times. Raw materials based on vegetable oils are important in our life because they have a number of excellent properties for producing valuable polymers such as polyurethane, polyester, amide and epoxy resins. There is a growing worldwide interest in the development of vegetable oil based polyurethane. This interest is economically driven because vegetable oils are relatively inexpensive and a renewable resource [26], [27]. The potential for polyols derived from vegetable oils to replace petrochemical- based polyols began garnering attention around 2004, partly due to rising costs of petrochemical feedstock's and partially due enhanced public desire for environmentally friendly green products. Although the development of commodities derived from petrochemical polymers has brought many benefits to mankind. However, it is becoming more evident that the ecosystem is considerably disturbed and damaged as a result of pollution occasioned by discharge of heavy metals and the non- degradable materials used. To produce materials that are competitive with synthetic ones is gaining attention over the last decade, because of availability of materials, and their low cost [28], [29]. Bio-based polymers and biocomposites are a relatively new and growing market in light of recent societal concerns including dwindling petroleum reserves, environmental and end of- live disposal issues [30,31] Polymers derived from plants, especially those from non-food resources, are gaining the attention of governments, industries and institutes, primarily due to their environmental compatibility, superior physical properties and low stable market prices which are becoming competitive with petroleum-derived polymers.Vegetable oils are abundant renewablesources available worldwide. They have relatively low costand offer possibilities of biodegradation [32]. Oilsare triglyceride molecules composed of saturated and unsaturatedfatty acids. These oils can be functionalized byhydroxylation of the carbon-carbon double bonds using enzymes or chemicalsand can be induced a hydroxyl value useful forelastomeric or rigid polyurethane production [33,34]. Although many types of vegetable oils have been tested and reported for polyol and polyurethane applications for example soyabean oil, sunflower oil, castor oil, palm oil and rice-barn oil [35]. Castor oil is the most promising one to partially replacing petroleum to make polyols due to its volume and price stability. Castor oil differs from other oils from its high acetyl or hydroxyl value also; it is miscible with alcohol but only slightly soluble in petroleum ether at room temperature. . India is the world'slargest exporter of castor oil; other major producers areChina and Brazil.Castor oil is a vegetable oil obtained from the seeds of the castor plant (Ricinuscommunis), found in Nigeria. Castor oil is a colorless to very pale yellow liquid with mild or no odor or taste. Its boiling point is 313 °C (595 °F) and its density is 961 kg/m^3. It is a triglyceride which contains about 85% ricinoleic acid, Cis-1, 2-hydroxyoctadec-9-enoic acid [36]. Oleic and linoleic acids are the other significant components that can be used for many industrial applications. Ehrilich et al., 1959 and Leitheiser et al., 1969 reported that castor oil can be used to replace the petroleum-based polyol to make polyurethane foams [37, 38].

1.6 Origin of Research Problem

The production cost of polyurethane foam is significantly dependent on the cost of polyol, which constitute the largest percentage of materials used in foam production with the characteristics to induce superior mechanical properties. It is well accepted that fillers, that are relatively cheap, can be introduced in the foam matrix as replacement for polyol. The purpose of adding the fillers is to reduce the cost of the material without much compromising on properties. The addition of fillers has reported to have significant effect on the mechanical and structural properties of the polyurethane foam. These increase cell density and decrease cell size. By affecting the macroscopic cell geometry in this way they act as the reinforcement material in polyurethane foam. It is important to improve the mechanical and structural properties of the core material used for any engineering application. As the rigid polyurethane foam is one of the commonly used cellular materials for various important industrial applications especially in construction industries, this study aims to produce low cost, environment friendly rigid polyurethane foams with enhanced mechanical and structural properties. For this purpose, studies have been carried out for the effect of various fillers on the properties of the rigid polyurethane foam.

In order to make the RPUFs low cost and environmental-friendly, the polyol used in this study has been derived from vegetable oil i.e. Castor oil. Raw materials based on vegetable oils are found promising because they have a number of excellent properties for producing polymers like polyurethanes. The potential for polyols derived from vegetable oils to replace petrochemical- based polyols is gaining attention, because

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

In view of the environmental and sustainability aspects, polyols can be prepared from vegetable oils like canola oil, soybean oil, castor oil and palm oil. This interest is economically driven because vegetable oils are relatively inexpensive and a renewable resource.

1.7 Objective of Research Work

The aim of this project is **Studies on the Effect of Various Fillers on the Properties of Rigid Polyurethane Foams".** During these studies, I have synthesized low cost bio-based rigid polyurethane foam with enhanced properties by incorporating fillers viz: calcium carbonate, glass fiber, talc, fly-ash and mica in different amounts. Castor oil was found most promising one to replace petroleum in the formation of polyols due to its volume and price stability. Also it differs from other oils, as it is the only oil which bears hydroxyl groups naturally. Here I summarise my objectives of the research programme.

The objectives of the work are:

a) Determination of the properties of Castor Oil and Glycerol.
b) Modification of the Castor Oil for the synthesis of Polyol.
c) Characterization of Castor Oil based Polyol.
d) Development of Castor Oil based Rigid Polyurethane Foam with Various Fillers (Calcium Carbonate, Glass Fiber, Talc, Fly-Ash and Mica).
e) Characterization of Castor Oil based Rigid Polyurethane Foam Reinforced with Various Fillers.

CHAPTER- 2

LETERATURE

REVIEW

2.1 History of Polyurethane

In 1937 the German scientist Otto Bayer, also known as “father” of polyurethane, and his co-workers discovered the polyaddition reaction for the formation of polyurethane. In polyaddition reaction, Polyurethane was formed by the addition of isocyanate and polyol under mild conditions without any by-product or elimination of small molecules during the reaction process. The initial works focussed on PU products obtained from aliphatic diisocyanate and diamine forming polyurea, till the interesting properties of PU obtained from an aliphatic diisocyanate and glycol, were realized. Polyisocyanates became commercially available in the year 1952, soon after the commercial scale production of PU was witnessed (after World War II) from toluene diisocyanate (TDI) and polyester polyols. In the years that followed (1952-1954), different polyester-polyisocyanate systems were developed by Bayer [39]. In 1954, a commercial production of flexible foam began, based on toluene diisocyanate (TDI) and polyester polyols. The invention of these foams was thanks to water accidentally introduced in the reaction mix.It was first developed as a replacement for rubber. The versatility of this new organic polymer and its ability to substitute for scarce materials spurred numerous applications. During World War II, polyurethane coatings were used for the impregnation of paper and the manufacture of mustard gas resistant garments, high-gloss airplane finishes and chemical and corrosion-resistant coatings to protect metal, wood and masonry. By the end of the war, polyurethane coatings were being manufactured and used on an industrial scale and could be custom formulated for specific applications. . Since that time they have been finding use in an ever-increasing number of applications and polyurethanes are now all around us, playing a vital role in many industries. They could be found in coatings and adhesives, elastomers and rigid foams. It was not until the late-50’s that comfortable cushioning flexible foams were commercially available. With the development of a low-cost polyether polyol, flexible foams opened the door to the upholstery and automotive applications [40]. Today, the world of PU has come a long way from PU hybrids, PU composites, non-isocyanate PU, with versatile applications in several diverse fields. Interests in PU arose due to their simple synthesis and application protocol, simple/few basic reactants and superior properties of the final product.

2.2 Vegetable oil based polyurethane foam

Presently, most polyols used in PU industry are petrochemicals based where crude oil and coal are used as raw materials. 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.As the world’s energy and raw material demands keep increasing, imposing a large burden on the fossil fuel resources. Unfortunately, fossil fuel resources are not sustainable and are very likely to be mostly depleted in a few decades. Also, the significant amount of CO_2 emission from fossil fuel usage is also increasing steadily, which might cause irreversible damage to the environment and climate. One solution to these problems is to utilize renewable resources and gradually transfer the global economy towards more sustainable future. Moreover 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 fulfill our requirements, exhibiting similar or better properties. Vegetable oils have shown great potential to produce different kinds of polymeric resins [41-44]. Unsaturated triglyceride oils such as soybean, crambe, linseed and castor oil constitute one major class of renewable resources [45]. The main composition ofthese triglyceride oils is saturated and unsaturated fatty acids. Castor oil, a triglyceride of ricinoleic, is a naturally occurring and suitable monomer for PU production, whose viscosity depends on the chain length and unsaturation degree of the fatty acid [46, 47]. The castor oil is a versatile vegetableoil due to its unique composition in which the main component is the 12-hydroxy -9-cis-octadecenoic acid, the so-called ricinoleic acid, which represents 90 % ofits fatty acid content. The rich chemistry of raw castoroil is attributed to its structure (one double C C an done –OH group per fatty acid chain), which makes ita good starting material for a wide range of applications. The castor oil is suitable for use in isocyanate reactions to make polyurethane elastomers [46], polyurethan emillable [47, 48], castables [48, 49], adhesives and coatings [50- 52], interpenetrating polymer network fromcastor oil-based polyurethane [53, 54] and polyurethane foam [55]. Ehrilich et al., 1959 and Leitheiser et al., 1969 reported that castor oil can be used to replace the petroleum-based polyol to make polyurethane foams [56,57]. Lu et al., 2005 used waterborne polyurethane made from rapeseed oil-based polyol to modify glycerol-plasticized starch and develop biodegradable films[58]. Chang et al., 2001a and 2001b added commercial soy flours into water-blown rigid polyurethane foams to improve the physical properties and lower the cost of these foams[59,60]. Rigid polyurethane foams had also been reported to be synthesized from rhodium catalyzed hydroformylated polyols. Petrovic et al [61], 2000and Zlatanic et al., 2004 [62], investigated the structure and properties of vegetable oil-based polyols, their applications in polyurethane foams, and the foam's biodegradation behaviour and thermal stability. Kumar and Kaur, 2013, reported the effect of NCO/OH ratio on the properties of Castor Oil based Rigid Polyurethane Foam [63]. The work carried out by different researchers on the bio-based polymers is given in Table 2.1

Table 2.1: Work Carried Out By Different Researchers on Bio-based Polymers

Sr. No.	**Author's Name**	**Year of Publication**	**Title**	**Outcome**
1	Ogunniyi, D. S. et al	1996	Preparation and Properties	Tensile strength of resulted PUF was found

	[64].		of Polyurethane Foams from Toluene Diisocyanate and Mixtures of Castor Oil and Polyol	to be increased with increase in the concentration of castor oil.Compression set increase dramatically with increase in concentration of castor oil.
2	Guo, A. et al.[65]	2002	Polyols and Polyurethanes from Hydroformylation of Soybean Oil	The rhodium catalyzed reaction give a polyol with 95% conversion giving rise to rigid polyurethane. The cobalt catalyzed reaction gave a polyol with a 67% conversion, giving a hard rubber having lower mechanical strength. Glycerine was used as a cross- linker to improve the properties of PUs.
3	KendagannaSwamy, B. K. et al.[66]	2003	Structure-property relationship of castor oil based diol chain extended polyurethanes (PUs)	High density chain extended PUs were produced. 1,6-hexane diol system yields higher dimensional stability compared to 1,4-butane diol system. Higher tensile strength value are observed for 1,4-butanediol system than 1,6-hexane diol system.MDI based chain extended PUs show higher tensile strength of 1.10 and 1.29 MPa for 1,6-diol and 1,4-diol based PU system respectively.The variation of tensile strength with respect to diisocyanate is in the order: MDI > TDI > HMDI.
4	Badri, K. H. et al.[67]	2004	Rigid polyurethane foams from oil palm resources	The foam produced exhibited good mechanical properties. Silane was used as a coupling agent for surface modification.
5	Mythili, C. V. et al [68]	2004	Synthesis, mechanical, thermal and chemical properties of polyurethane based on cardanol	The addition of commercial polyol, PPG-2000 along with cardanol formaldehyde resin introduces some degree of flexibility in the tough polyurethane. The TGA analysis of polyurethane showed higher thermal stability in RPUFs. The PUs were found to be stable in acid, alkali, 1 N sodium chloride, toluene, ether and ethanol.
6	Zhang, L. et al.[69]	2007	Substituting soybean oil-based polyol into polyurethane flexible foams	Compressive properties of the resulted PUs were found to be improved.. Substituting SAN copolymer filled polyol results in slightly smaller cell size and does not change phase separated morphology in the polymer phase. The use of crosslinkerpolyol

				alters polymer phase morphology, especially that of hard domains.
7	Lee, C. S. et al.[70]	2007	Rigid Polyurethane Foam Production from Palm Oil Based EpoxidizedDiethanolamides	The increase in the isocyanate index from 1.0 to 1.4 had led to an increase in the density &compression strength. With further increase in NCO index, i.e. to 1.5, a decrease in the density &compression strength was recorded, which subsequently increased, but the brittleness increased as well. PUFs were produced with a higher percentage of close cell contents and exhibited lower thermal conductivity.
8	Chuayjuljit, S. et al.[71]	2007	Processing and Properties of Palm Oil-Based Rigid Polyurethane Foam	The obtained palm oil based polyol was a viscous yellowish liquid with much higher viscosity than that of the regular palm oil. This high viscosity was reported due to hydrogen bonding associated with the hydroxyl groups. The densities of the PUFs decreased with the increased amount of catalyst (DMCHA). Compressive strength of PUFswas found to be increased with an increase in DMCHA. Increased amount of surfactant showed negligible effect on the density and compressive strength of the PUFs.
9	Ogunleye, O. O. et al.[72]	2007	Effect of Castor Oil on the Physical Properties of Polyether Based Flexible Polyurethane Foam	Making a partial substitution of silicone oil by castor oil significantly increased density and hardness index. The tensile strength and elongation of samples declined with increased castor oil.
10	Narine, S. S. et al.[73]	2007	Physical Properties of Polyurethanes Produced from Polyols from Seed Oils: II. Foams	Canola PU was the most reactive system with the shortest cream, rising and gel times and Soybean PU was the least reactive one with the longest times. Castor oil PU has a cream time 50% larger, a rising time 35% larger and a gel time 25% larger than those of Canola PU. Canola PUF showed better compressive properties than Soyabean PUF but less than Castor oil PUF.
11	Ghosh, S. B. et al.[74]	2010	Synthesis of Soy-Polyol by Two Step Continuous	PUF produced from soybean polyol was found to have density and compressive

			Route and Development of Soy-Based Polyurethane Foam	strength comparable to commercial polyols. The cellular microstructure of soy foam shows polygonal cell structure.
12	Corcuera, M. A. et al.[75]	2010	Microstructure and properties of polyurethanes derived from castor oil	Both melting temperature and enthalpy increased as hard segment content increases for both PUBD and PUPD polyurethane. Shore D hardness, tensile modulus and tensile strength and lower strain were measured by mechanical tests. As seen in mechanical tests, the higher hard segment crystallinity degree observed in PUBD polyurethanes at high hard segment contents did not improved the mechanical strength. The thermal decomposition mechanism followed the same behaviour in both synthesized polyurethanes. PUs synthesized with PD as the chain extender structure showed a thermal stability comparable to that of synthesized from petroleum-derived chain extender.
13	Palanisamy, A. et al.[76]	2011	Development and Characterization of Water-Blown Polyurethane Foam from Diethanolamides of Karanja Oil	The two step synthesis involved hydroxylation followed by transamidationleading to a polyol with OH value of 225 mg KOH/g. The foams produced were found to have good mechanical properties such as compression and flexural strengthas compared to semi-rigid PUFs.
14	Palanisamy, A. et al [77]	2011	Diethanolamides of Castor Oil as Polyols for the Development of Water – Blown Polyurethane Foam	The density increased with hydroxyamide content and molecular weight of PPG while the reverse trend was observed in flexural strength measurements. The compression strength increased with the content of hydroxyamide and the molecular weight of PPG.
15	Kashif, M. et al.[78]	2011	Synthesis and Characterization of Ricinoleamide – Based Polyurethane	The synthesized polymer showed moderate antibacterial activity. Thermal degradation of the resin was more or less similar to virgin polyurethane.
16	Tan, S. et al.[79]	2011	Rigid polyurethane foams	The Tgwas found to be increased and foams

			from a soybean oil based Polyol	had comparable foaming kinetics, density, cellular morphology, and initial thermal conductivity. Compressive strength of the soy-based RPUFs were superior to those of petroleum-based foams possibly due to smaller cell size. Foams with 50% SBOP showed thermal conductivity comparable to those of commercially available PUFs.Foams with 100% SBOP showed more aging.
17	Kong, X. et al.[80]	2012	Novel polyurethane produced from canola oil based poly(ether ester) polyols: Synthesis, characterization and properties	Foams were produced using Liprol 270 and Liprol 320 MDI. Both Liprol 270-MDI PU and Liprol 320-MDI PU networks were found highly cross-linked. Compared to Liprol 320-MDI PU, Liprol 270-MDI PU displays shorter gelation time and better initial thermal degradation properties, whereas Liprol 320-MDI PU have a higher Tg, higher cross-linking density.
18	Pawlik, H. and Prociak, A.[81]	2012	Influence of Palm Oil Based Polyol on the Properties of Flexible Polyurethane Foams	The palm oil polyolupto 15 wt% in the polyol premix resulted in more uniform cell size, increased density, compressive strength and resilience, but slightly decrease of $T_g$was observed.
19	Cardoso, G. T. et al.[82]	2012	Rigid foam polyurethane (PU) derived from castor oil (Ricinuscommunis) for thermal insulation in roof systems	The TGA showed that PUFs had higher resistance to degradation by heat.
20	Yang, L. T. et al.[83]	2012	Thermal and Mechanical Properties of Polyurethane Rigid Foam Based on Epoxidized Soybean Oil	The mass fraction of the soybean oil-based polyol at 60% presents higher compressive strength and density. Two glass transition temperatures of each foam were reported and Tg_1increased with OH value.
21	Silva, V. R. D. et al.[84]	2013	Polyurethane foams based on modified tung oil and reinforced with rice husk ashI: Synthesis & physical chemical characterization	Rice husk ash filled RPUF showed a higher thermal conductivity than that of the unfilled samples. TGA analysis showed that thermal stability was almost unaffected by ash content.
22	Silva, V. R. D. et	2013	Polyurethane foams based	Both unreinforced and RHA filled samples

	al.[85]		on modified tung oil and reinforced with rice husk ash II: Mechanical Characterization	exhibited a density gradient in the foam rise direction due to the free rise method selected for the preparation. The addition of rice husk ash led to reduced compression modulus, compressive strength, thermal transitions and storage modulus respect to the unfilled foam.
23	Kumar, M. and Kaur, R.[86]	2013	Effect of Different Formulations of MDI on Rigid Polyurethane Foams based on Castor Oil	Glycerol modification of castor oil results in more cross-linked and stiffer polymer. The tensile and compressive strength of RPUF were found to be increased with MDI content. The highest values were obtained for the high MDI: Polyol ratio. SEM studies had revealed more closed packing with increased MDI content.

2.3 Polyurethane incorporated with various Fillers

The term filler is very broad and encompasses a very wide range of materials. Fillers may be classified as inorganic or organic substances and further subdivided according to chemical family or according to their shape and size or aspect ratio. Wypych, 2000 reported more than 70 types of particulates or flakes and more than 15 types of fibers of natural or synthetic origin that have been used or evaluated as fillers in thermoplastics and thermosets [87].

The first generation of fillers soon after the commercialization of polypropylene included talc platelets and asbestos fibers due to their beneficial effects on stiffness and heat resistance.[88] The search for an asbestos replacement due to health issues led to calcium carbonate particles and mica flakes as the second-generation fillers. Mica was found to be more effective than talc for increasing stiffness and heat resistance, whereas calcium carbonate was less effective in increasing stiffness but increased the impact resistance of PP homo-polymers.

Surface modification of mica with coupling agents to enhance adhesion and stearate modification of the calcium carbonate to assist dispersion were found to enhance these functions and introduce additional benefits such as improved processability, a means of controlling color, and reduced long-term heat aging. Other fillers imparted entirely different functions. For example, barium sulfate enhances sound absorption, wollastonite enhances scratch resistance, solid glass spheres add dimensional stability and increase hardness, hollow glass spheres lower density, and combinations of glass fibers with particulate fillers provide unique properties that cannot be attained with single fillers.

An additional example of families of fillers imparting distinct new properties comprise platelets of mica, silica, alumina, or glass substrates coated with films of oxide nanoparticles, for example, TiO2, Fe2O3, Fe3O4, andCr_2O_3. In addition to conventional decorative applications, new functional applications such as solar heat reflection, laser marking of plastics, and electrical conductivity are possible through the proper selection of substrate/coating combinations.

For some years, study has been extended to composite foams reinforced by the introduction of fibres [89] or metallic or mineral fillers/ particles [90]. Some notable ones include inorganic materials such as calcium carbonate, dolomite, aluminum silica, titanium dioxide, and talc [90] while some of the organic materials used as filler are carbon black and natural fibers [91, 92]. Particulate fillers are used in many composites to improve mechanical properties, impart color, or reduce material cost [93]. Homogenous and multi-functional PU composites can be achieved with Nano-fillers, such as carbon nanotube carbon black, graphene and, nanocellulose, nanoclay and nanosilica. Particularly, in polyurethane foam, presence of filler can create void fractions and enhance nucleation sites, on the polymer/filler interfaces, where gasses may be trapped [94]. The filler serve as solid surfaces for heterogeneous cell nucleation. Moreover, a typical effect of theaddition of fillers to the reaction mixture is an increase inits viscosity [95].It is expected that fillers as nucleating agent can influence the cellular structure of polyurethane foam and promote increase in density and hardness characteristics. However, they reduce other properties such as resiliency and tear strength and contribute to the increase in permanent deformation [96]. Multi-functional homogeneous PU composites can be achieved with Nano-fillers, such as carbon nanotube carbon black, graphene and, nanocellulose, nanoclay and nanosilica.

In the last few years some works have been performed by researchers on glass fibre reinforced polyurethane (GFRP). Saint- Michel et al. [97, 98] studied the mechanical properties of polyurethane foam with different densities and filler size. Husic et al. [99] investigated the thermal and mechanical properties of the polyurethane resin derived from soybean oil, reinforced with glass fibres.

Wilberforce and Hashemi [100] studied the effect of fibre concentration, strain rate and weldline on mechanical properties of short glass fibre polyurethane composites. The long-term properties of polyurethane reinforced composites were investigated by Bruckmeier and Wellnitz [101] with the intention of using the composites in the automotive industry due to its lightweight, strength and damage tolerance. Recently,Deceuninck North America, among the leading designers and manufacturers of high-quality systems for windows, doors, and outdoor living, is introducing an advanced fiberglass technology based on materials from Bayer Material Science. Rovex is a polyurethane composite technology that includes bio-based materials and offers superior structural, thermal, and environmental performance.Recently, relatively low-expanded, high-density PUF reinforced with glass fibers have been used for structural material. However, the physical properties of PUF reinforced with milled glass fiber have not been substantially improved except for the modulus of elasticity, impact resistance, and dimensional stability [102].Meanwhile, PUF reinforced with long fiber has not been commercialized successfully owing to its difficult moldability, although the flexural and tensile characteristics are expected to be remarkably improved [103, 104].

Bahrambeygiet. al,2013 prepared flexible polyurethane (PU) nanocomposite foams[105]. The effects of incorporation of nanoparticles on the morphological and structural developments and the relation between this development and mechanical properties of the PU foam were demonstrated. It had been found that by adding multiwall carbon nanotubes and nanoclay in foams, the foam morphology improved, in which cell density increased and smaller cells were obtained. The mechanical properties of foam especially tensile strength have increased in the presence of nanoparticles. An increase in nanoparticle amount leads to a lower cell density. Tekeei et al.,2012 studied the effect of incorporation of microspheres and nanoclay on soyabean oil based rigid polyurethane foams[106]. With increase in filler content density of the foam increasing filler percentage reduced the PU foam density. The compressive strength of PU foams decreased slightly when increasing the microsphere content from 1 to 3% and then increased. For PU foams reinforced with nanoclay, their compressive strength changed little from 1 to 5%, but decreased at 7% due to a lower density and weaker matrix structure. Foams containing 5 to 7%microspheres or 3 to 7% nanoclay had density-compressive strength comparable or superior to the control. Foams reinforced with fillers had more cells and smaller cell size than foams made from 15% soy-polyol but without fillers.

Michel et a, 2006 studied the mechanical behaviour of rigid polyurethane reinforced by mineral fillers [107]. The filler used was Calcium Carbonate in two different size ranges i.e. 1 and 30 μm, respectively and crystallised silica particles with an intermediate size. The microstructural characterisation had been performed by electron microscopy. It had shown closed spherical cells whose size is decreased when the fillers are added. the results showed that the reinforcement of foam is not efficient if the filler added are bigger than the bubble size. They concluded that the the filler size in the range studied is a key parameter to take into account in the reinforcement level. Saha et al, 2008 investigated the effects of different types of nanoparticles on thermal and mechanical performance of rigid polyurethane (PUR) foam [108]. Three different types of nanoparticles, namely spherical TiO_2, platelet nanoclay, and rod-shaped carbon nanofibers (CNFs) were used. Significant thermal and mechanical properties enhancement of the nanophased foam was observed among nanoparticles, CNFs infused PUR foam showed maximum enhancement, whereas TiO2 infused PUR foam showed the minimum. Cell shapes are changed from spherical to elliptical for nanoparticles with aspect ratio more than unity. A consistent enhancement of thermal and mechanical properties was observed with infusion of nanoparticles.

Morlmoto et al,1984 investigated the flexural properties of rigid polyurethane foams **(PUF)** and glass fiber reinforced rigid polyurethane foams **(FRU)** with different expansion ratios by the bending test[109]. Both the flexural modulus and **the** flexural strength increased and the temperature dependencies decreased when the longer fiber was used to reinforce the polyurethane foam. Kumar 2012, fabricated thermoplastic polyurethane (TPU) - glass fibre (GF) composites by using compression moulding machine[110]. This technique was used with a specific alternative multilayer sandwich model. The multilayer sandwich model enhanced the Tensile, Modulus and Impact properties of TPU-GF composite. The key to obtain significant properties enhancement is to be attributed to the additional interaction site between the polymer matrix and reinforcing agents. Use of polymer-fibre alternative layer sandwich model gives advantages of high aspect ratio, interacted surface area and higher stiffness with better strength. The properties of the composites were believed to be predominantly influenced by the type of processing conditions and technique used.

Ana et. al,2008 carried out the physico-chemical analyses of the flexible polyurethane foams with different contents of $CaCO_3$[111] .It was observed that the excess of commercial $CaCO_3$ caused the increase of hysteresis, possibly causing permanent deformations and damaging the quality of the final product. The carbonate did not disperse well in the matrix since it has variable particle size and presents interactions that tend to form agglomerates, making it so that there is not a distribution of force between the carbonate and the matrix during the utilization of the flexible foam. Although the flexible polyurethane foam factories use calcium carbonate as a filler, the introduction of high quantities corroborates with the increase in hysteresis values, leading to a loss in quality. Latinwo et al,2010 studied the effects of calcium carbonate of different compositions and particle size distributions on the mechanical properties of flexible polyurethane foam[112]. The mechanical properties such as Tensile strength, and Elongation at break were measured with the aid of a Hampden testing machine. The finely divided filler material increased the hardness characteristics of the foam to compositions of up to 35wt%, while coarse filler did not show any appreciable improvement in the property. For all particle sizes, the tensile strength and elongation at break decreased while increasing the load of the filler weight percentages. However, the tendency with which the coarse filler reduce the properties is not as much as for the fine fillers. Scanning Electron Microphotography of the foam samples showed the effect of the fillers on the foam cellular structure and cell size distributions. Babaloia, 2012 studied he effects of calcium carbonate (calcite – CaCo3) and dolomite [CaMg(Co3)2] as fillers on the structural and mechanical properties of the PU[113]. For calcium carbonate as filler, all properties tested are approximately maximized at 10% concentration except for tensile strength while for dolomite; all properties are appreciably maximized at 20% except for maximum strain. Usman et al, 2012 investigated the effect of $CaCO_3$ filler in flexible polyurethane foam matrix [114]. The optimum $CaCO_3$ composition was found to be 20 wt % representing a concomitant 18.54% reduction in cost of production. The cost of production was reduced by about 18.54% while the foam qualities andproperties were either maintained or improved upon as the $CaCO_3$ filler was introduced into thefoam formulation to an optimum 20% content.

Balo, 2011 reported the results of a study conducted to evaluate the influence of class C fly ash (FA), clay (C), expanded perlite(EP), pumice powder (PP) and epoxidized castor oil (ECO) on the density, thermal conductivity, compressive strength, tensile strength, abrasion loss and water absorption of building material[115]. Density, thermal conductivity, compressive strength and tensile strength decreased with the increase of ECO and FA as replacement for building material. . The addition of clay in the building material had an increasing effect on these properties. The thermal, mechanical and physical properties of productions weremeasured according to relevant standards and the resultswere compared to the values of other investigation. The density of samples decreases with an increase in FA ratios. The lower density of sample due to FA is probably related to the higherair content that results in less density and partly to theamorphous structure of FA.Pinto etal, 2001 added two types of fillers i.e. mica and aluminium trihalide and studied the mechanical properties of the resulted thermoplastic urethane elastomers[116]. It was observed that incorporation of mica enhanced the tensile strength of TPU in comparasion to aluminium trihalide. The use of mica in combination with aluminium trihalide did not contributed much towards mechanical properties of the TPU, however the addition of the mica facilitated the processing and reduced the cost of TPU.

Deshmukh and Rao, 2012 prepared mica filled PVC composites of different concentrations using untreated and surface treated water ground mica of different particle size[117]. Mica filled PVC composites were compounded for various compositions and test samples were prepared using compression moulding process. These samples were tested for electrical insulation and mechanical properties. The results shows enhancement in dielectric properties with improvement in Young's modulus, stiffness, reduction in elongation at break and slight increase in shore D hardness of composites. Scanning electron microscopy was used to test the morphology of the samples which has shown proper distributions and adhesion of the filler mica in PVC matrix. AltafimI et al, 2003, studied the behaviour of fillers, such as carbon black, silica and mica added to castor oil-derived polyurethane resins[118]. Several thermal, mechanical and electrical tests were conducted on samples and insulators produced. The results of these tests clearly demonstrated that this type of resin and its composites can be used to manufacture indoor electrical insulators and that the fillers analyzed in this study improve or maintain the characteristics of the pure resins. **Sreekanth et al., 2009 studied the** the effects of mica with varying concentration on the mechanical, thermal, electrical, rheological and morphological properties of polyester thermoplastic elastomers [119]. Mechanical properties such as flexural strength and modulus were found to increase with mica concentration, whereas tensile strength was found to decrease at higher concentrations. Electrical and thermal properties of composite were found to increase with filler concentration. Morphological studies revealed that there is a good dispersion of filler in the polymer matrix at lower concentrations.

Kim et al, 2010 fabricated the rigid polyurethane foam (RPUF)/glass fiber composites from glass fiber, polymeric 4,40-di-phenylmethane diisocyanate (PMDI) and polypropylene glycols (PPG) using HFC 365mfc as blowing agent[120]. Glass fiber was added in the form of mat. Thermal conductivity, glass transition and decomposition temperatures and the mechanical strengths of the foam increased with the addition of glass fiber. Foam density increased with the addition and increasing amount of glass fiber in accordance with the decreased cell size which is due to the decreased interface energy of the foam. Compression strength, tensile modulus and strength increased with the addition of glass fiber implying that the glass fibers are properly incorporated into the polymer matrix. The increase was also in accordance with the increased foam density. Young et al., 2014 reinforced the PUF with chopped E-glass fiber because of its good dispersion and distribution characteristics[121]. The compression, tension and the fracture toughness test were conducted with respect to the amount of the chopped E-glass fiber both at the room (25^0C) and cryogenic (_150^0C) temperatures. From the experimental results, it was found that the chopped E-glass fiber reinforcement increased the fracture toughness of the PUF much, especially at the cryogenic temperature. Nikje et al, 2006 [122] reported on the properties of polyurethane rigid foams by addind talc as a filler. Physical and comparative tests were performed on various compositions of polyurethane foam to chart their insulating capabilities, and our comparative analysis indicated that advances had been achieved with respect to its properties. **Studies carried out by different researchers on various fillers incorporated in Polymeric Resins is given in Table 2.2**

Table 2.2: Studies Carried out by Different Researchers on Various Fillers Incorporated in Polymeric Resin

S.No	Authors Name	Year of publication	Title	Outcome
1	M. A. Usman [123]	2012	Optimum Calcium Carbonate Filler Concentration for	$CaCO_3$ increases tensile strength & elastic qualities &

			Flexible Polyurethane Foam Composite	improves the foam resilience ability as the desired load bearing ability is enhanced
2	Chan Wen Shan [124]	2012	Study of Flexible Polyurethane Foams Reinforced with Coir Fibres and Tyre Particles	SEM images indicated that structures of foams are anisotropic. During the foam production, effect of fillers on viscosity increase in PU mixture causes the foam composites easily to become failed or imperfect.
3	Fabrice Saint-Michel [125]	2006	Mechanical properties of high density polyurethane foams: II Effect of the filler size	the reinforcement of foam is not efficient if the filler added are bigger than the bubble size.
4	Faith U. Babalola [126]	2012	A Comparative Analysis of The Effects of Calcium Carbonate and Dolomite as Fillers in Polyether Polyurethane Foam Production	Dolomite at 20% concentration is preferred to calcium carbonate at 10% as this will translate to cost reduction
5	Yang Li [127]		Cellulose Nano Whiskers as a Reinforcing Filler in Polyurethanes	Improvements of thermal and mechanical properties of cellulose nano whiskers reinforced nanocomposites
6	Manasa Nayani [128]	2013	Synthesis and Characterization of Polyurethane-Nanoclay Composites	The thermal properties, tensile properties, flexural strength, and abrasion resistance were significantly enhanced
7	FIGEN BALO [129]	2011	castor oil-based building materials reinforced with fly ash, clay, expanded perlite and pumice powder	FA and ECO together were effective admixtures for decreasing significantly both the compressive-tensile Strength and the thermal conductivity of sample.
8	Ruy Alberto Corrêa AltafimI [130]	2003	The effects of fillers on polyurethane resin-based electrical insulators	according to the mass proportion of mica, showing increased moduli of storage elasticity and loss.

9	J.M.L. Reis [131]	2013	Tensile behaviour of glass fibre reinforced polyurethane at different strain rates	The modulus of elasticity increases with the strain rate and higher ultimate strengths are obtained for higher strain rates.
10	Klyotake Morlmoto [132]	1984	Flexural Properties of Glass Fiber Reinforced Rigid Polyurethane Foam	Both the flexural modulus and the flexural strength Increased
11	S. H. Kim [133]	2010	Glass fiber reinforced rigid polyurethane foams	Compression strength, tensile modulus and strength increased with the addition of glass fiber
12	Ryutoku Yosomlya [134]	1984	Compressive Properties of Glass Fiber Reinforced Rigid Polyurethane Foam	compressive strength increases linearly with increasing volume fraction of glass fiber
13	NARESH KR SHARMA [135]	2012	Thermoplastic polyurethane - glass fibre mat reinforced composite: effect of alternative multilayer sandwich model on mechanical properties	As the glass fibre content increased, impact strength continuously increases. Flexural testing results showed that as the glass fibre content increased, modulus increased
14	Edmund B. Semme [136]	2004	Nano-aramid fiber reinforced polyurethane foam	The addition of ~0.5% Kevlar® results in an approximate two-fold increase in tensile and compressive strength without sacrificing density, thermal conductivity, processibility or any other key parameters.

CHAPTER-3

EXPERIMENTAL WORK

3.1 Raw Materials

Castor oil (99.9%) and 4, 4’-diphenylmethane diisocyanate (AR grade) was obtained from Shivathene Linopack ltd. Parwanoo, Himachal Pardesh. tertraethylenediamine (99%), n-Pentane (99.5%) and Silicon oil, were purchased from Standard Chemicals (ISO 9001:2008 certified), Chawari Bazar, Delhi. Glycerol (99%) was supplied by Sisco Industries Pvt. Ltd, Mumbai.E-glass fibre (Chopped) was supplied by Gujwool Glass fibre Pvt. Ltd. Delhi. Mica, Talc and Calcium Carbonate was supplied by CDH, Mumbai.The other chemicals usedfor analysis purpose i.e. Acetone, Amidosulphonic acid, Methanol, Mono methyl glycol, Ethyl methyl ketone, Ethylene diamine, Triethyl phosphate (flame retardant), Triethyl amine, Dibutyl amine, Toluene, Phenolphthalein, Bromophenol blue, Pyridine, Acetic anhydride, Sodium hydroxide, Ethanol, Diethyl ether, Hydrochloric acid, Potassium hydroxide, Hexane1,6-diol (crosslinker).Fly-Ash was obtained by Bathinda Thermal Power Plant, Punjab.All the reagents were of A.R. grade.

3.1.1 Analytical Testing of the Raw Materials

The precision of the results is not only dependent on the instrument and experiment performed, but also to some extent to the purity of the substance/materials used. The properties of the raw materials determine the characteristics of the final product. The characterization of the raw materials is thus essential to control the quality as well as properties of the product. The commercially available Castor Oil, Glycerol and 4, 4-diphenylmethane diisocyanate (MDI) had been tested for their properties. The properties of Castor Oil and Glycerol as determined by various experimental procedures are reported in Table 3.1 and Table 3.2 respectively.The values obtained are almost similar to that available in literature[137,138] Characterization of available Castor Oil and Glycerol for the determination of these properties is as given in Appendix-1.

Table 3.1:Properties of Castor Oil

Property	Value
Color and Appearance	Clear/ Dark Yellow
OH value (mg KOH/g)	161.98
Viscosity (cP at 25 °C)	600-650
Water content (%)	0.5
Acid number	0.96

Specific gravity (25 °C)	0.95
Solubility in Alcohol	Completely Soluble /Mixing

Table 3.2: Properties of Glycerol

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

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

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

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

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

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

FTIR spectra of the MDI were recorded in A Nicolet 380 FTIR spectrophotometer. Small quantities of the liquid samples were spread in pure dried KBr for analysis. The characteristic absorptions peaks and respective bonds are observed at 3694.95 cm^{-1}(O-H stretch, free strong, sharp intensity), 3396.19 cm^{-1}(N-H stretching frequency), 3027.36 cm^{-1}(C-H aromatic stretching medium), 2917.78 cm^{-1}(C-H stretching strong intensity), 2593.69 cm^{-1}(O-H acid stretching strong, very broad), 2277 cm^{-1}(--N=C=O isocyanate stretch), 1731.8 cm^{-1}(C=O stretch strong), 1577.92 cm^{-1}(-NO_2 aliphatic nitro group), 1609.01 cm^{-1}(N-H amides bend), 1524.96 cm^{-1}(N-H bend 1^0), 1435.74 cm^{-1}(C=C aromatic stretch medium-weak, multiple bands), 1376.49 cm^{-1}(-C-H alkane bending variable), 1296.32 cm^{-1} (C-O anhydrides stretch), 1206.02 cm^{-1}(C-C stretch), 1018.57 cm^{-1}(C-O stretch), 945.85 cm^{-1} (C-H bend), 802.06 cm^{-1} (C-H bend trisubstituted), 756.03 cm^{-1}(C-H bend mono aromatic), 694.21 cm^{-1}(C-H bend disubstituted-z), 658.89 cm^{-1}(C-Cl stretch), 621.9 cm^{-1}(C-Br stretch), 564 503.39- cm^{-1}(C-I stretch) frequency in the FTIR for 4, 4-Diphenylmethane Diisocyanate.

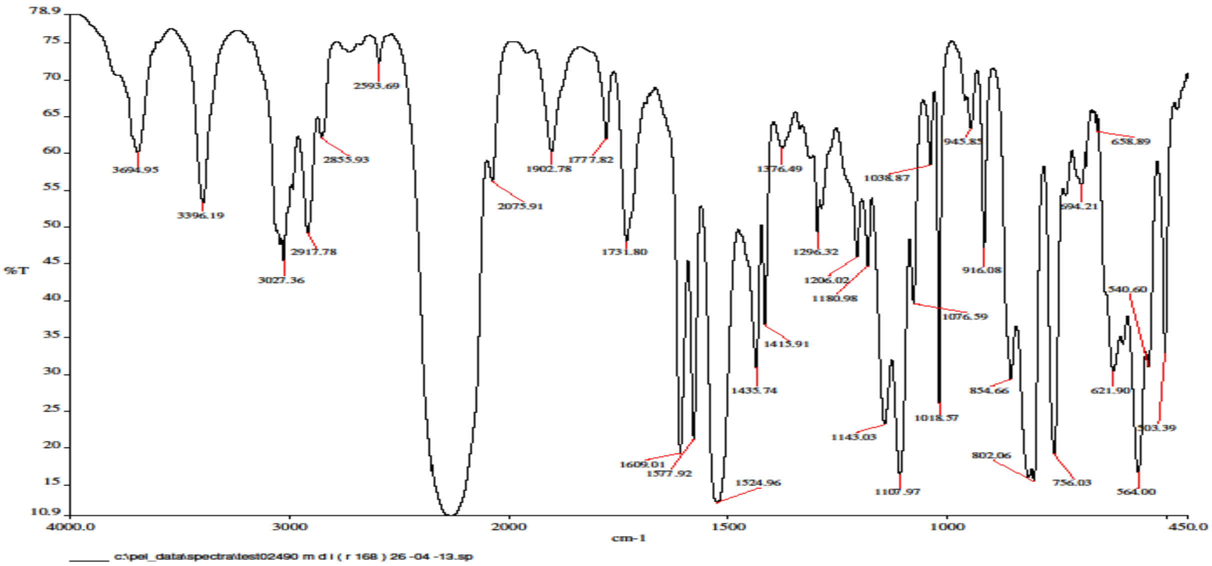


Figure 3.1: FTIR for 4, 4-Diphenylmethane Diisocyanate (MDI).

3.2 Modification of Castor Oil/Formation of Polyol

3.2.1 Experimental Setup and Procedure

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

Figure 3.2: Arrangement for Modification of Castor Oil

3.2.2 Procedure:

The reaction kettle was charged with castor oil.Add Glycerol to the mixture drop wise over a period of 10 minutes. Castor oil and glycerol are taken in ratio of 3:1 (%w/w). The reacting contents were heated to a temperature of 220 ± 10^0C. The stirring speed is kept constant at 1000 rpm. The progress of condensation reaction and its stability were confirmed by checking its properties. For this purpose, the samples at regular intervals were taken out and checked for hydroxyl value, acid value, viscosity and water content. The heating was carried out till a hydroxyl value of 350-410 mg KOH/g is achieved. The time required to complete this reaction was nearly 4 hrs. The resulted polyol was stored in dark bottles away from direct sun light.The properties of Modified Castor Oil or Modified Polyol as determined by various experimental procedures are reported in Table 3.4. Characterization of Modified Polyol for the determination of these properties is as given in Appendix-1.

Table 3.5: Properties of Modified Polyols

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

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

3.2.3 FTIR Analysis of Modified Polyol

FTIR spectra of the modified polyols were recorded in A Nicolet 380 FTIR spectrophotometer. Small quantities of the liquid samples were spread in pure dried KBr for analysis. FTIR spectra of polyols are well known to be sensitive to hard domain organization.The characteristic absorptions peaks of the modified polyols are observed. Peaks ore obtained at frequency 3400.43 cm^{-1}(N-H stretching frequency), 3008.5 cm^{-1}(C-H stretching frequency), 2855.2 cm-^{1}(C-H stretching strong frequency), 2270.94 cm-1 (--N=C=O stretch), 1745.07 cm^{-1}(C=O stretching strong ester group), 1524.18 cm^{-1}(N-H amide bending), 1464.58 cm^{-1}(C=C aromatic stretch), 1377.73 cm^{-1}(-C-H alkane bending variables), 1165.77 cm^{-1}(C-N amine medium- weak stretch), 858.15 cm^{-1}(=C-H alkene bending strong intensity), 566.27 cm^{-1}(C-Br alkyl halide stretching strong intensity) respective to the bonds present.

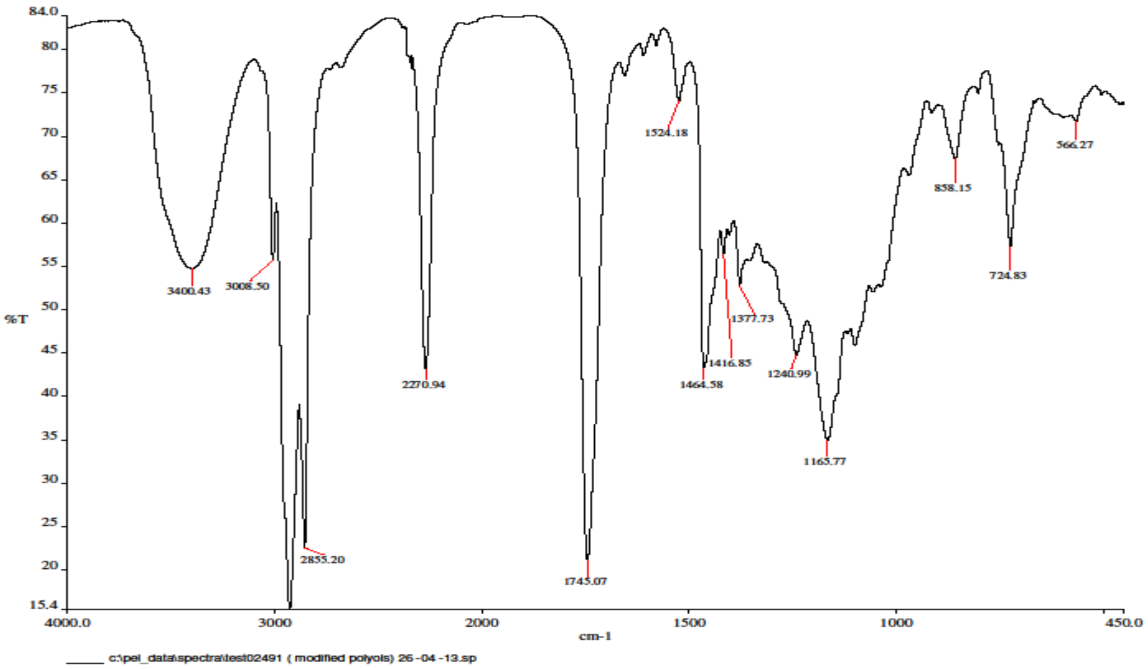


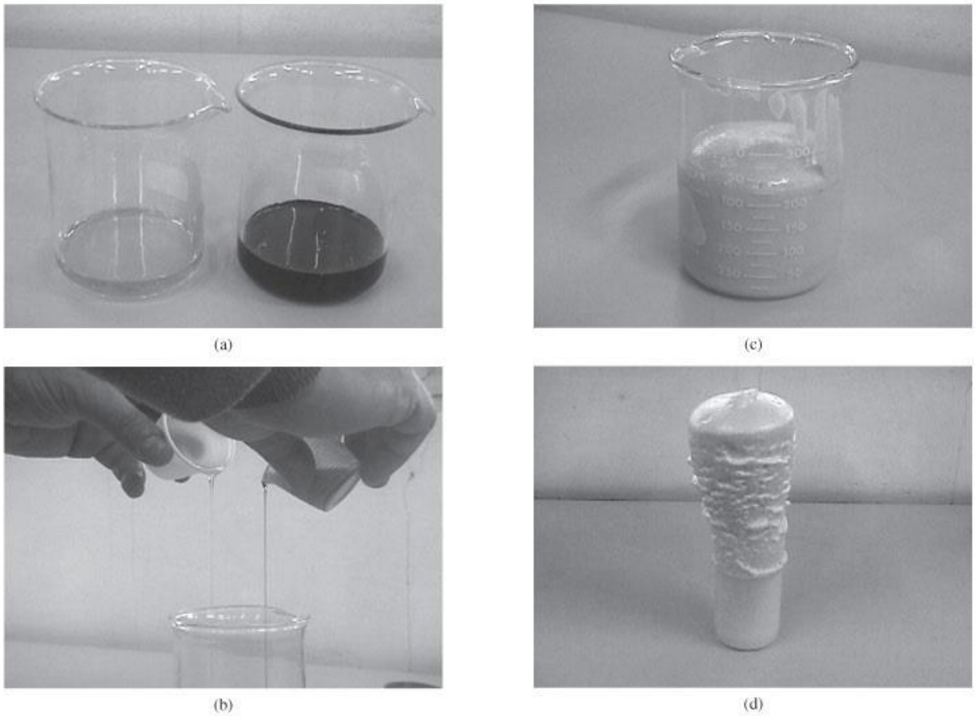
Figure 3.3: FTIR for Modified Polyol

The filler was mixed with modified polyol at 1600 rpm for 10 min by using a mechanical stirrer. Then, the catalyst, surfactant, and blowing agent in required amounts were added to the mixture and mixed for 1 min. afterward, the isocyanate was added to thismixture. The whole components weremixed again with the mechanical stirrer until foamingoccurred and then the mixture was immediatelypoured into an open mold. All foams were cured at ambient temperature (23◦C) for 24–48 h

3.3 Preparation of Castor Oil Based Rigid Polyurethane Foams with Various Fillers

The rigid polyurethane foams were obtained by a two step method. In the first step, the castor oil was modified to obtain polyol of desired hydroxyl value (already carried out). The subsequent step is the formation of castor oil based rigid polyurethane form incorporated with various fillers. The procedure is as follows:

Calculated amount of modified polyol is mixed with other ingredients as such as Catalyst: Tetraethlenediamine , Surfactant: Silicon Oil, Blowing Agent: Pentanein a beaker and thoroughly mixed under controlled temperature conditions at 35±2^{0}C to form Polyol-premix. The predetermined quantity of the filler is added to the contents of the beaker. The fillers were dehydrated in a vacuum oven at 60^0 C for 4 h before addition. The heating and mixing is continued for next 5-10 minutes. A calculated amount of MDI is then added to the contents of the beaker. The contents of the beaker are then stirred by means of a high speed mechanical stirrer operating at 1000 rpm. Heating the contents can also result into the fastening of the reaction. After the heating and stirring of approximately two minutes, the viscosity of the reaction mixture increases and a cream like formation takes place with a color change from orange-yellow to pale yellow. The reaction mixture was poured into a metal mould, coated with releasing agent i.e. silicon oil. The mould was thus closed and kept under a load of about 10 kN. To ensure complete curing, the moulds were left to stand for 24 hours. After demoulding , the resulted Filled Castor Oil based Rigid Polyurethane foamwas cut into desired dimensions and tested for its visual colour, tensile strength, compression strength, flexural strength, morphology structure and biodegradability. Different concentrations of the fillers viz: Glass Fiber, Calcium Carbonate, Mica, Talc and Fly-Ash were used to carry out **Studies on the Effect of Various Fillers on the Properties of Rigid Polyurethane Foams.**To insure that a complete reaction takes place, the raw material formulation had NCO Index equal to 105. Different formulations of raw materials used in these studies are given in Tables 3.5 to 3.9. The procedure for the calculation of NCO Index is as given in Appendix-2.



(a) (c)

(b) (d)

Figure 3.4 a)-Modified Polyol and MDI, b) Mixing of Two Components

c) Beginning of Foam Process and d) Rigid Foam

Table 3.5: Composition of Rigid Foam Incorporated with $CaCO_3$ as Filler

Modified Polyol	20 gm
Tetraethylenediamine (catalyst)	2 pbw
n-Pentane (blowing agent)	10-15 pbw
Silicone oil	3 pbw
$CaCO_3$	5 pbw, 10 pbw, 15pbw
MDI	25 gm

Pbw = parts by weight of polyol

Table 3.6: Composition of Rigid Foam Incorporated with Mica as Filler

Modified Polyoll	20 gm
Tetraethylenediamine (catalyst)	2 pbw
n-Pentane (blowing agent)	10-15 pbw
Silicone oil	3 pbw
Mica	5 pbw, 10 pbw, 15pbw
MDI	25 gm

Pbw = parts by weight of polyol

Table 3.7 : Composition of Rigid Foam Incorporated with Talc (Hydrated Magnesium Silicate) as Filler

Modified Polyol	20 gm
Tetraethylenediamine (catalyst)	2 pbw
n-Pentane (blowing agent)	10-15 pbw
Silicone oil	3 pbw
Mica	5 pbw, 10 pbw, 15pbw
MDI	25 gm

Pbw = parts by weight of polyol

Table 3.8: Composition of Rigid Foam Incorporated with Fly-ash Filler

Modified castor oil	20 gm
Tetraethylenediamine (catalyst)	2 pbw
n-pentane (blowing agent)	10-15 pbw
Silicone oil	3 pbw
Fly-ash	5 pbw, 10 pbw, 15pbw
MDI	25 gm

Pbw = parts by weight of polyol

Table 3.9: Composition of Rigid Foam Incorporated with Glass Fiber as Filler

Modified Polyol	20 gm
Tetraethylenediamine (catalyst)	2 pbw

n-Pentane (blowing agent)	10-15 pbw
Silicone oil	3 pbw
Glass fibre	5 pbw, 10 pbw, 15pbw
MDI	25 gm

Pbw = parts by weight of polyol

CHAPTER-4

CHARACTERIZATION

Analysis of resulted castor oil based PUF incorporated with various fillers

The Castor oil based rigid polyurethane foams incorporated with various fillers in different concentration were subjected to the morphological, mechanical and positron analyses to verify the alterations provoked by the progressive introduction of the fillers. The various characterization techniques used were:

4.1 FTIR Analysis

4.2 Mechanical Testing, including

4.2.1 Tensile Testing

4.2,2 Flexural Testing

4.3 SEM Analysis

4.1 FTIR Analysis

Fourier Transform Infrared spectra of rigid polyurethane foams unreinforced and reinforced had been recorded on a Nicolet 380 spectrometer (Figure 4.1), in the range 400–4,000 cm-1 using the KBr pallets technique. A molecule absorbs radiation only when the natural frequency of vibration of some part of molecule (i.e. atoms or group of atoms comprising it) is the same as the frequency of the incident radiation. After absorbing the correct wavelength of radiation, the molecule vibrates at increased amplitude. This occurs at the expense of the energy of the IR radiation, which has been absorbed. Infrared spectroscopy is one of the most powerful analytical technique , which offers the possibility over the other usual method of structural analysis (X-ray diffraction , electron spin resonance etc) and provides useful information about the structure of the molecules and bonding quickly, without tire-some evaluation method . Moreover, FT-IR provides a very faster of identifying chemical structures especially those of the organic ones. FT-IR spectroscopy employs an interferometer in place of monochromatic. This device generates the Fourier transform of the infra-red spectrum, which is converted to spectrum itself by a computer. This approach has the advantageous of providing much higher source radiation throughout, increased signals-to-noise (SN) ratio and higher wave number accuracy than is possible with a conventional light dispersive spectrometer [139].

Figure 4.1. FTIR (Nicolet 380) Spectrometer

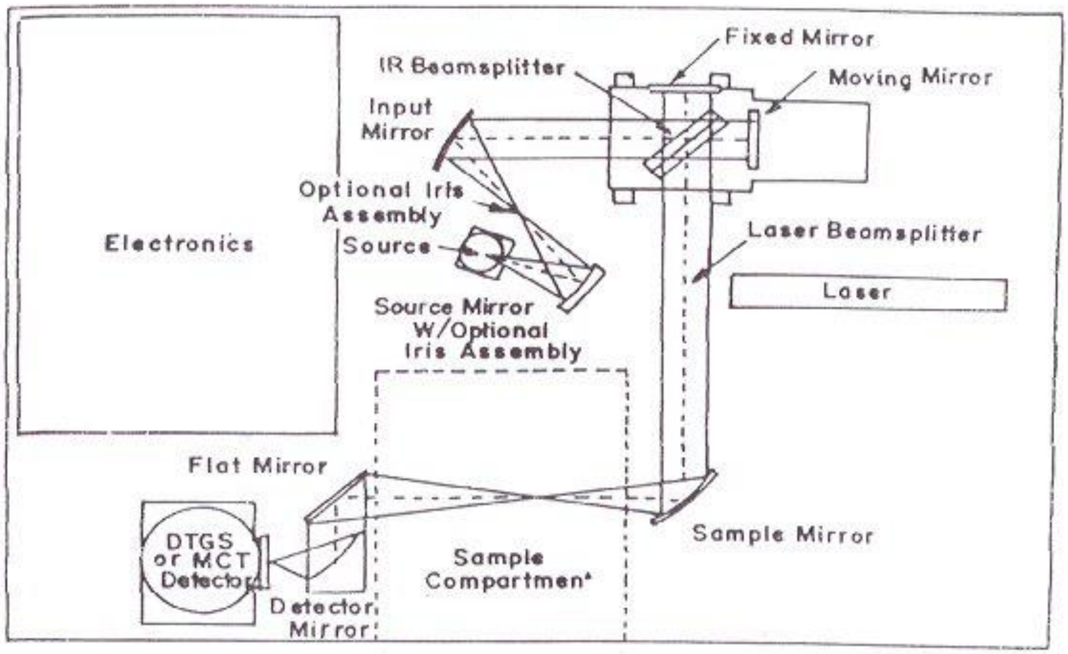


Figure 4.2: Schematic representation of FTIR Set-up

The technique is based upon the simple fact that a chemical substance shows marked selective absorption in infrared region giving rise to close-packed absorption bands, called an IR absorption spectrum, which may extend over a wide wavelength range. Various bands in all IR spectrum correspond to characteristic functional groups and bonds present in the chemical substance. IR spectrum of a chemical substance is thus a fingerprint for its identification. Band position in infrared may be expressed conveniently by wave number ν, whose unit is cm-1. The relation between velocity c, wavelength λ and frequency ν is as follows;

$$\nu = c/\lambda \text{ or } \nu/\text{cm-1} = l\lambda$$

Band intensities in IR spectrum may be expressed either as transmittance (T) or absorbance (A). Transmittance is defined as the ratio of the radiant power transmitted by a sample to the radiant power incident on the sample. In most spectra transmittance (T) versus wave number (cm-1) has been plotted.

4.2 Mechanical Properties

The mechanical properties of the castor oil based rigid polyurethane samples were determined according to the standard procedures. Samples were cut at ambient temperature to the required dimensions. Tensile and flexural properties of the resulted foams were measured at room temperature using Instron (model No. 3369) universal testing machine (Figure 4.13) as per ASTM D-638 and ASTM D-790 method respectively.

Figure 4.3 Instron (model No. 3369) Universal Testing Machine

4.2.1 TENSILE TEST:

Tensile testing, also known as tension testing, is a fundamental materials science test in which a sample is subjected to a controlled tension until failure. The results from the test are commonly used to select a material for an application, for quality control, and to predict how a material will react under other types of forces. Properties that are directly measured via a tensile test are ultimate tensile strength, maximum elongation and reduction in area. From these measurements the following properties can also be determined: Young's modulus, Poisson's ratio, yield strength, and strain-hardening characteristics. Uniaxial tensile testing is the most commonly used for obtaining the mechanical characteristics of isotropic materials. For anisotropic materials, such as composite materials and textiles, biaxial tensile testing is required [140].

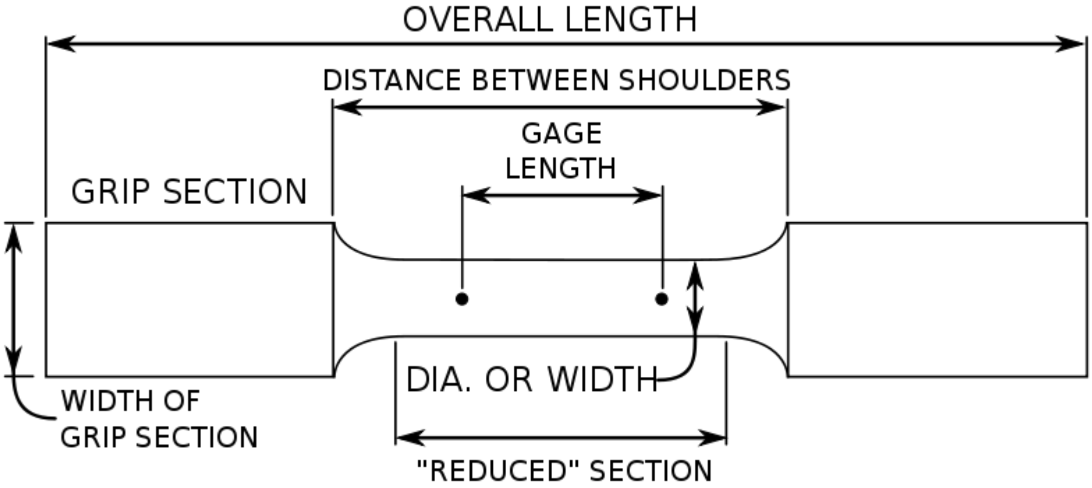


Figure 4.4: Sample Used for Tensile Test

Equipment used:

The most common testing machine used in tensile testing is the universal testing machine. This type of machine has two crossheads; one is adjusted for the length of the specimen and the other is driven to apply tension to the test specimen. There are two types: hydraulic powered and electromagnetically powered machines. The machine must have the proper capabilities for the test specimen being tested. There are three main parameters: force capacity, speed, and precision and accuracy. Force capacity refers to the fact that the machine must be able to generate enough force to fracture the specimen. The machine must be able to apply the force quickly or slowly enough to properly mimic the actual application. Finally, the machine must be able to accurately and precisely measure the gauge length and forces applied; for instance, a large machine that is designed to measure long elongations may not work with a brittle material that experiences short elongations prior to fracturing. Alignment of the test specimen in the testing machine is critical, because if the specimen is misaligned, either at an angle or offset to one side, the machine will exert a bending force results on the specimen. This is especially bad for brittle materials, because it will dramatically skew the results [141**].**

Figure 4.5 :Tensile UTM machine

Test procedure:

The test procedure involves placing the test specimen in the testing machine and applying tension to it until it fractures. During the application of tension, the elongation of the gauge section is recorded against the applied force. The data is manipulated so that it is not specific to the geometry of the test sample. The elongation measurement is used to calculate the engineering strain, ε, using the following equation:

$$\varepsilon = \frac{\Delta L}{L_0} = \frac{L - L_0}{L_0}$$

where ΔL is the change in gauge length, L_0 is the initial gauge length, and L is the final length. The force measurement is used to calculate the engineering stress, σ, using the following equation:

$$\sigma = \frac{F_n}{A}$$

Where, F is the force and A is the cross-section of the gauge section. The machine does these calculations as the force increases, so that the data points can be graphed into a stress-strain curve.

4.2.2 FLEXURAL TEST:

Flexural strength is the ability of the material to withstand bending forces applied perpendicular to its longitudinal axis. The stresses induced by the flexural load are a combination of compressive and tensile stress [51]. In general, 3-point bending flexural test is used to determine the flexural properties of the RPUFs. The three-point bending flexural test provides values for the modulus of elasticity in bending E_f, flexural stress σ_f, flexural strain ϵ_f and the flexural stress-strain response of the material. The main advantage of a three point flexural test is the ease of the specimen preparation and testing. However, this method has also some disadvantages: the results of the testing method are sensitive to specimen and loading geometry and strain rate.

Testing method:

Calculation of the flexural stress σ_f

$$\sigma_f = \frac{3PL}{2bd^2}$$ for a rectangular cross section

$$\sigma_f = \frac{PL}{\pi R^3}$$ for a circular cross section

Calculation of the flexural strain ϵ_f

$$\epsilon_f = \frac{6Dd}{L^2}$$

Calculation of flexural modulus E_f

$$E_f = \frac{L^3 m}{4bd^3}$$

In the above formulas the following parameters are used:

- σ_f = Stress in outer fibers at midpoint, (MPa)
- ϵ_f = Strain in the outer surface, (mm/mm)
- E_f = flexural Modulus of elasticity,(MPa)
- P = load at a given point on the load deflection curve, (N)
- L = Support span, (mm)
- b = Width of test beam, (mm)
- d = Depth of tested beam, (mm)
- D = maximum deflection of the centre of the beam, (mm)
- m = The gradient (i.e., slope) of the initial straight-line portion of the load deflection curve,(P/D), (N/mm)
- R = The radius of the beam, (mm)

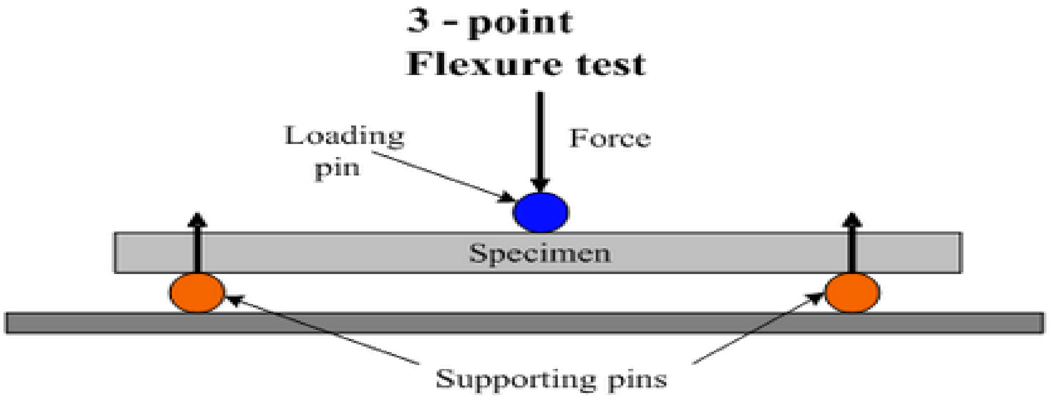


Figure 4.6: Schematic representation of 3-point Flexure Test

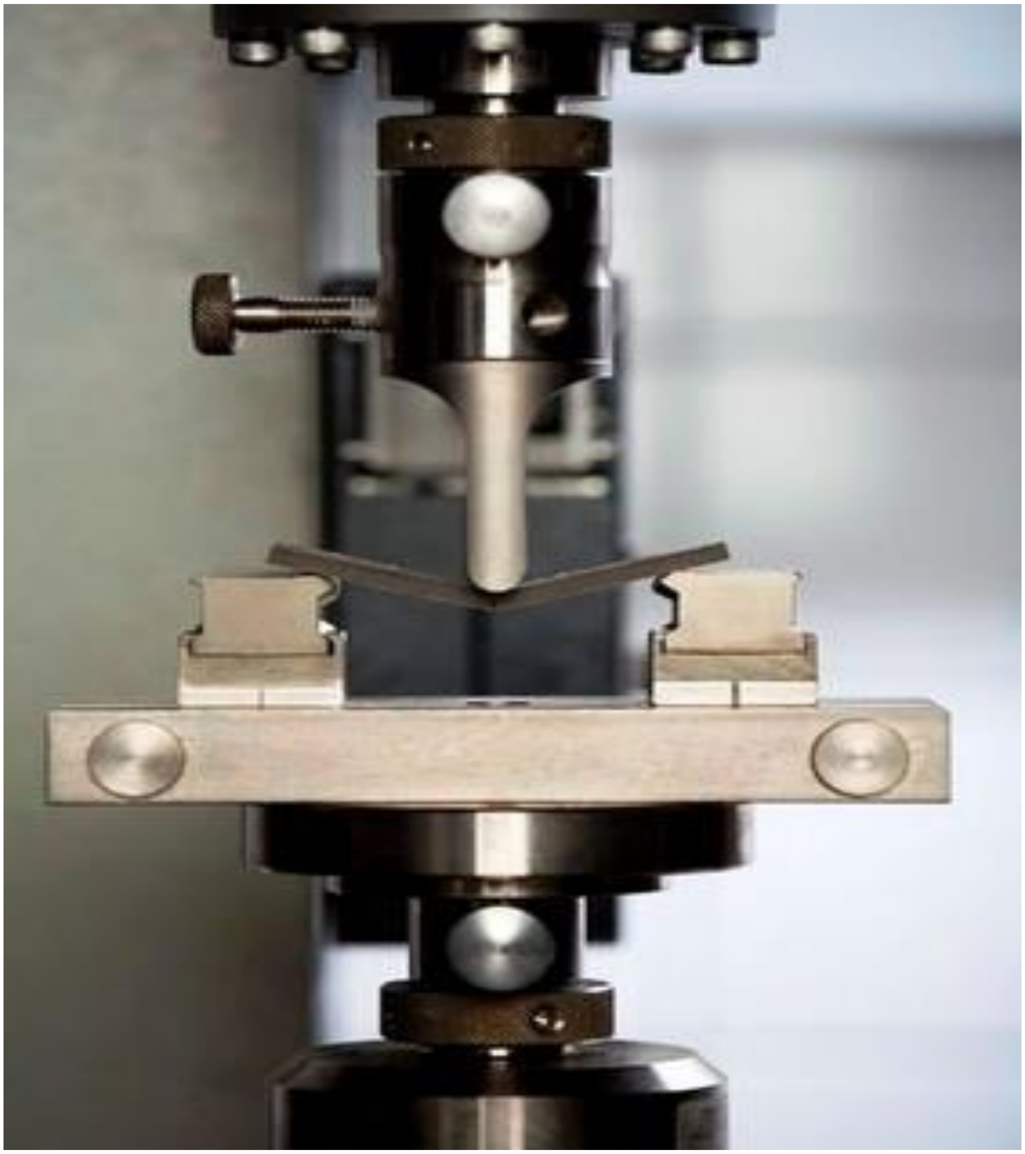


Figure 4.7: Flexural UTM machine

4.3 SEM ANALYSIS:

In general, the physical properties of foams do not only depend on the rigidity of the polymer matrix, but are also related to the foam cell structure. Thus, it is of interest to observe the structure of the foam specimen using SEM. The cell structures of the samples were characterized with a Hitachi S 3700 SEM (Scanning Electron Microscope) using an acceleration of 15 kV as shown in Figure 4.8.

Figure 4.8: Scanning Electron Microscopic (Hitachi S-3700N)

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with electrons in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image. SEM can achieve resolution better than 1 nanometre. Specimens can be observed in high vacuum, low vacuum and in environmental SEM specimens can be observed in wet conditions [142].

In the SEM, specimens must be electrically conductive, at least at the surface, and electrically grounded to prevent the accumulation of electrostatic charge at the surface. Metal objects require little special preparation for SEM except for cleaning and mounting on a specimen stub. Nonconductive specimens tend to charge when scanned by the electron beam, and especially in secondary electron imaging mode, this causes scanning faults and other image artifacts . They are therefore usually coated with an ultrathin coating of electrically conducting material, deposited on the sample either by low-vacuum sputter coating or by high-vacuum evaporation. Conductive materials in current use for specimen coating include gold,gold/palladium alloy, platinum, osmium,iridium, tungsten,chromium, and graphite.

Test process:

In a typical SEM, an electron beam is thermionically emitted from an electron gun fitted with a tungsten filament cathode. Tungsten is normally used in thermionic electron guns because it has the highest melting point and lowest vapour pressure of all metals, thereby allowing it to be heated for electron emission, and because of its low cost.

The electron beam, which typically has an energy ranging from 0.2keV to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the x and y axes so that it scans in a raster fashion over a rectangular area of the sample surface.When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 µm into the surface. The size of the interaction volume depends on the electron's landing energy, the atomic number of the specimen and the specimen's density. The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current. Electronic amplifiers of various types are used to amplify the signals, which are displayed as variations in brightness on a computer monitor (or, for vintage models, on a cathode ray tube). Each pixel of computer video memory is synchronized with the position of the beam on the specimen in the microscope, and the resulting image is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen. In older microscopes image may be captured by photography from a high-resolution cathode ray tube, but in modern machines image is saved to a computer data storage [142, 143].

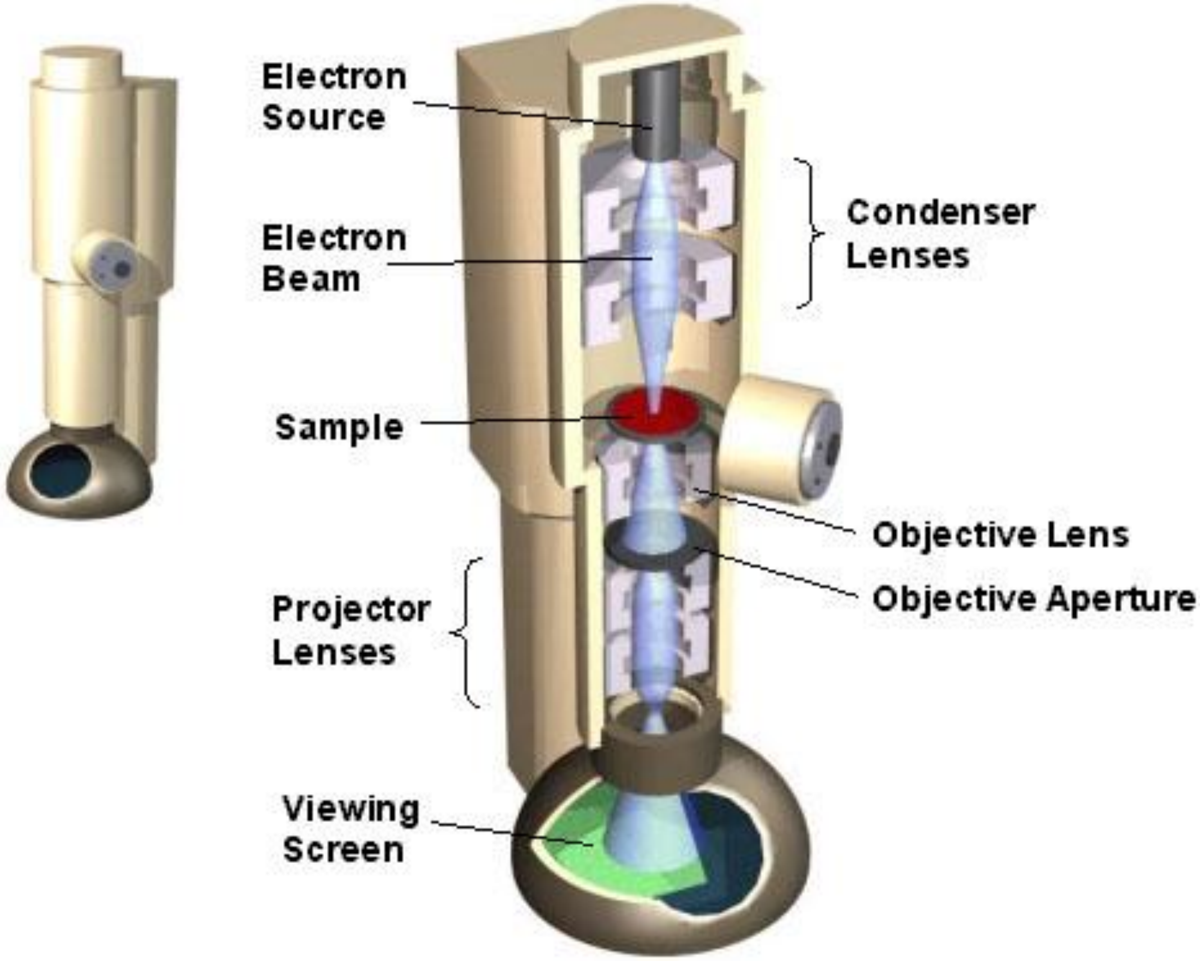


Figure 4.9 Different Parts of Scanning Electron Microscope

CHAPTER-5

RESULTS

AND

DISCUSSIONS

Studies had been carried out on the effect of various fillers on the properties of castor oil based rigid polyurethane foams. Fillers are added to polyurethane foam in order to reduce cost and provide some desired structural and mechanical properties. Filler used in these studies are glass fiber, mica, calcium carbonate, fly-ash and talc in concentration 5%, 10% and 15% by weight of the modified polyol. The surface state and the filler type are important parameters governing the mechanical properties. The foam architecture depends on the filler dispersion, and the particle size. The mechanical properties of the foam being also governed by the mechanical properties of the constitutive material, the reinforcement level of the foam depends on the interaction between the filler and the polymer matrix. When a filler is added to a polymer, a conjugated biphasic material get formed and the tension applied to the polymeric matrix will be transferred in part to the disperse filler phase, thus imparting properties superior to the pure polymer.The filler reported in these studies significantly contributed towards the improvement (in few case retardance) in the properties of the RPUs. For the comparison purpose, properties of neat polyurethane are measured and reported first. Then subsequently, the effect of addition of fillers on RPUF has been reported one by one.

5.1 Properties of Castor Oil Based Polyurethane (neat: without the addition of fillers)

5.1.1 FTIR Analysis

To understand the possible reactions that may occur among the reactants i.e. modified polyols and MDI with different formulations of blowing agents, Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 380 spectrometer in the range 400–4,000 cm-1. KBr pellets was used to verify the completion of the resin curing reaction and the presence of free isocyanate groups (NCO) in cured Rigid Polyurethane Foam. FTIR spectra of PUs (and modified polyol-based polyurethanes) are well known to be sensitive to hard domain organization and the urea and urethane hydrogen bonding. The characteristic absorptions peaks of the Castor Oil based rigid PU foams are as shown in Figure 5.1.

Almost every absorption peak is obtained in the unreinforced rigid polyurethane foam produced by the reaction of castor oil with the MDI. The peak at 3310 cm^{-1}is associated with an overlap between hydroxyl groups (O-H) and amino groups (N-H), 2928.8 cm^{-1} due to Alkyl C-H stretch, 1708 cm^{-1} due to ester C=O stretch which is very close to urethane linkage that is observed at 1795, 1596-1510 cm^{-1} is of aromatic C ═ C bending, 811.46-764.53 cm^{-1} is due to aromatic C-H bending.

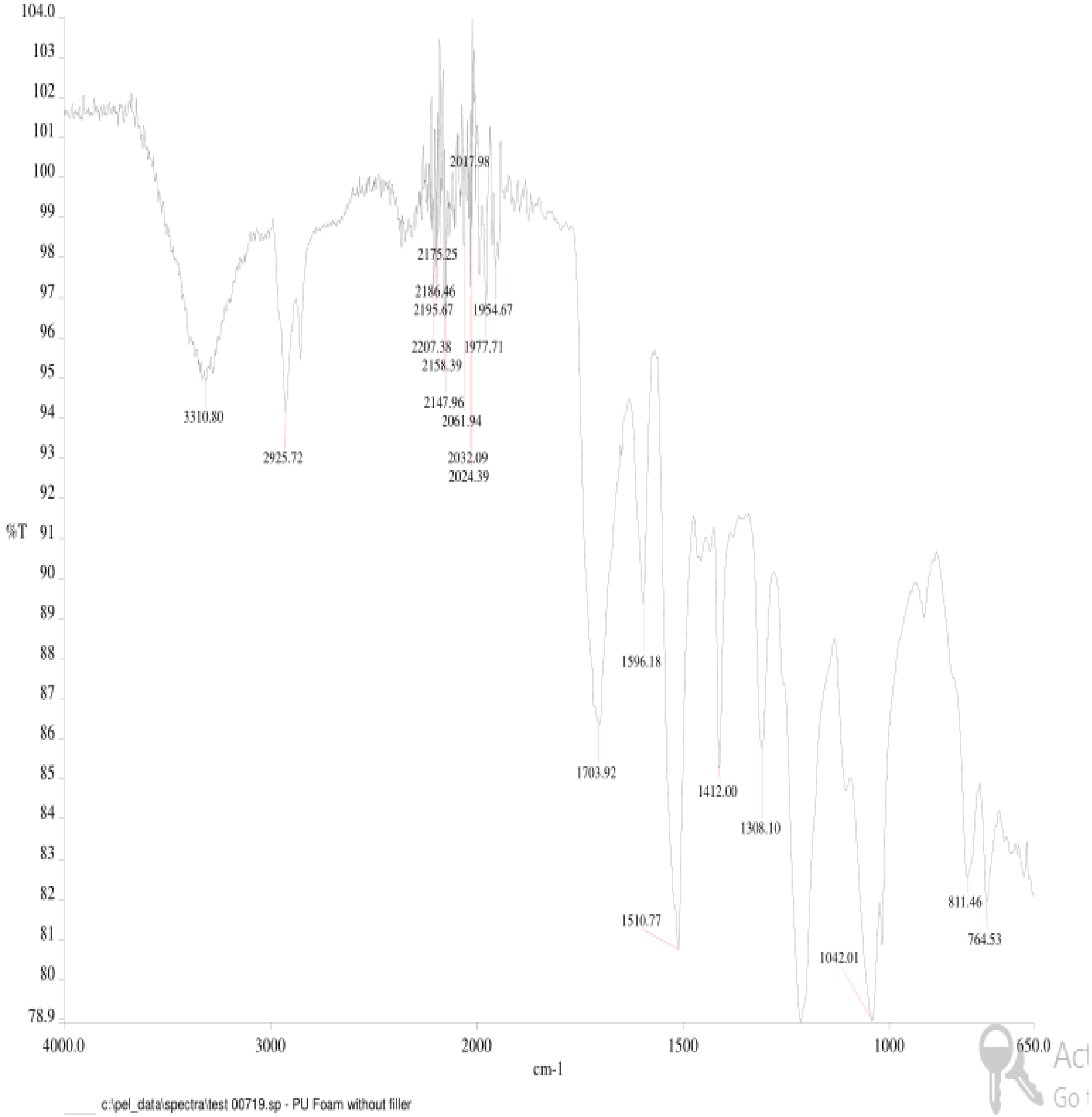


Figure 5.1: FTIR of of Caster oil based Rigid Polyurethanes Foam.

5.1.2 Tensile Strength

The tensile strengths of the resulted castor oil based polyurethane foam was found good and comparable to that of commercially derive petrochemical dased RPU. The relationship between tensile stress and tensile strain for the castor oil based rigid polyurethane rigid foams is as shown in Figure 6.2.The initial portion of the stress-strain curve is linear and it follows Hooke’s Law according to which for an elastic material the stress is proportional to the strain. The elongation of the rigid foam continued after that break or rupture of the foam is observed at 209.45081 Mpa.

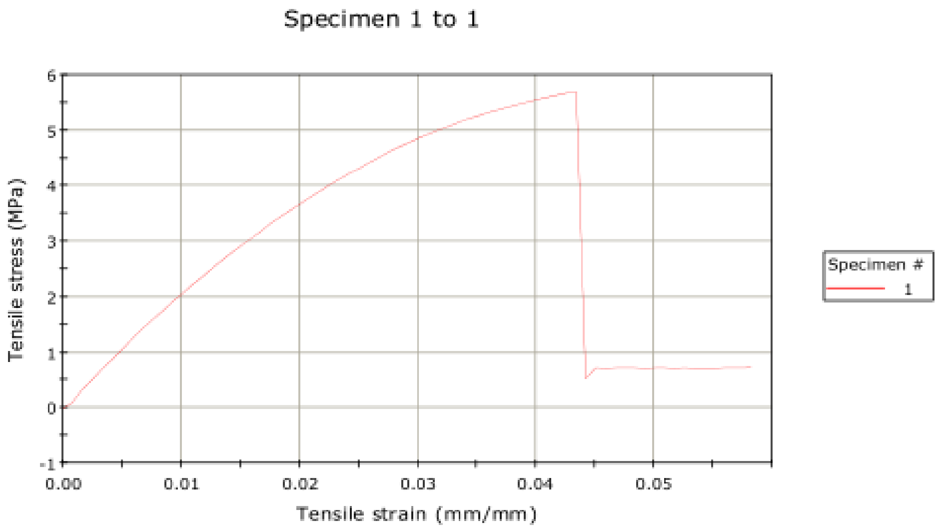


Figure: 5.2 Relationship between Tensile stress and Tensile strain for Castor oil Based Rigid Polyurethane

5.1.3Flexural Strength

Flexural strength is the ability of the material to withstand bending forces applied perpendicular to its longitudinal axis. The stresses induced by the flexural load are a combination of compressive and tensile stress. The relationship between flexure load (kN) and flexure extension (mm) for the castor oil based rigid polyurethane rigid foams is as shown in Figure 6.3. From the curve, it is clear that the resulted rigid foam is being subjected to flexural bending and it can withstand the flexural extension upto 2.12506 mm after that it breaks. Initial linear portion of thre curves is due to linear elastic deformation of the cell structures. As the cell begins to rupture due to stretching, the slope of the load-deflection curve changes and the foam almost uncontrollably deforms and finally fail at maximum loadFlexural strength and flexural extension is excellent in the modified castor oil based RPU.

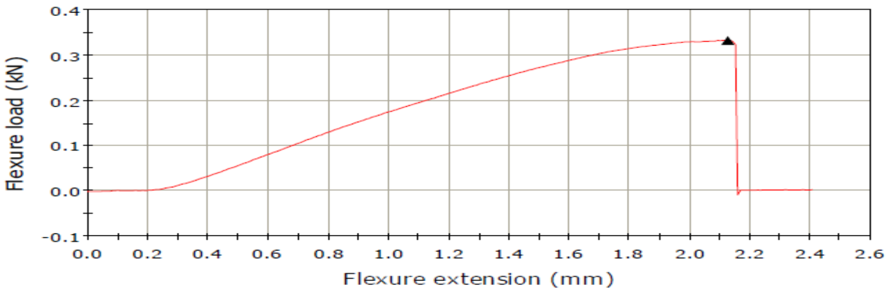


Figure 5.3: Relationship between Flexural Load and Flexural extension for Castor oil Based Rigid Polyurethane

5.1.4 SEM Analysis

In general, the physical properties of foams do not only depend on the rigidity of the polymer matrix, but are also related to the foam cell structure. Thus, it is of interest to observe the structure of the foam specimen using SEM. The cell structures of the samples were characterized with a Hitachi S 3700 SEM (Scanning Electron Microscope) using an acceleration of 15 kVat 40 X zoom. The un-reinforced foams present a smaller cell density with a higher pore size. The size of pores was mostly in range of 847 µm and a few are in the range of 1.03-1.06 mm, whereas after reinforcement with the glass fibre the cell density increases and pore size was reducing appreciably. The SEM Analysis graphs of of Caster oil based Rigid Polyurethanes is as shown in Figure 6.4.

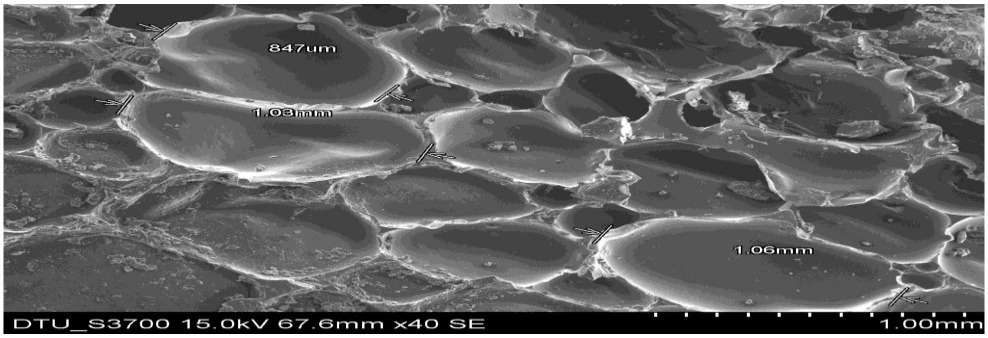


Figure 5.4 SEM of Caster oil based Rigid Polyurethanes Foam

5.2 Effect of Addition of Glass fibre on Castor Oil Based RPU

5.2.1 FT-IR analysis

Infrared spectroscopic (IR) on nanophased PUR foams areperformed using a Thermo Nicolet Omnic 6.0, Fourier transforminfrared spectrometer (FT-IR) to determine the chemical bondingbetween the nanoparticles and polymer chains. The microdomain structures of both neat and nanophased PUR foams areanalyzed by FT-IR.

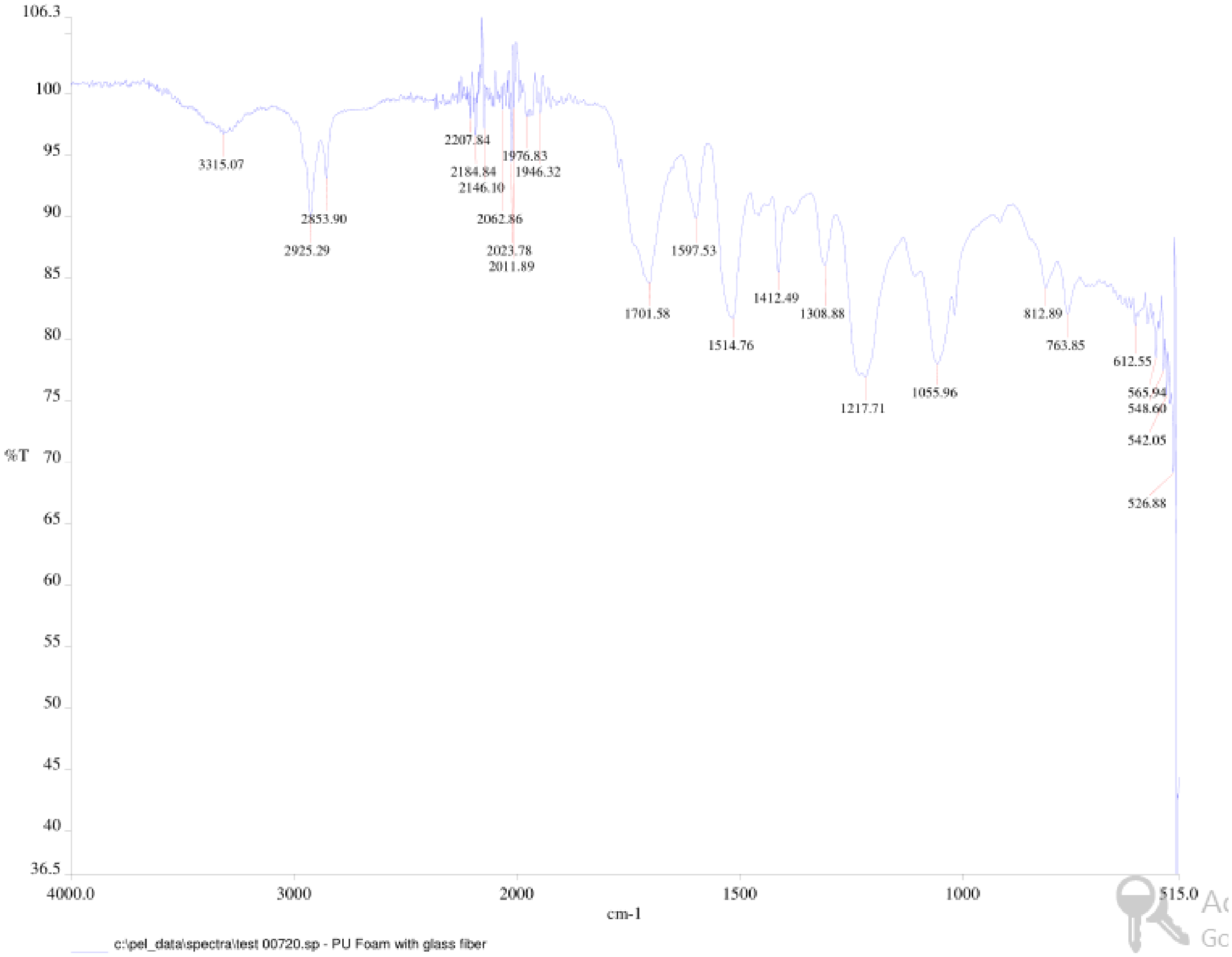


Figure 5.5: FTIR of of Caster oil based Rigid Polyurethanes Foam Incorporated with Glass Fillers

FTIR of the filled PU foam (filled with glass fiber) are used to determine the chemical bondingbetween the filler and polymer chains. The microdomain structures of both neat and nanophased PUR foams areanalyzed by FT-IR.The FT-IR graph analysis reveals a new absorption peak at 2853.9 cm^{-1}very close to peak at2928.8 cm^{-1} due to Alkyl C-H stretchthis absorption peak occurred due to reaction between the raw materials of foam i.e. castor oil and MDI with mica powder filler rest of peaks are obtained as same in unreinforced polyurethane sample like the prominent peak at 3387.8 cm^{-1} is associated with an overlap between hydroxyl groups (O-H) and amino groups (N-H), 2928.8 cm^{-1} due to Alkyl C-H stretch, 1708 cm^{-1} due to $C{=}O$ stretching.

5.2.2 Tensile Strength

Tensile strength and Tensile Modulus of the Castor oil based Rigid Polyurethane Foams incorporated with glass fibers is as given in Table 6.1. The tensile strengths of the resulted foam samples were found good and was first found to be increased with increase in the concentration of the filler i.e. glass fiber

Table No.5.1: Effect of Glass Fiber Concentrations on the Tensile Properties of RPUFs.

Filler concentration in grams	Effect on Modulus
0 gm	209.45081
1 gm	289.77756
2 gm	323.20069
3 gm	347.59394

Upon reinforcing rigid polyurethane foam with glass fibre there is increase in tensile modulus 289.7776 (1 gm), 323.2007 (2 gm), 347.5939 (3 gm) as compare to unreinforced polyurethane foam 209.45081 (figure 19). So the percentage increase in tensile modulus is 42%. The relationship between tensile stress and tensile strain for glass fiber filled castor oil based rigid polyurethane rigid foams is as shown in Figure 6.6 (a) to (c). From the graph, it is clear that tensile strength increases with increase of glass fiber in the concentration from 5% to 15%,

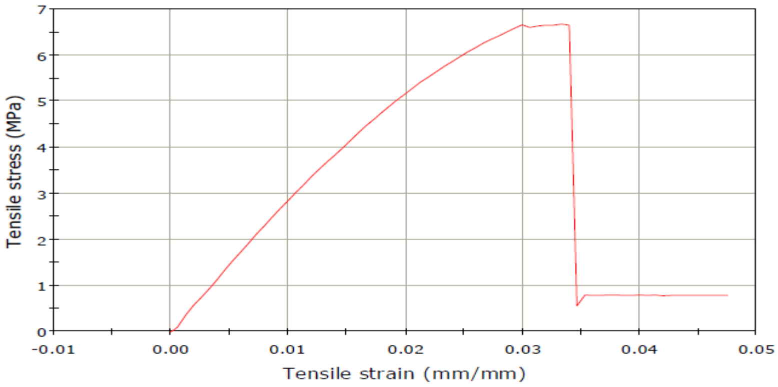


Figure 5.6 (a): Relationship between Tensile stress and Tensile strain for Castor oil Based Rigid Polyurethane Incorporated with 5% of Glass Fiber

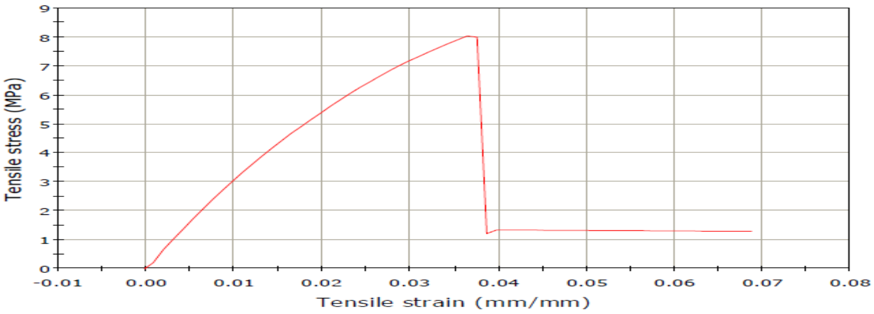


Figure 5.6 (b): Relationship between Tensile stress and Tensile strain for Castor oil Based Rigid Polyurethane Incorporated with 10% of Glass Fiber

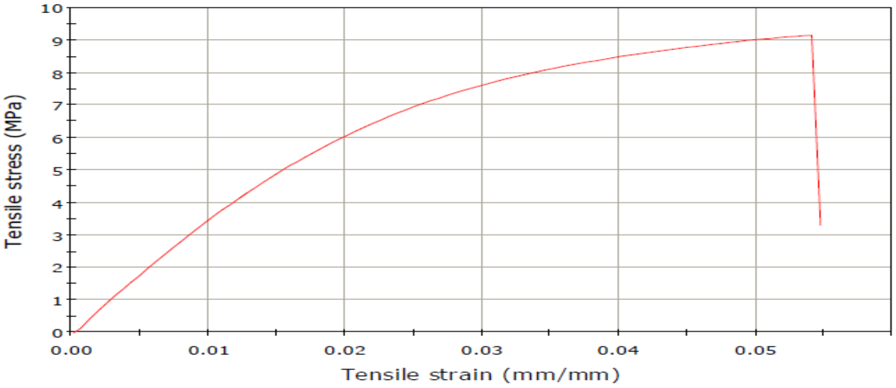


Figure 5.6 (c): Relationship between Tensile stress and Tensile strain for Castor oil Based Rigid Polyurethane Incorporated with 15% of Glass Fiber

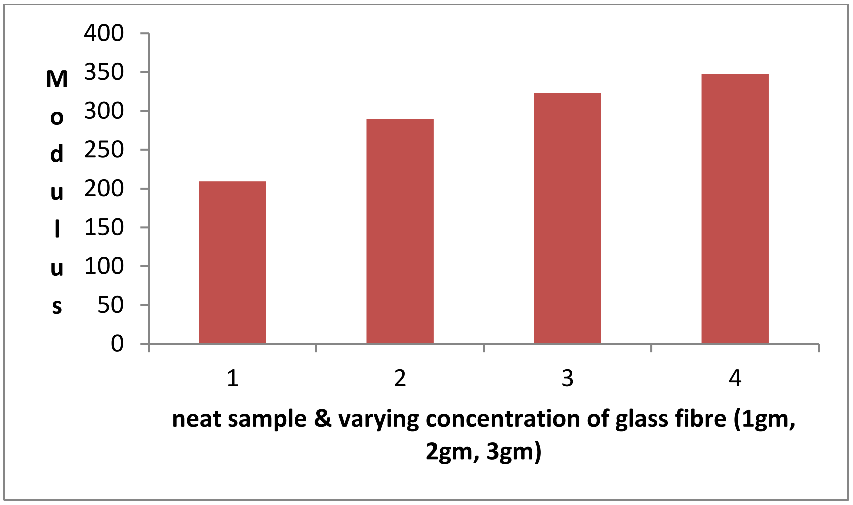


Figure 5.7:Various of Tensile Modulus with Percentage Loading of Glass Fiber

On Comparing the results obtained by at three levels of loading, It was seen from the Figure 6.7,with the increase on the quantity of the glass fiber in rigid polyurethane foam, tensile strength of the foam also increased.

5.2.3 Flexural Strength

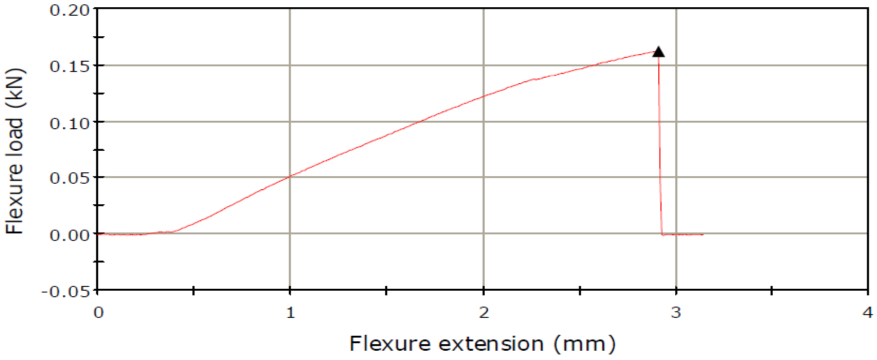


Figure 5.8 (a): Relationship between Flexure Load and Flexure Extension for Castor oil Based Rigid Polyurethane Incorporated with 5% of Glass Fiber

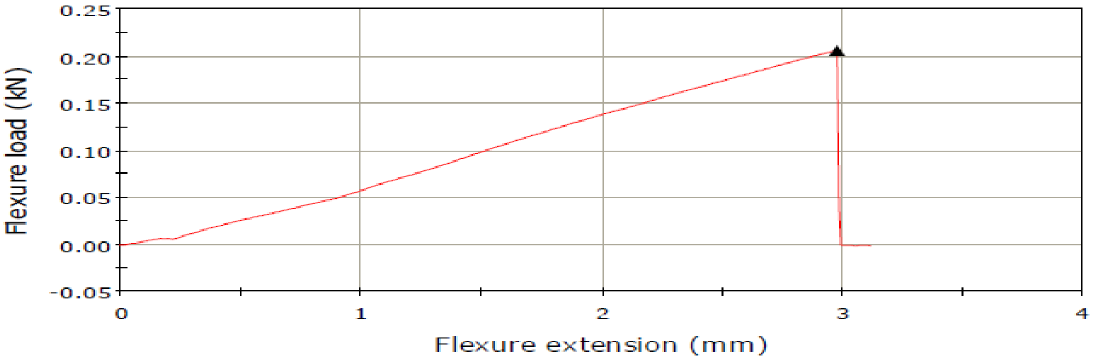


Figure 5.8 (b): Relationship between Flexure Load and Flexure Extension for Castor oil Based Rigid Polyurethane Incorporated with 10% of Glass Fiber

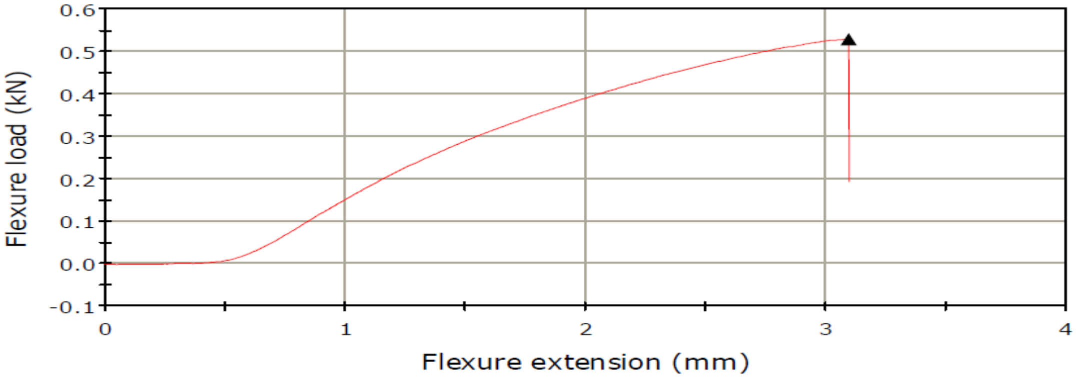


Figure 5.8 (c): Relationship between Flexure Load and Flexure Extension for Castor oil Based Rigid Polyurethane Incorporated with 15% of Glass Fiber

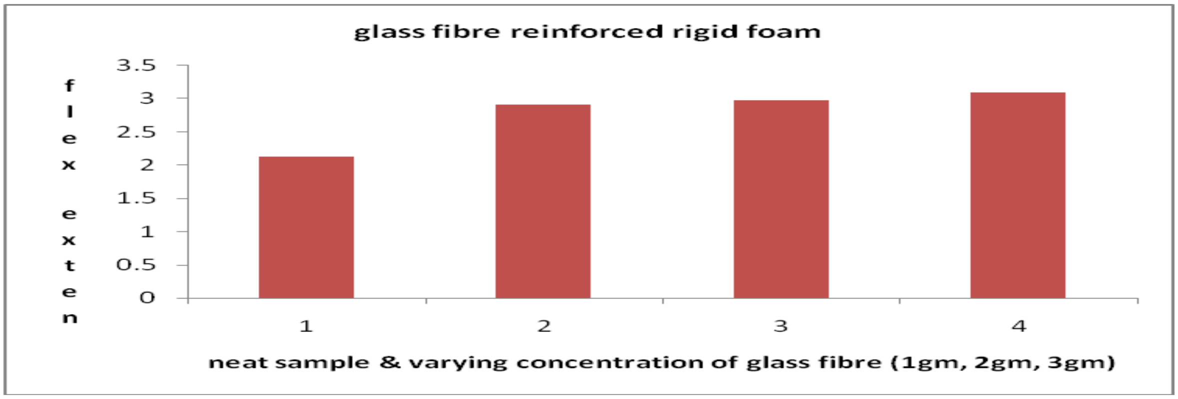


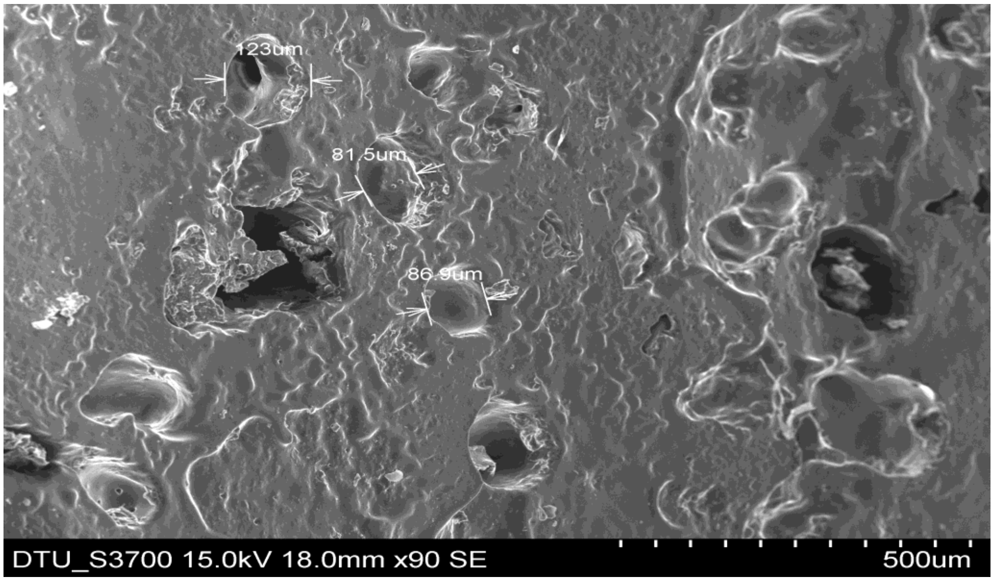
Figure 5.9:Various of Flexural Extension with Percentage Loading of Glass Fiber

Table No.5.2: Effect of Glass Fiber Concentrations on the Flexural Properties of RPUFs.

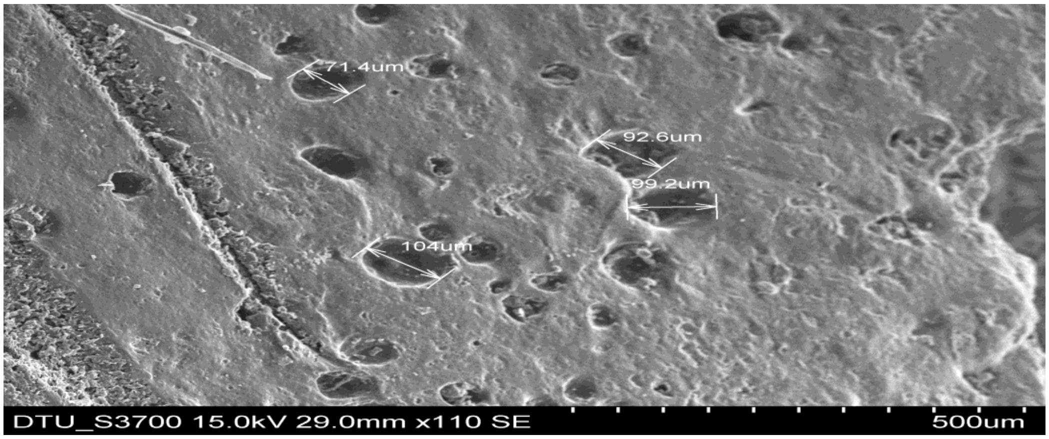
Filler concentration in grams	**Flexural Extension**
0 gm	**2.12506**
1 gm	**2.90831**
2 gm	**2.975**
3 gm	**3.09169**

Upon reinforcing rigid polyurethane foam with glass fibre there is increase in flexural extension 2.90831 (1 gm), 2.975 (2 gm), 3.09169 (3 gm) as compare to unreinforced polyurethane foam 2.12506 (figure 20). So the percentage increase in the flexural extension is 40-45%.

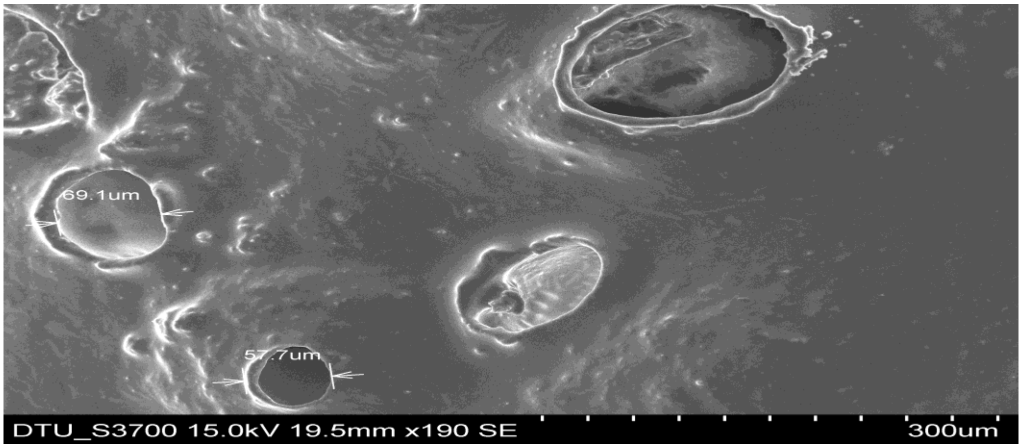
5.2.4 SEM Analysis



a) 1gm



b) 2gm



c) 3gm

Figure 5.10(a) SEM of Caster oil based Rigid Polyurethanes Foam for5% Glass Fiber Loading (a), For 10 % Glass Fiber Loading (b) and For 15% Glass Fiber Loading(c)

The average pore size of glass fibre reinforced rigid [polyurethane foam is 84.66 µm compare to 847 µm of neat sample (Figure 6.1), thus, there is nearly 90% reduction in pore size after the glass fibre reinforcement. The reduced pore size indicates that the 3-D structure of foam was more packed and consequently resulted in increased density and increased compressive strength. The cells are spherical in shape and having an open cell type structure.

5.3 Effect of Addition of Mica on Castor Oil based RPU

5.3.1 FT-IR Analysis

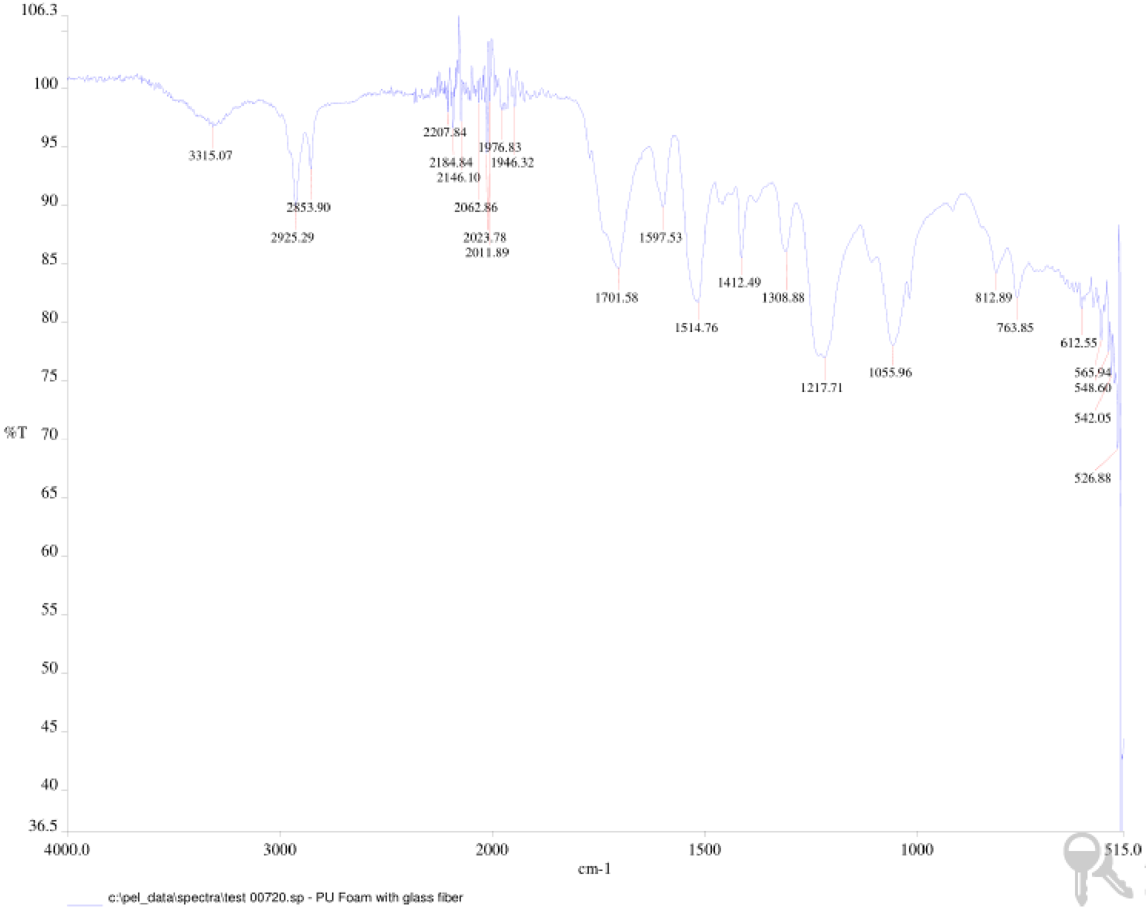


Figure 5.11: FTIR of of Caster oil based Rigid Polyurethanes Foam Incorporated with Mica Filler.

The FT-IR graph analysis reveals a new absorption peak at 2853.9 cm^{-1} very close to peak at 2928.8 cm^{-1} due to Alkyl C-H stretch this absorption peak occurred due to reaction between the raw materials of foam i.e. castor oil and MDI with mica powder filler rest of peaks are obtained as same in unreinforced polyurethane sample like the prominent peak at 3387.8 cm^{-1} is associated with an overlap between hydroxyl groups (O-H) and amino groups (N-H), 2928.8 cm^{-1} due to Alkyl C-H stretch, 1708 cm^{-1} due to C ═ O stretching.

5.3.2 Tensile Strength

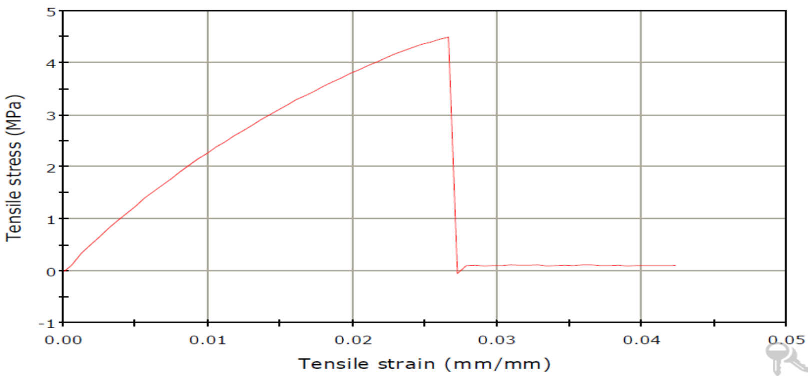


Figure 5.12 (a): Relationship between Tensile stress and Tensile strain for Castor oil Based Rigid Polyurethane Incorporated with 5% of Glass Fiber

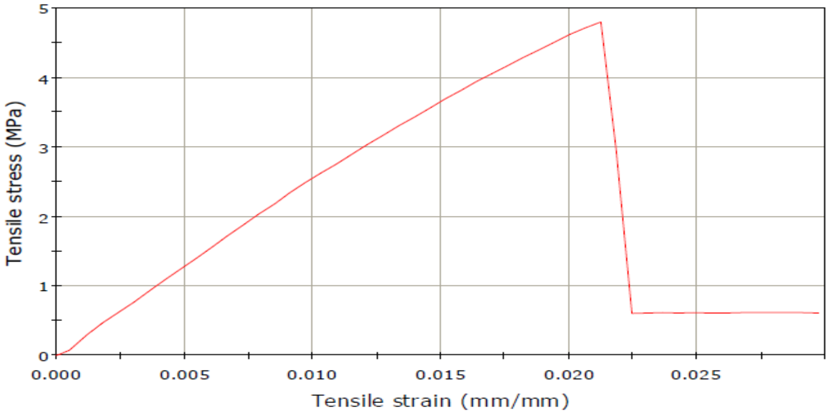


Figure 5.12 (b): Relationship between Tensile stress and Tensile strain for Castor oil Based Rigid Polyurethane Incorporated with 10% of Glass Fiber

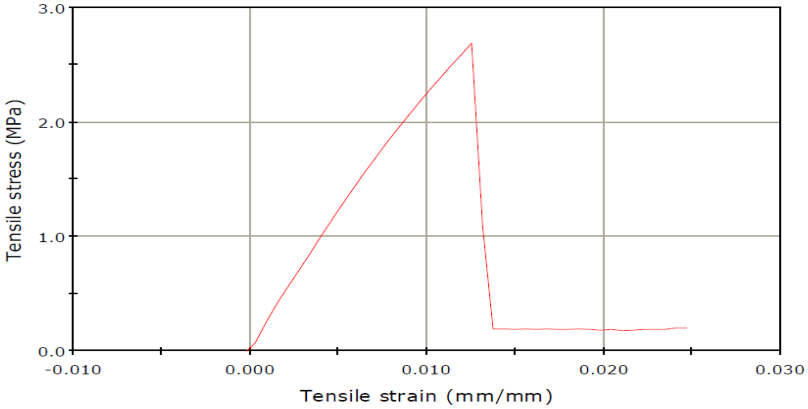


Figure 5.12 (c): Relationship between Tensile stress and Tensile strain for Castor oil Based Rigid Polyurethane Incorporated with 15% of Glass Fiber

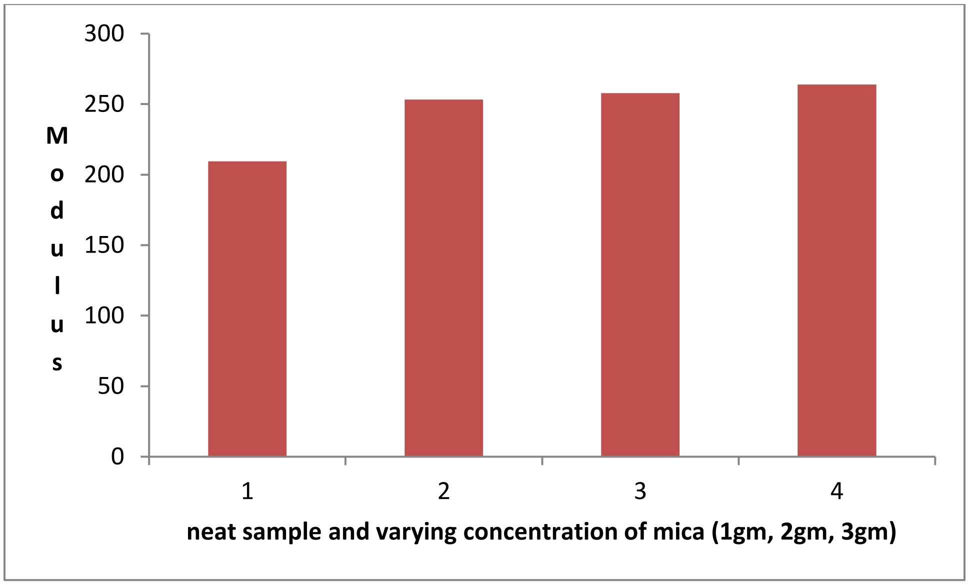


Figure 5.13: Various of Tensile Modulus with Percentage Loading of Mica

Table No.5.3: Effect of Glass Fiber Concentrations on the Tensile Properties of RPUFs.

Filler concentration in grams	**Modulus**
0 gm	**209.45081**
1 gm	**253.16725**
2 gm	**257.73223**
3 gm	**263.91595**

It is clearly evident that after reinforcing rigid polyurethane foam with the mica filler its tensile modulus increases linearly with the increase in the concentration of the mica filler as compare to unreinforced neat rigid polyurethane foam. In unreinforced neat sample tensile strength is 209.4508 (figure 6.2) but upon reinforcing with the mica it becomes 253.1673 (in 1 gm) 257.7322 (2 gm) 263.916(3 gm). So the percentage increase in tensile modulus is 11%.

5.3.3 Flexural Strength

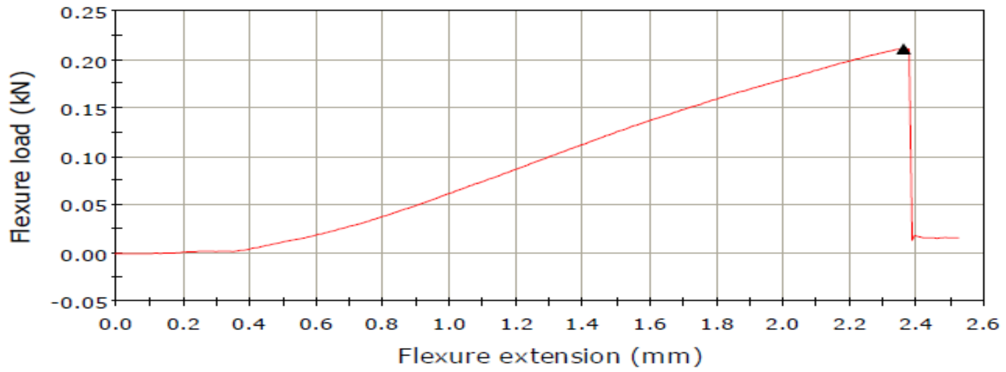


Figure 5.14 (a): Relationship between Flexure Load and Flexure Extension for Castor oil Based Rigid Polyurethane Incorporated with 5% of Mica

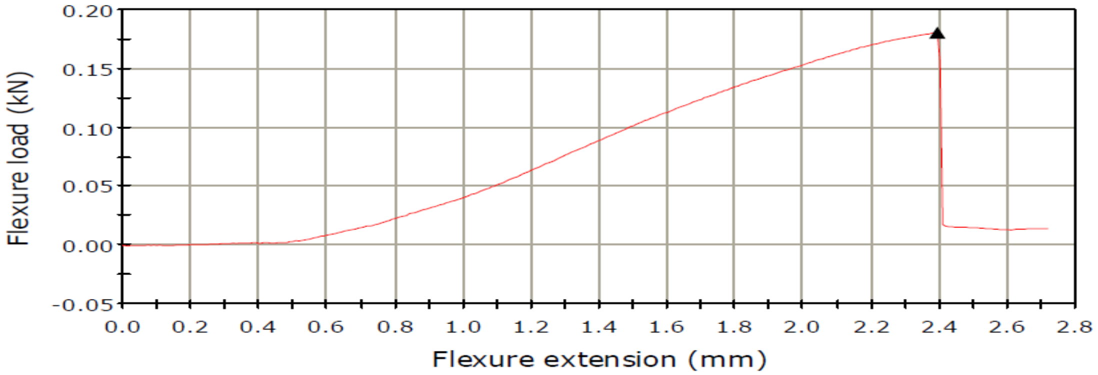


Figure 5.14 (b): Relationship between Flexure Load and Flexure Extension for Castor oil Based Rigid Polyurethane Incorporated with 10% of Mica

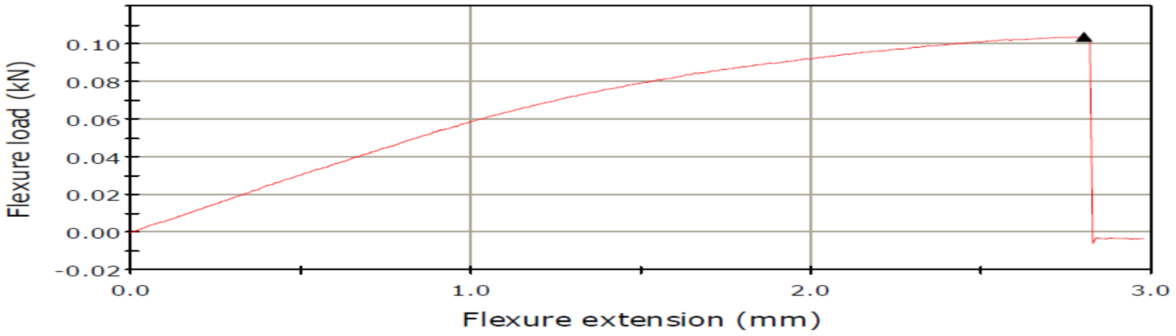


Figure 5.14 (c): Relationship between Flexure Load and Flexure Extension for Castor oil Based Rigid Polyurethane Incorporated with 15% of Mica

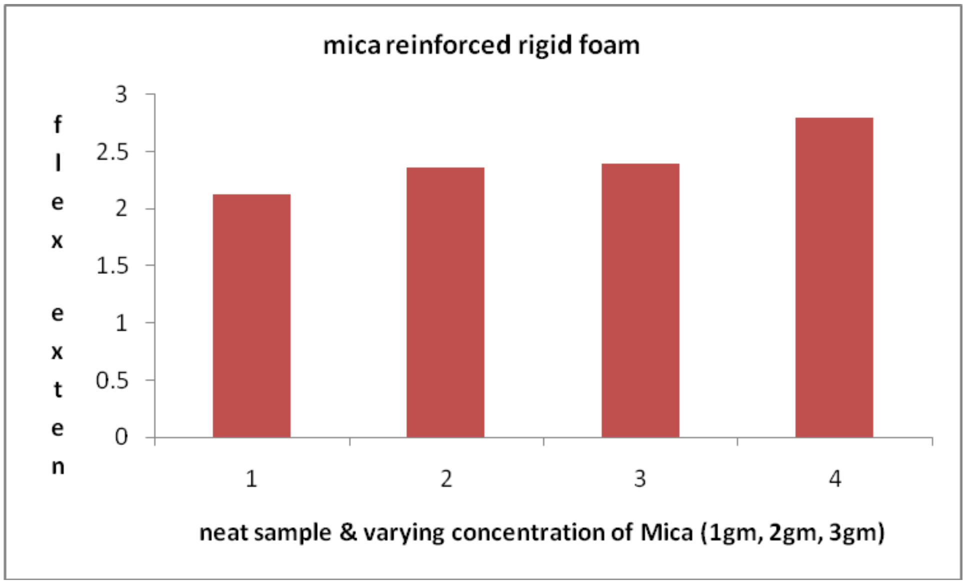


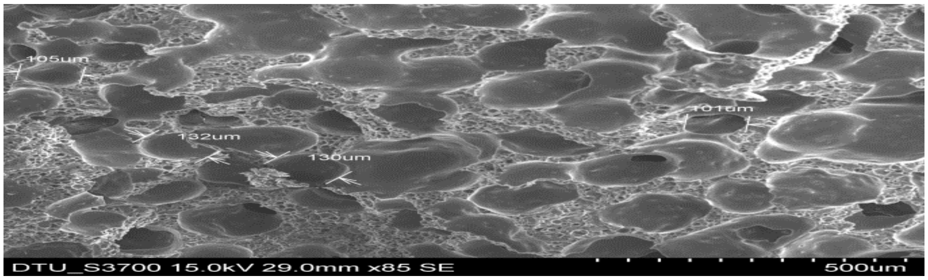
Figure 5.15 Various of Flexural Extension with Percentage Loading of Mica

Table No.5.4: Effect of Mica Concentrations on the Flexural Properties of RPUFs.

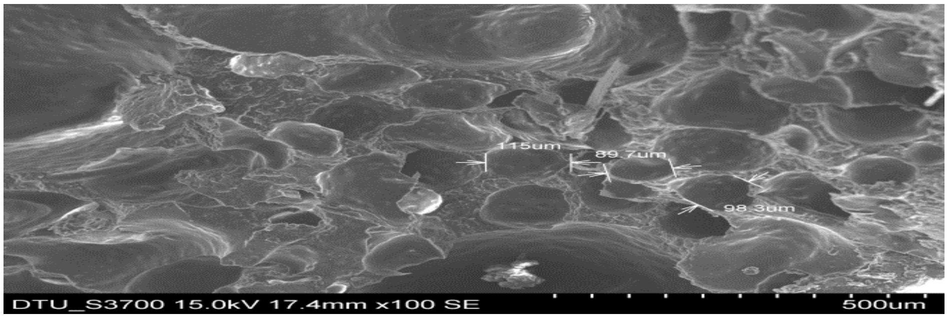
Filler concentration in grams	**Flexural Extension**
0 gm	**2.12506**
1 gm	**2.35831**
2 gm	**2.39156**
3 gm	**2.80013**

It is clearly evident that after reinforcing rigid polyurethane foam with the mica filler its flexural strength increases linearly with the increase in the concentration of the mica filler as compare to unreinforced neat rigid polyurethane foam. In unreinforced neat sample flexural strength is 2.12506 (figure 20) but upon reinforcing with the mica it becomes 2.35831 (in 1 gm) 2.39156 (2 gm) 2.80013 (3 gm). So the percentage increase in the flexural extension is11-13%.

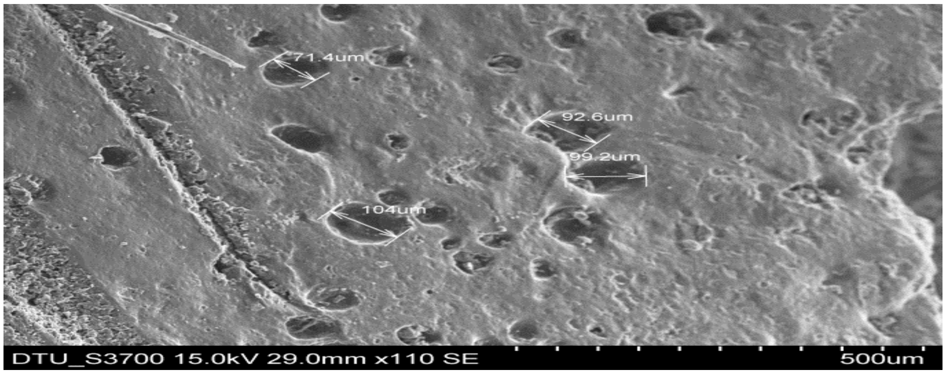
5.3.4 SEM Analysis



a) 1gm



b) 2gm



c) 3gm

Figure 5.16(a) SEM of Caster oil based Rigid Polyurethanes Foam for 5% Mica Loading (a), For 10 % Mica Loading (b) and For 15% Mica Loading (c)

The average pore size in case of mica filled rigid polyurethane is 99.96 µm compare to 847 (figure 5.2) µm of neat sample thus, there is nearly 82% reduction in pore size after the mica reinforcement. The reduced pore size indicates that the 3-D structure of foam was more packed and consequently resulted in increased density and increased compressive strength.

The pores are in spherical in shape and are open type in structure.

5.4 Effect of Addition of Calcium Carbonate on Castor Oil based RPU

5.4.1 FT-IR Analysis

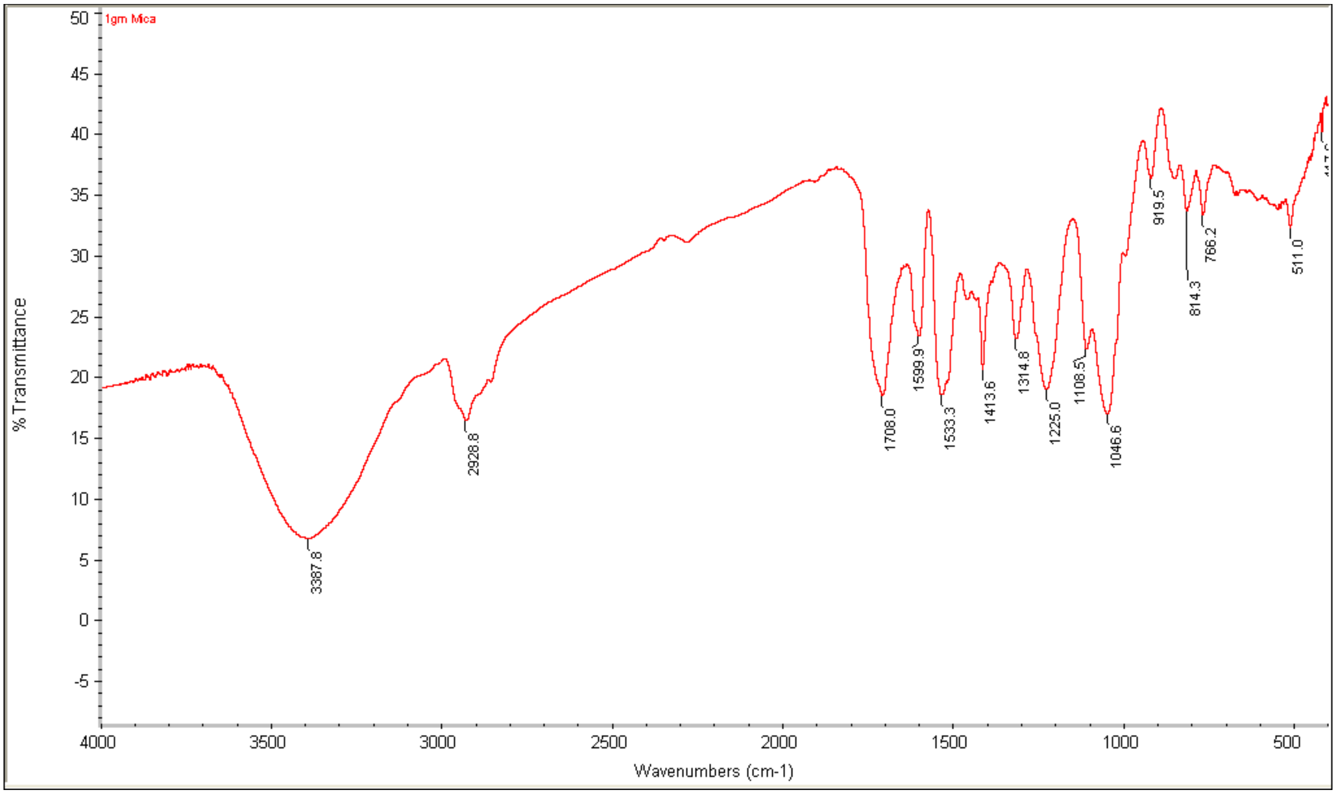


Figure 5.17: FTIR of of Caster oil based Rigid Polyurethanes Foam Incorporated with Calcium Chloride Filler

The FT-IR graph analysis reveals some new absorption peaks at 1225 cm^{-1} and 1108.5 cm^{-1} due to reaction between the raw materials of foam i.e. castor oil and MDI with mica powder filler Rest of peaks are obtained as same in unreinforced polyurethane sample like the prominent peak at 3387.8 cm^{-1} is associated with an overlap between hydroxyl groups (O-H) and amino groups (N-H), 2928.8 cm^{-1} due to Alkyl C-H stretch, 1708 cm^{-1} due to C$=$O stretching.

5.4.2 Tensile Strength

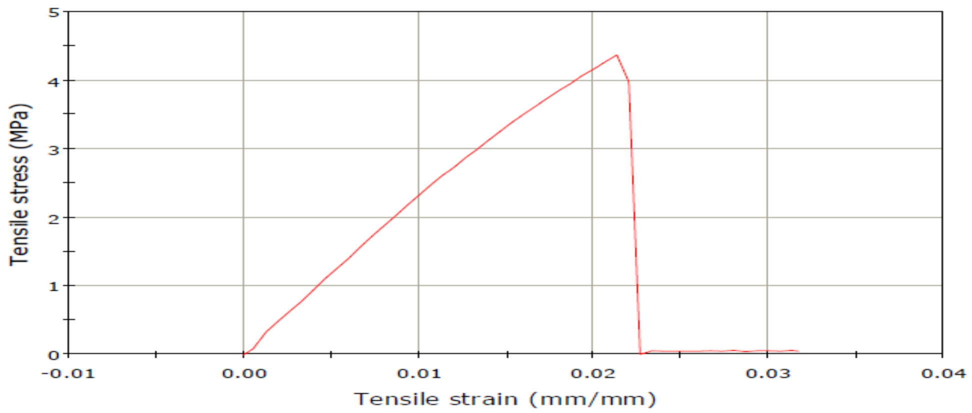


Figure 5.18 (b): Relationship between Tensile stress and Tensile strain for Castor oil Based Rigid Polyurethane Incorporated with 10% of $CaCO_3$

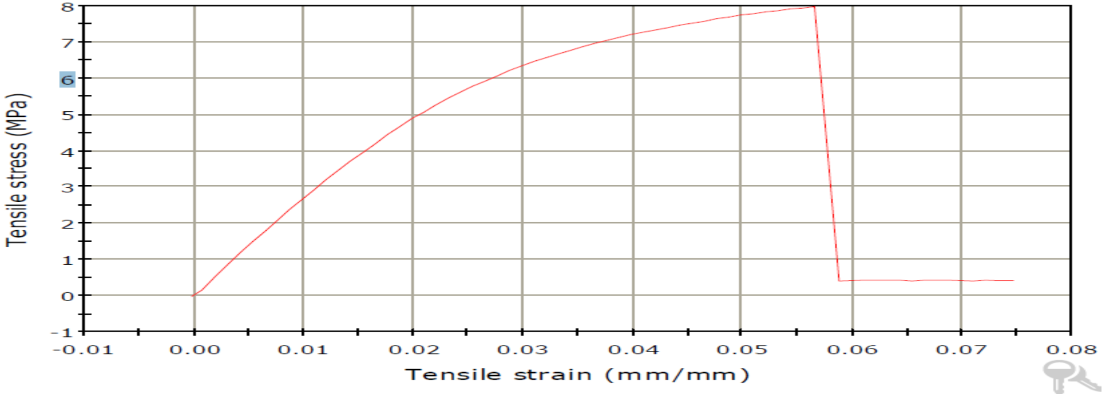


Figure 5.18 (c): Relationship between Tensile stress and Tensile strain for Castor oil Based Rigid Polyurethane Incorporated with 15% of $CaCO_3$

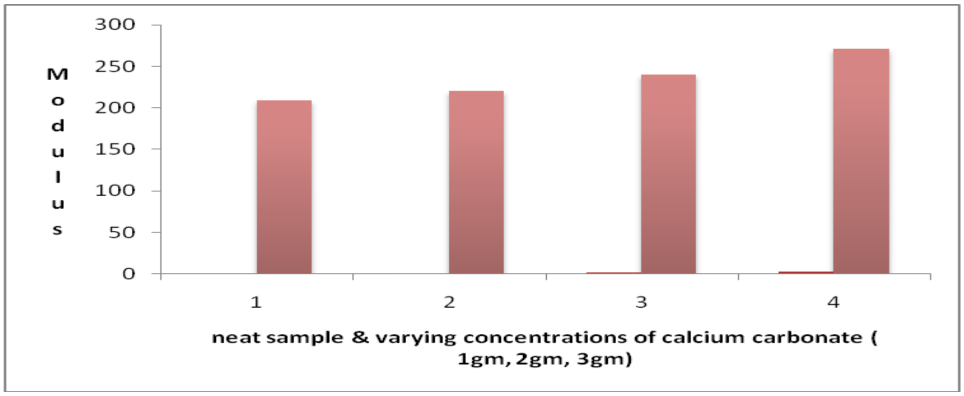


Figure 5.19: Various of Tensile Modulus with Percentage Loading of $CaCO_3$

Table No.5.5: Effect of $CaCO_3$ Concentrations on the Tensile Properties of RPUFs.

Filler concentration in grams	**Modulus**
0 gm	**209.45081**
1gm	**220.6969**
2 gm	**239.6357**
3 gm	**271.49413**

Reinforcing with the calcium carbonate filler in the rigid polyurethane foam results in the increase in the flexural modulus of the rigid polyurethane foam with the increase in amount of calcium carbonate filler 220.6969 (1 gm), 239.6357 (2 gm), 271.49413 (3 gm) compare to 209.45081 of neat sample (figure 19). So the percentage increase in tensile modulus is 40%.

5.4.3 Flexural Strength

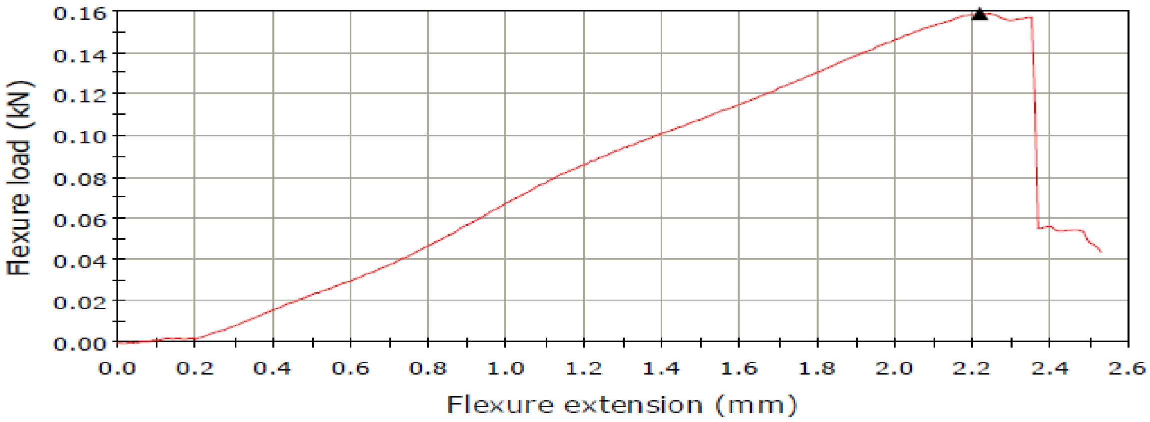


Figure 5.20 (a): Relationship between Flexure Load and Flexure Extension for Castor oil Based Rigid Polyurethane Incorporated with 5% of $CaCO_3$

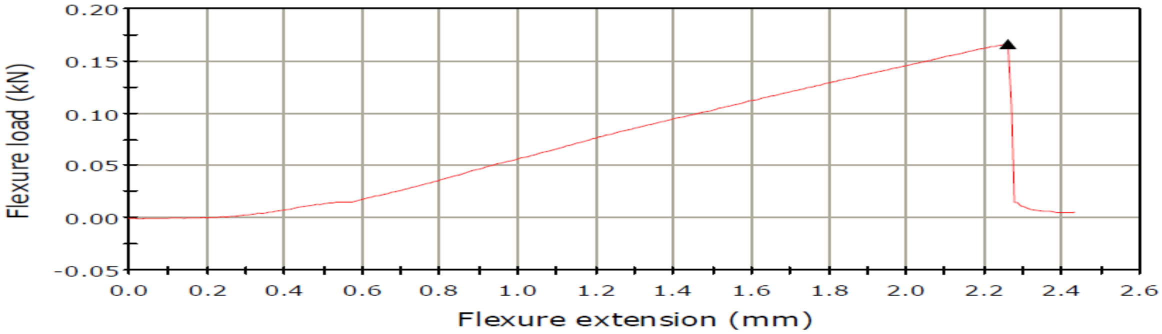


Figure 5.20 (b): Relationship between Flexure Load and Flexure Extension for Castor oil Based Rigid Polyurethane Incorporated with 10% of $CaCO_3$

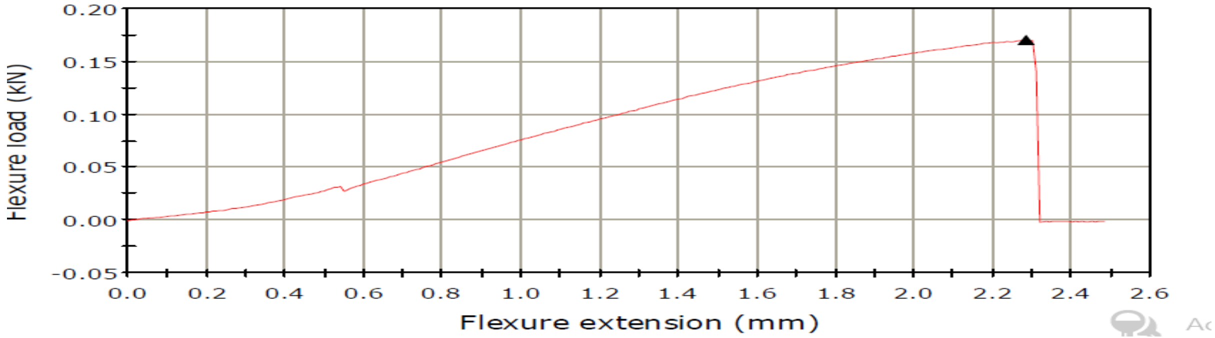


Figure 5.20 (c): Relationship between Flexure Load and Flexure Extension for Castor oil Based Rigid Polyurethane Incorporated with 15% of $CaCO_3$

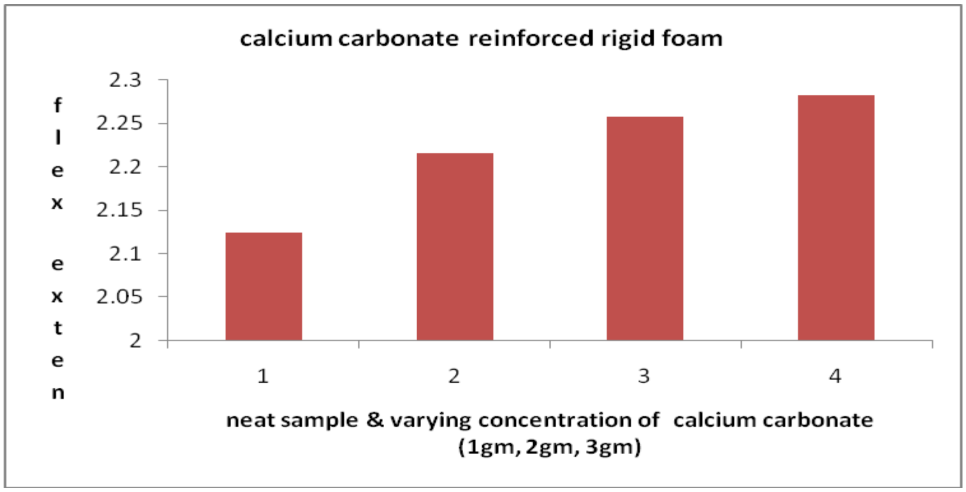


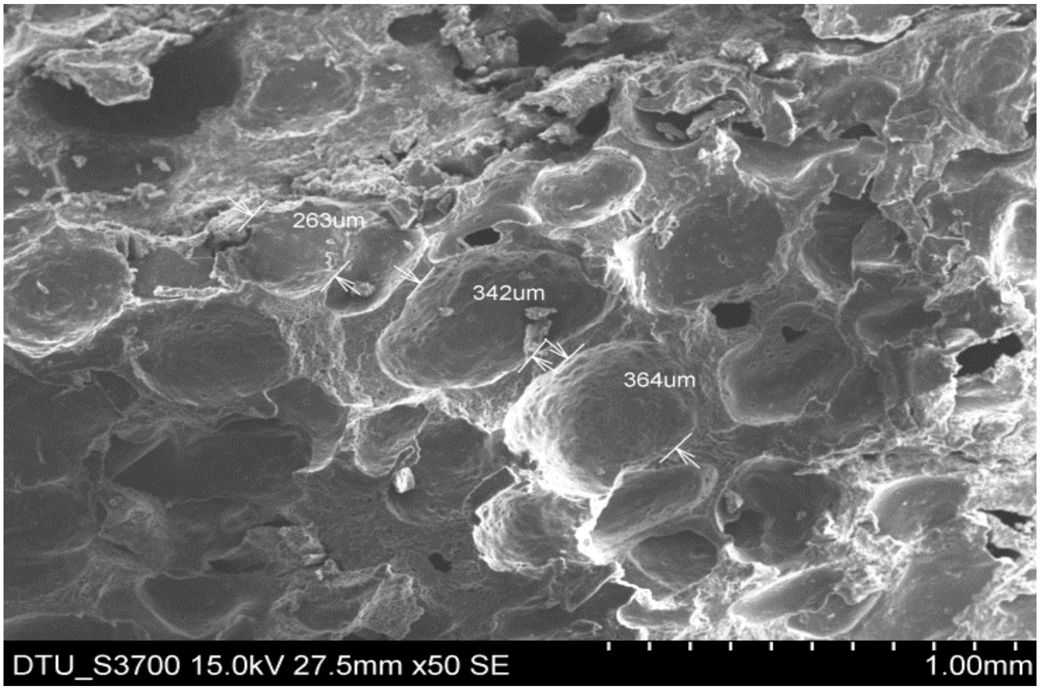
Figure 5.21: Various of Flexural Extension with Percentage Loading of $CaCO_3$

Table No. 5.6 Effect of $CaCO_3$ Concentrations on the Flexural Properties of RPUFs.

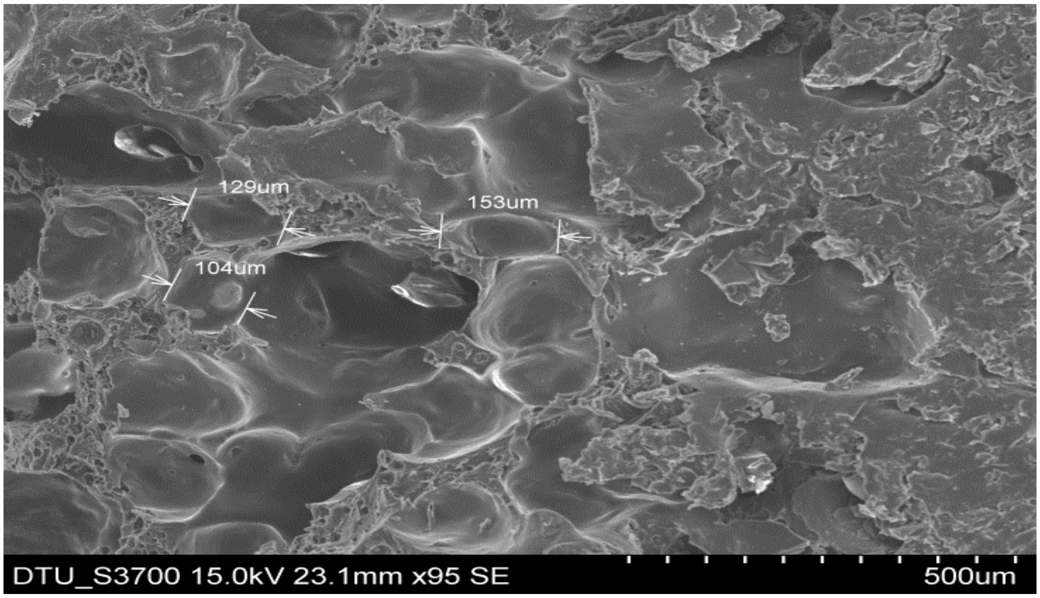
Filler concentration in grams	Flexural extension
0 gm	2.12506
1 gm	2.21656
2 gm	2.25819
3 gm	2.28319

Reinforcing with the calcium carbonate filler in the rigid polyurethane foam results in the increase in the flexural strength of the rigid polyurethane foam with the increase in amount of calcium carbonate filler 2.21656 (1 gm), 2.25819 (2 gm), 2.28319 (3 gm) compare to 2.12506 of neat sample (figure 20). So the percentage increase in flexural extension is 39-45%

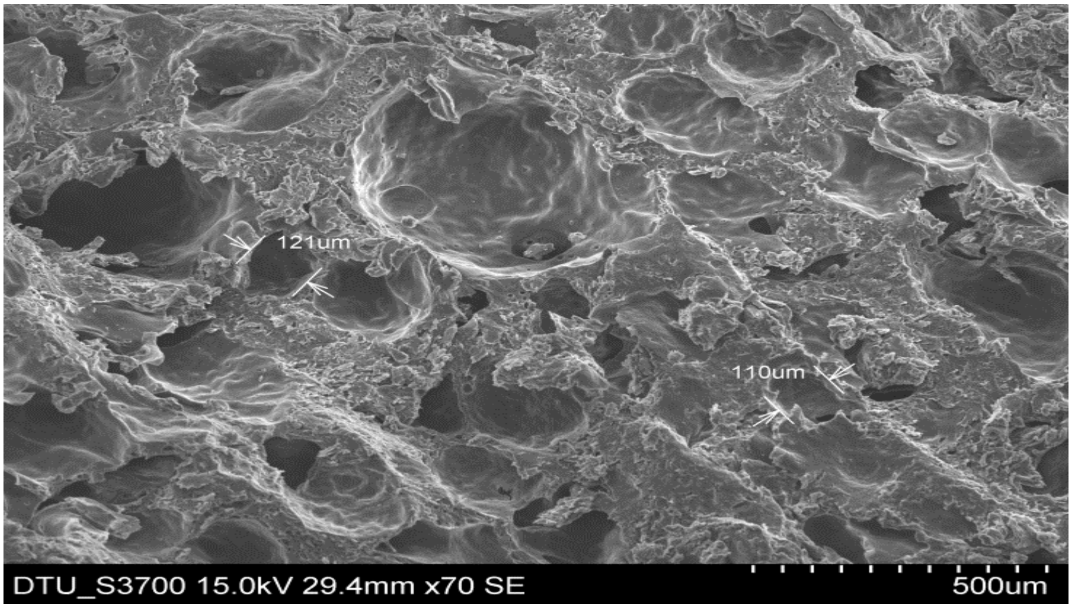
5.4.4 SEM analysis



a) 1gm



b) 2gm



c) 3gm

Figure 5.22(a) SEM of Caster oil based Rigid Polyurethanes Foam for 5% $CaCO_3$ Loading (a), For 10 % $CaCO_3$(b) and For 15% $CaCO_3$ Loading (c)

The average pore size of calcium carbonate filled rigid polyurethane is 193.66 μm compare to 847 μm of neat sample (figure 21), thus, there is nearly 57% reduction in pore size after the calcium carbonate reinforcement. The reduced pore size indicates that the 3-D structure of foam was more packed and consequently resulted in increased density and increased compressive strength.

5.5 Effect of Addition of Fly-Ash on Castor Oil based RPU

5.5.1 FT-IR Analysis

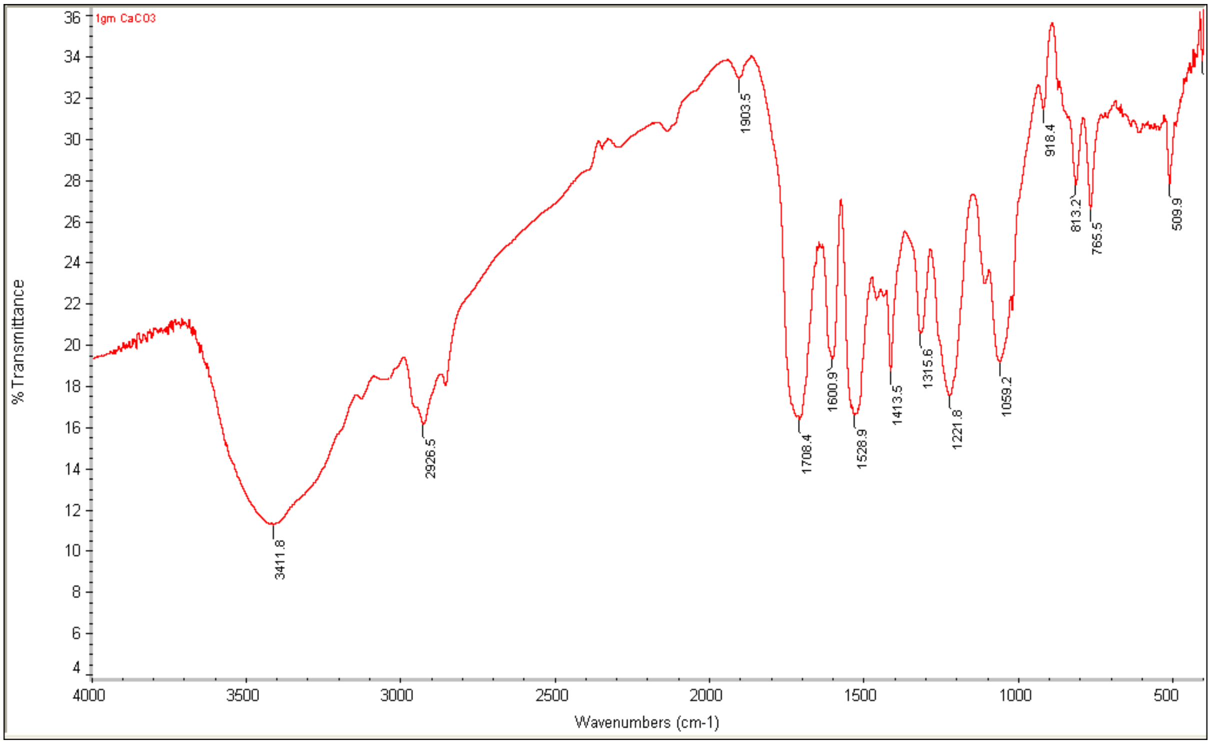
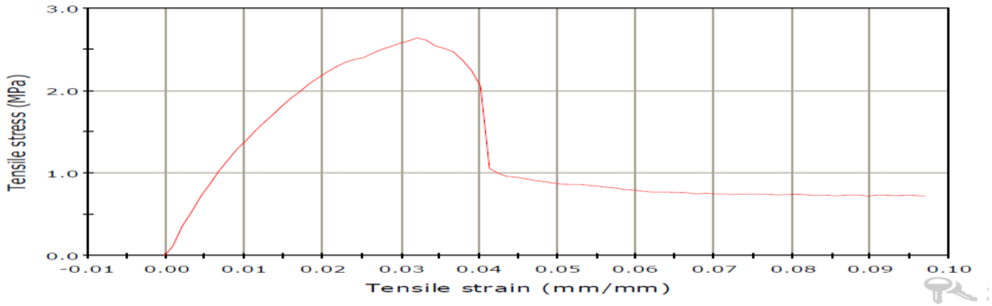


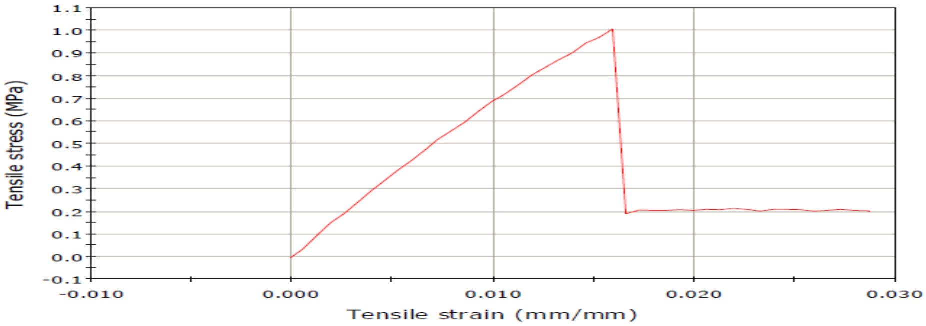
Figure 5.23: FTIR of of Caster oil based Rigid Polyurethanes Foam Incorporated with Fly-Ah Filler.

In case of calcium carbonate filled rigid polyurethane foam FT-IR graph a new peak of absorption have obtained which is at 1903.5 cm^{-1} due to interaction between the calcium carbonate and the raw materials of foam i.e. castor oil and MDI. Rest of peaks are obtained as same in unreinforced polyurethane sample like the prominent peak at 3274 cm^{-1} is associated with an overlap between hydroxyl groups (O-H) and amino groups (N-H), 2925.5 cm^{-1} due to Alkyl C-H stretch, 1708 cm^{-1} due to C$=$O stretching.

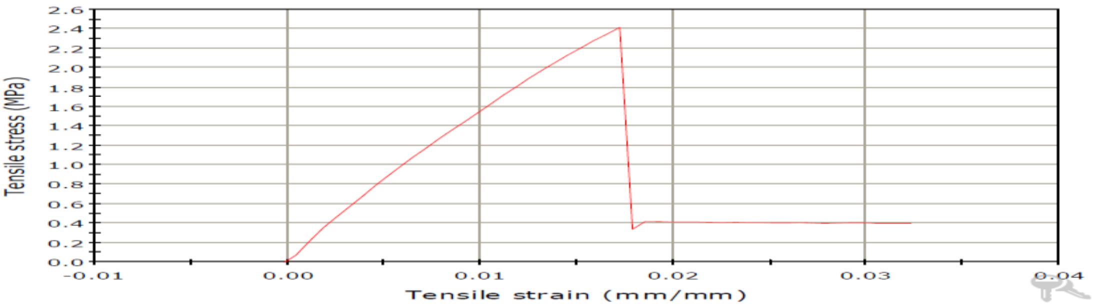
5.5.2- Tensile Strength



5.24 (a): Relationship between Tensile stress and Tensile strain for Castor oil Based Rigid Polyurethane Incorporated with 5% of Fly-Ash



5.24 (b): Relationship between Tensile stress and Tensile strain for Castor oil Based Rigid Polyurethane Incorporated with 10% of Fly-Ash



5.24 (c): Relationship between Tensile stress and Tensile strain for Castor oil Based Rigid Polyurethane Incorporated with 15% of Fly-Ash

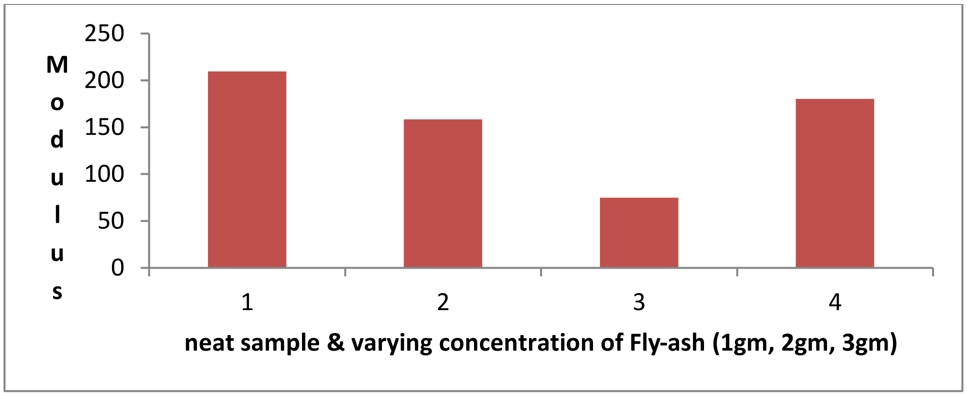


Figure 5.25: Various of Tensile Modulus with Percentage Loading of Fly Ash

Table No.5.7: Effect of Fly Ash Concentrations on the Tensile Properties of RPUFs.

Filler concentration in grams	Modulus
0 gm	209.45081
1gm	158.3119
2 gm	74.91106
3 gm	180.3.43

From the results obtained in case of fly-ash reinforced the tensile strength decreases as compare to unreinforced neat rigid foam 209.4508 (figure 19) upto 2 concentrations 158.3119 (1 gm), 74.91106 (2gm) but later strength increases 180.3043(3 gm) ,but still remains less in compare to neat rigid foam. So the decrease in tensile modulus is 24% .

5.5.3 Flexural Strength

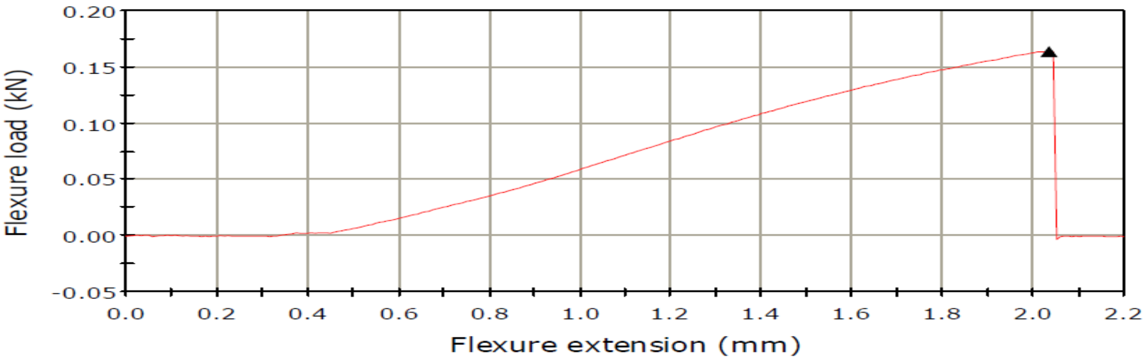


Figure 5.26 (a): Relationship between Flexure Load and Flexure Extension for Castor Based Rigid Polyurethane Incorporated with 5% of Fly Ashl

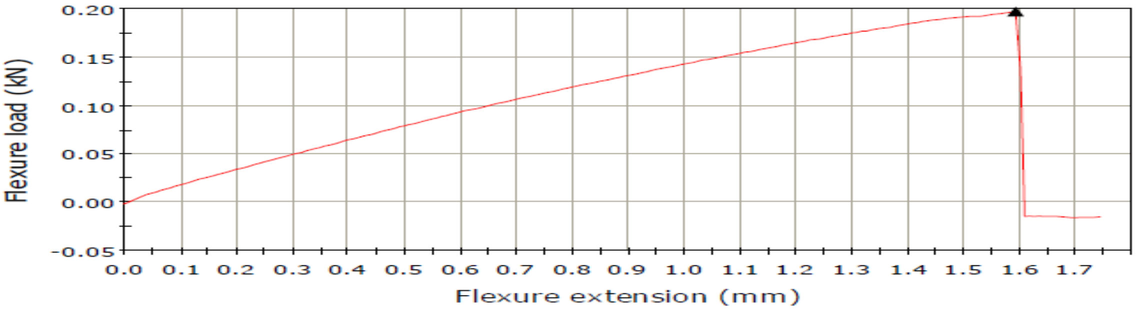


Figure 5.26 (b): Relationship between Flexure Load and Flexure Extension for Castor Based Rigid Polyurethane Incorporated with 10% of Fly Ashl

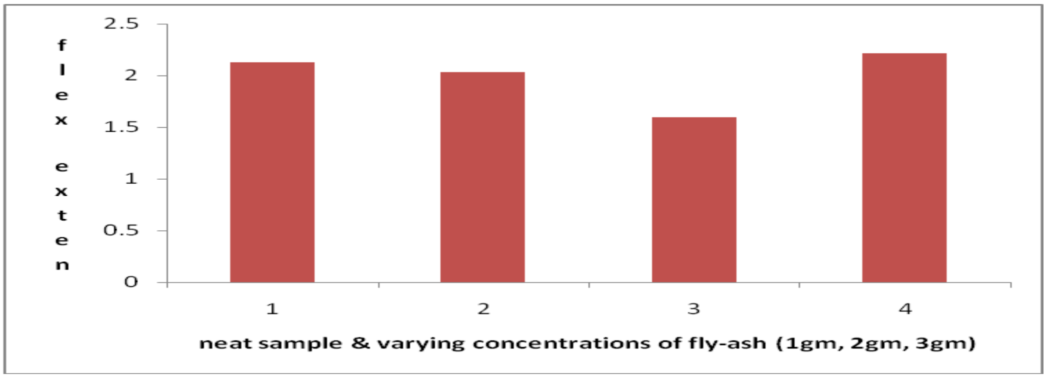


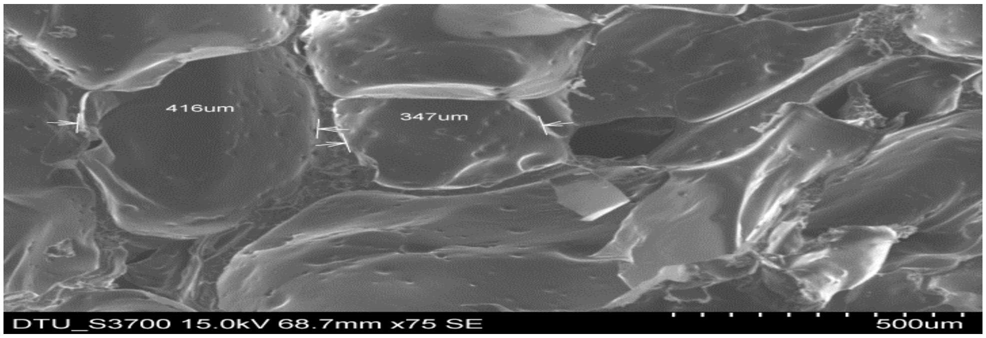
Figure 5.27 : Various of Flexural Extension with Percentage Loading of Fly Ash

Table No. 5.7: Effect of Fly Ash Concentrations on the Flexural Properties of RPUFs.

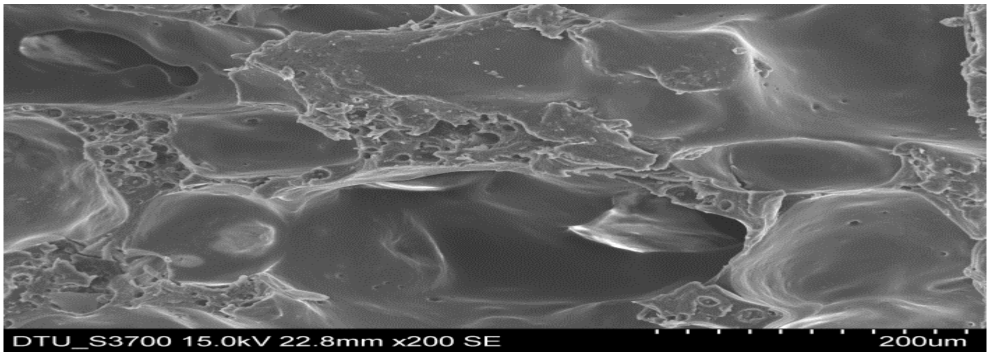
Filler concentration in grams	**Flexural extension**
0 gm	**2.12506**
1 gm	**2.03331**
2 gm	**1.59156**
3 gm	**2.21526**

From the results obtained in case of fly-ash reinforced the flexural extension decreases as compare to unreinforced neat rigid foam 2.12506 (figure 20) upto 2 concentrations 2.03331 (1 gm), 1.59156 (2gm) but later strength increases 2.21526 (3 gm) ,but still remains less in compare to neat rigid foam. So the decrease in flexural extension is 25%.

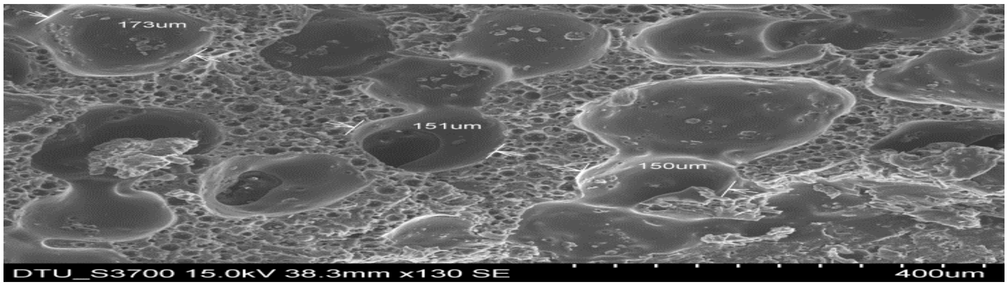
5.5.4- SEM Analysis



a) 1gm



b) 2gm



c) 3gm

Figure 5.28 SEM of Caster oil based Rigid Polyurethanes Foam for 5% Fly Ash Loading (a), For 10 % Fly Ash Loading (b) and For 15% Fly Ash Loading (c)

The average pore size of Fly-ash reinforced rigid polyurethane foam is 249 µm as compare to 847µm of neat sample (figure 21), thus, there is nearly 50% reduction in pore size after the fly-ash reinforcement. The reduced pore size indicates that the 3-D structure of foam was more packed and consequently resulted in increased density and increased compressive strength. The cells are in nearly spherical shape and have open cell type structure.

5.6 Effect of Addition of Talc on Castor Oil based RPU

5.6.1FT-IR analysis

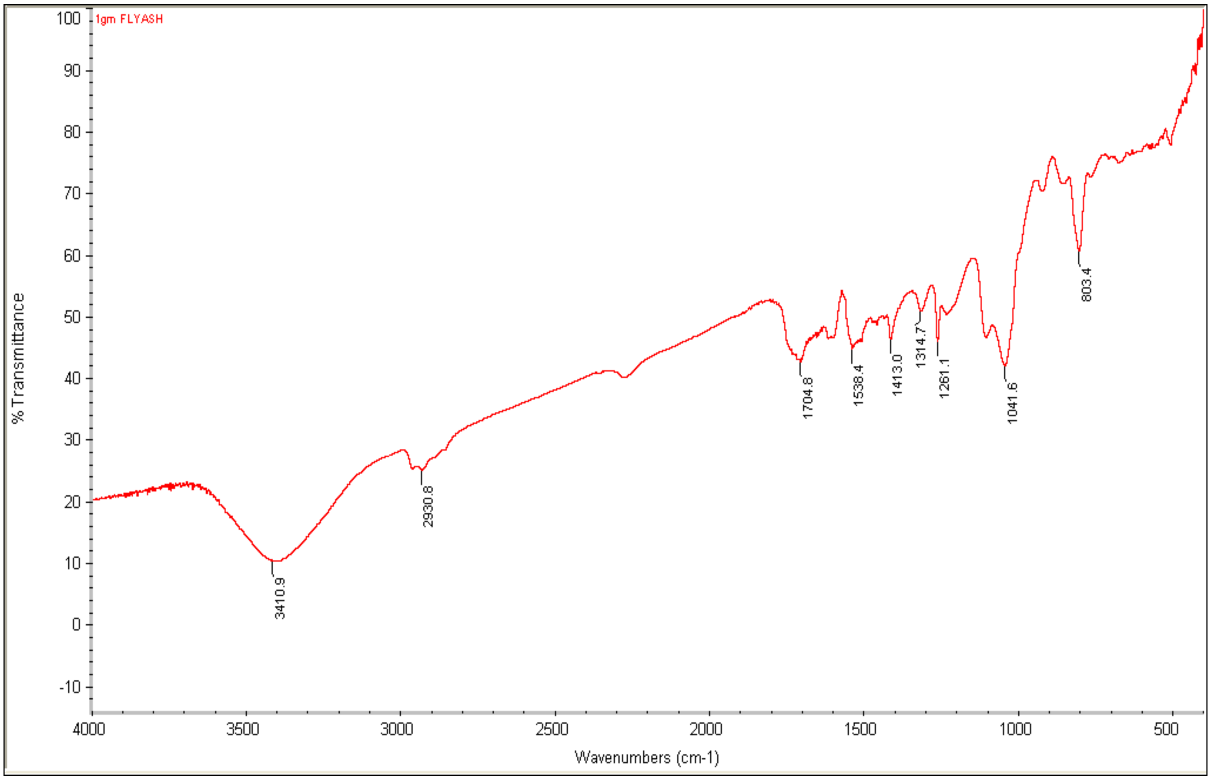
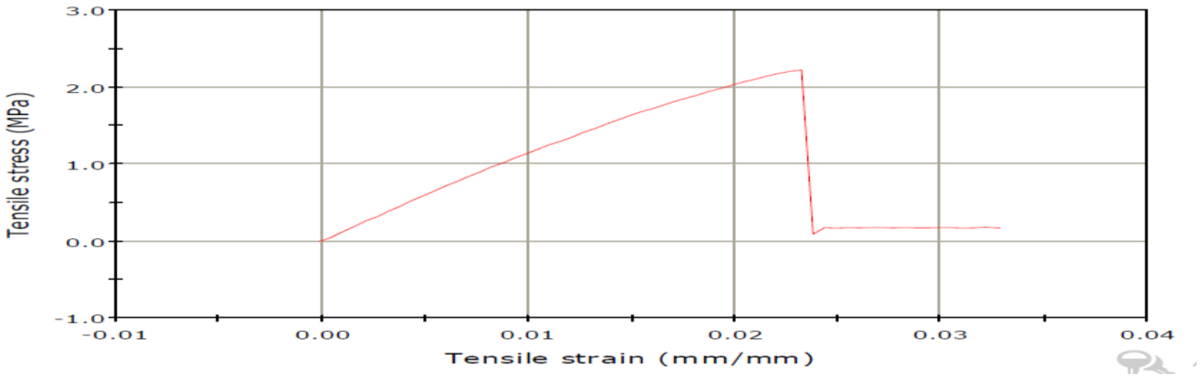


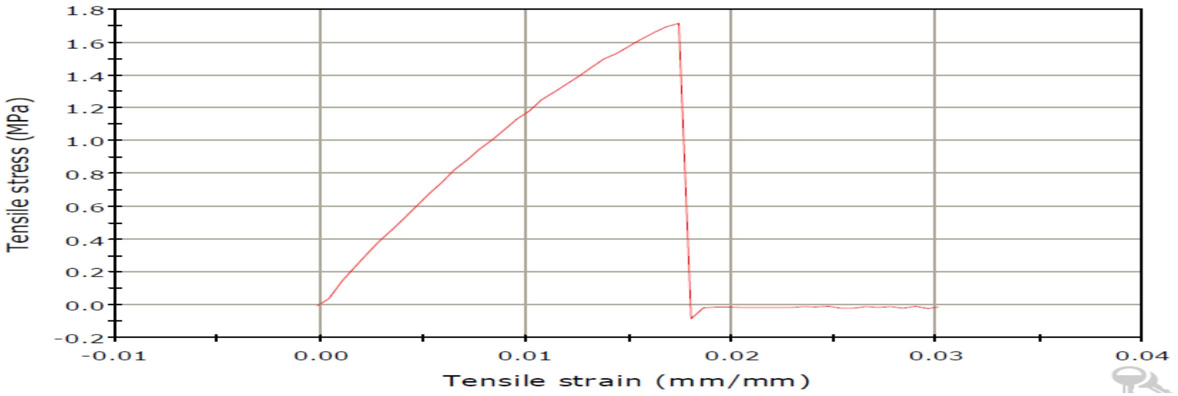
Figure 5.29 FTIR of of Caster oil based Rigid Polyurethanes Foam Incorporated with Talc Filler.

In case of talc reinforced rigid polyurethane foam the peaks have been shifted a lot due to interaction between the talc powder and the basic raw materials of polyurethane foam i.e. modified castor oil and MDI. The The prominent peak at 3397 cm^{-1} is associated with an overlap between hydroxyl groups (O-H) and amino groups (N-H). The Alkyl C-H stretch at 2925 cm^{-1} is being completely removed from the IR- graph

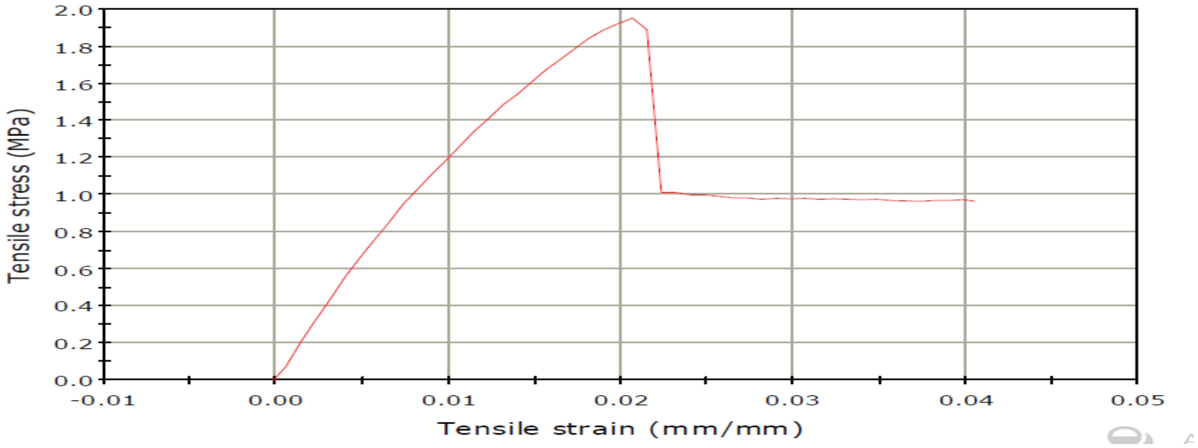
5.6.1 Tensile test



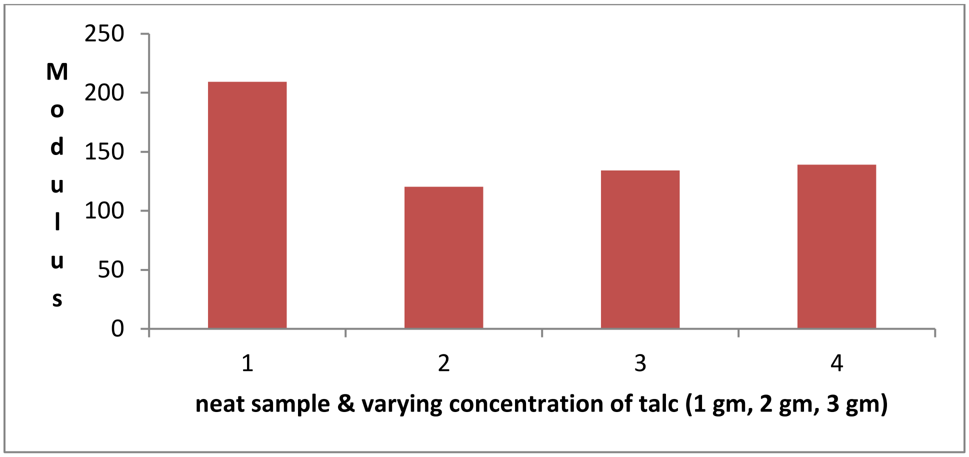
5.30 (a): Relationship between Tensile stress and Tensile strain for Castor oil Based Rigid Polyurethane Incorporated with 5% of Talc



5.31 (b): Relationship between Tensile stress and Tensile strain for Castor oil Based Rigid Polyurethane Incorporated with 10% of Talc



5.32 (c): Relationship between Tensile stress and Tensile strain for Castor oil Based Rigid Polyurethane Incorporated with 15% of Talc



5.33: Various of Tensile Modulus with Percentage Loading of Talc

Table No.5.8 Different concentration of talc and their effect on tensile modulus

Filler concentration in grams	**Modulus**
0 gm	**209.45081**
1 gm	**120.2613**
2 gm	**134.1368**
3 gm	**138.9838**

Results in case of talc reinforced polyurethane rigid foam indicates that there in increase in tensile strength 120.2613(1 gm), 134.1368 (2 gm), 138.9838 (3 gm) with the increasing amount of talc filler but the tensile strength remains low as compare to unreinforced neat sample 209.45081 (figure 19). So the decrease in the tensile modulus is 37 %.

5.6.2 Flexural Test

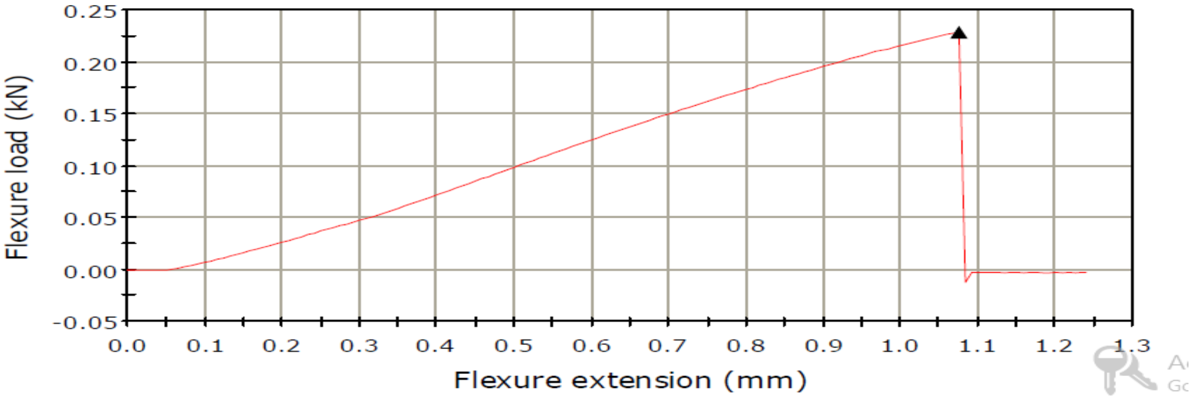


Figure 5.34(a): Relationship between Flexure Load and Flexure Extension for Castor Based Rigid Polyurethane Incorporated with 5 % Talc

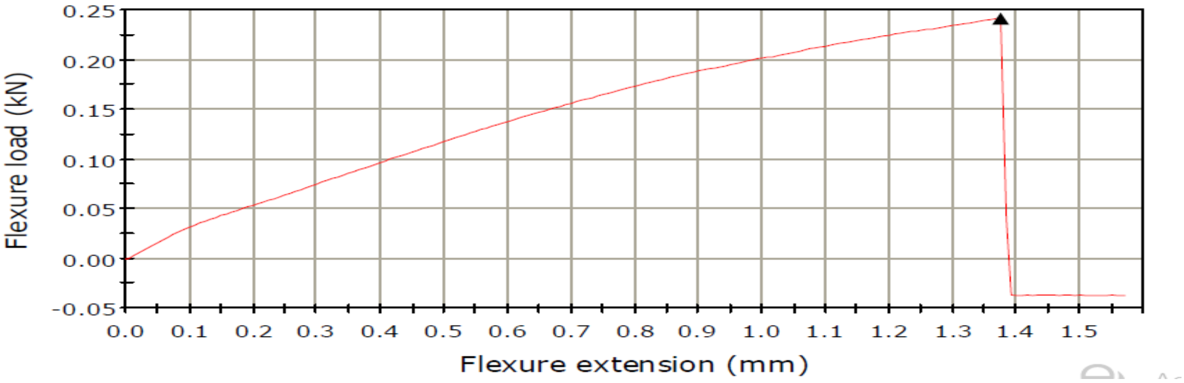


Figure 5.35 (b): Relationship between Flexure Load and Flexure Extension for Castor Based Rigid Polyurethane Incorporated with 10% of Talc

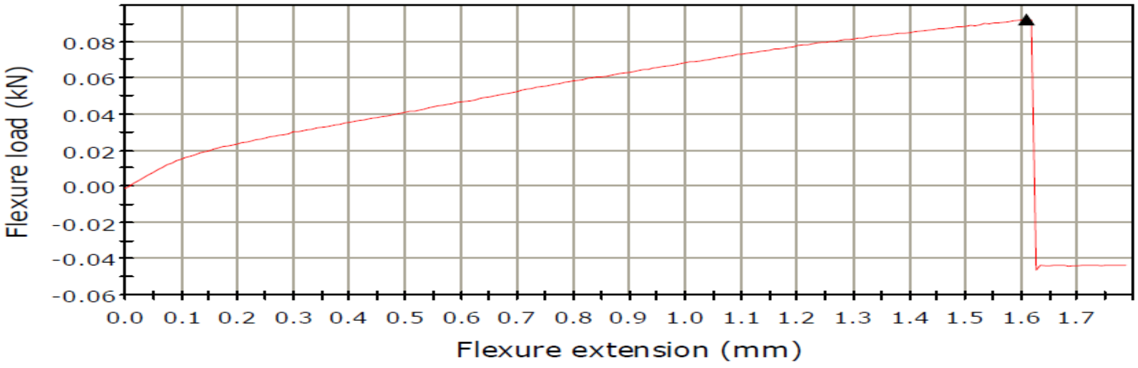


Figure 5.36 (b): Relationship between Flexure Load and Flexure Extension for Castor Based Rigid Polyurethane Incorporated with 15% of Talc

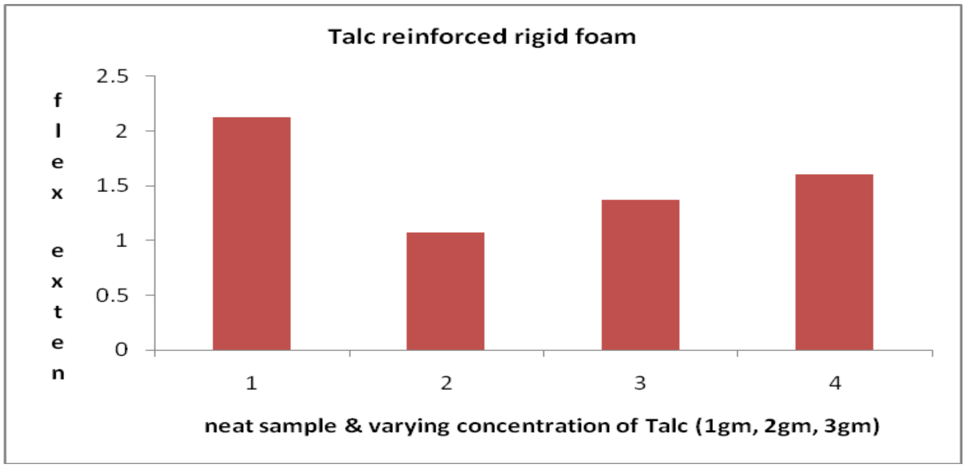


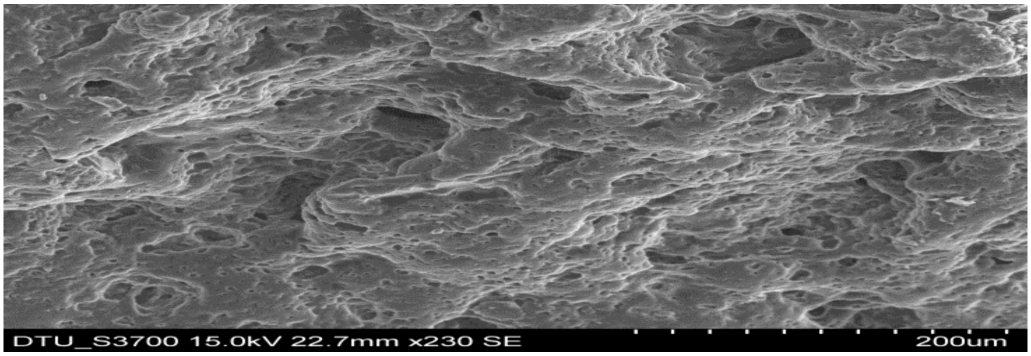
Figure 5.37 : Various of Flexural Extension with Percentage Loading of Talc

Table No. 5.9 Different concentration of talc and their effect on Flexural extension

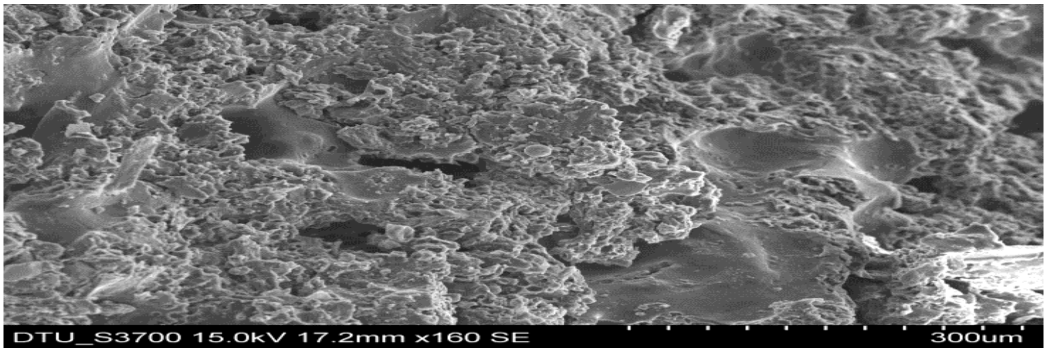
Filler concentration in grams	Flexural extension
0 gm	2.12506
1 gm	1.07506
2 gm	1.375
3 gm	1.60825

Results in case of talc reinforced polyurethane rigid foam indicates that there in increase in flexural strength 1.07506 (1 gm), 1.375 (2 gm), 1.60825 (3 gm) with the increasing amount of talc filler but the flexural strength remains low as compare to unreinforced neat sample 2.12506 (figure 20). So the percentage decrease in flexural extension is 36.61 %.

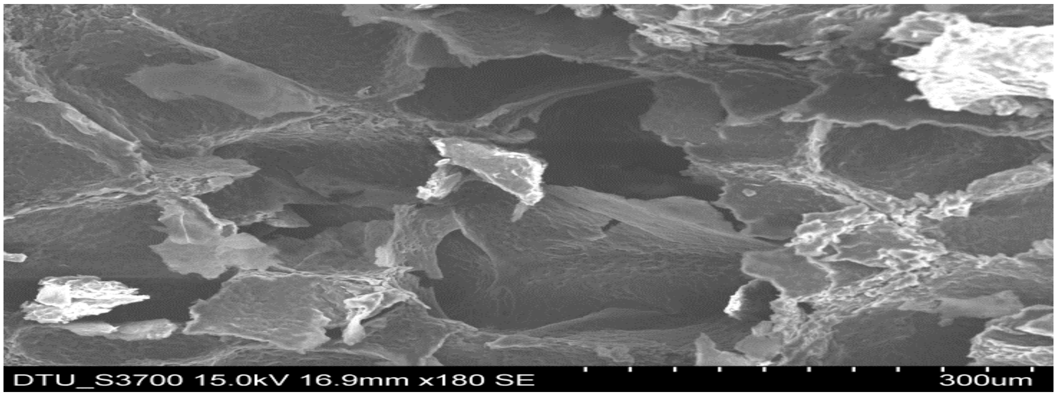
5.6.4 SEM analysis



a) 1gm



b) 2gm



c) 3gm

In this sample of 3 gm talc very fine closed pores can be easily seen in SEM figure

Table No. 5.10 comparison of tensile modulus of different fillers

Tensile Test					
Concentration	**Fillers**				
	Mica	**Glass fibre**	**Talc**	**Fly-ash**	**$CaCO_3$**
0 gm	**209.45081**	**209.45081**	**209.45081**	**209.45081**	**209.45081**
1 gm	**253.16725**	**289.77756**	**120.2613**	**158.3119**	**220.6969**
2 gm	**257.73223**	**323.20069**	**134.1368**	**74.91106**	**239.6357**
3 gm	**263.91595**	**347.59394**	**138.9838**	**180.3.43**	**271.49413**

On comparing the tensile modulus of these different fillers the strength of glass fibre filler is highest among the rest of the fillers in all the three concentration, but glass fibre is costly so from the cost point of view mica is proves to be a good reinforcing filler as well as its reinforcing increases the tensile modulus too after that $CaCO_3$ is also a option but it is costly as compare to mica. Talc and Fly-ash reinforcing results in the decrement of tensile modulus.

Table No.5.11 comparison of Flexural extension of different fillers

Flexural Test					
Concentration	**Fillers**				
	Mica	**Glass fibre**	**Talc**	**Fly-ash**	**$CaCO_3$**
0 gm	**2.12506**	**2.12506**	**2.12506**	**2.12506**	**2.12506**
1 gm	**2.35831**	**2.90831**	**1.07506**	**2.03331**	**2.21656**
2 gm	**2.39156**	**2.975**	**1.375**	**1.59156**	**2.25819**
3 gm	**2.80013**	**3.09169**	**1.60825**	**2.21526**	**2.8319**

On comparing the flexural extension of these different fillers the extension of glass fibre filler is highest among the rest of the fillers in all the three concentration, but glass fibre is costly so from the cost point of view mica is proves to be a good reinforcing filler as well as its reinforcing increases the extension too after that $CaCO_3$ is also a option but it is costly as compare to mica. Talc and Fly-ash reinforcing results in the decrement of flexural extension.

Table No.5.12 comparison of SEM of different fillers

SEM					
Concentration	**Fillers**				
	Mica	**Glass fibre**	**Talc**	**Fly-ash**	**$CaCO_3$**
0 gm	**847 µm**	**847 µm**	**847 µm**	**847 µm**	**847 µm**
1 gm	**132**	**99**	**Very fine pore**	**347**	**342 µm**
2 gm	**115**	**86**	**same**	**-**	**129 µm**
3 gm	**98**	**99**	**same**	**173**	**110 µm**

Reinforcement of fillers results in the decrease of pore size and increase of cell density. The cells obtained are slightly spherical with the open cell type structure. The percentage decrease in pore size upon reinforcing is highest in case of glass fibre upto 90%, 82 % in case of mica, 57 % in case of calcium carbonate and 50 % in case of fly-ash.

CHAPTER-6

CONCLUSION

Studies on the Effect of Various Fillers on the Properties of Rigid Polyurethane Foams have been carried out. Rigid PU foams based on modified castor oil were prepared and reinforced with fillers such as glass fiber, calcium carbonate, mica, talc and flyash. It was observed that, reinforced foams presented different (enhanced or reduced) characteristics than the neat one. Upon reinforcing of rigid polyurethane foams with various fillers like: calcium carbonate, glass fibre, mica, talc, fly-ash, changes were observed in the mechanical properties like tensile and flexural strength. Addition of calcium carbonate, mica, glass fibre shows improved properties, whereas in case of fly-ash and talc, there is decrease in tensile and flexural strength compare to neat unreinforced rigid polyurethane foam. SEM analysis revealed the decrease in pore size, thus making pores more compact by reinforcing it with the fillers. This in turn increased cell density and thus improves mechanical properties of the resulted foam. FT-IR analysis reveals some new absorption peaks in reinforced samples and some peaks have been shifted from its original position due to stretching. Being a part replacement of polyol with fillers, in PU manufacturing, foam derivatives with fillers could at least reduce the cost of foam production, as long as the desired characteristics of foam are retained. In addition to low cost, the foam produced are environment friendly because of the derivation of raw materials (at least one) from the plant origin. Nowadays, environmental concerns stimulate the use of renewable resources for producing economically convenient applications to maintain or even improve life quality. A current need of the polyurethane industry is to identify new sources of reagents for polymer synthesis to replace petrochemical raw materials by those obtained from renewable sources. In this sense, the use of polyols based/derived from natural oils is a very attractive alternative that can contribute positively to environmental protection.

APPENDIX-1

A1.1 Characterization of Raw Materials

A1.1.1Determination of Specific Gravity

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

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

Calculations:

Specific Gravity of Castor Oil

Weight of bottle (Mc) = 110.5 gm

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

Weight of water and bottle (Mw) =210.5 gm

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

Specific Gravity of Glycerol

Weight of bottle (Mc) = 110.5 gm

Weight of glycerol and bottle (Mo) =235.5 gm

Weight of water and bottle (Mw) =210.5 gm

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

Specific gravity of Modified Polyols

Weight of bottle (Mc) = 110.5 gm

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

Weight of water and bottle (Mw) =210.5 gm

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

Specific gravity of MDI

Weight of bottle (Mc) = 110.5 gm

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

Weight of water and bottle (Mw) =210.5

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

A1.1.2 Determination of pH

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

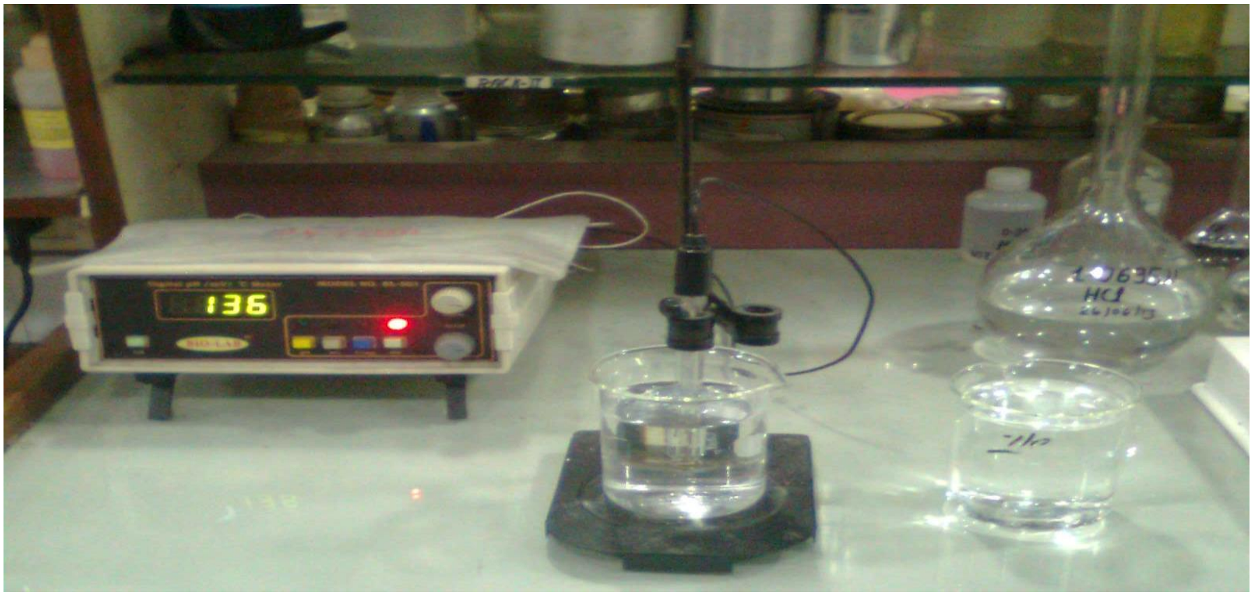


Figure A1.1: Digital pH Meter (Model no. BL-501)

A1.1.3 Determination of Acid Value

Approximately2 gm of sample was dissolved in 100 ml of Methyl Ethyl Ketone with slightly heating. The mixture was then cooled at room temperature and was titrated against 0.1 N KOH solution, using phenolphthalein as indicator. The Acid Value (in mg KOH/gm) can be given by using the equation:

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

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

Calculations:

Preparation of 0.1 N KOH solutions

Weight of KOH (W) = EVN/1000

Where, E = Equivalent weight = molecular weight/ functionality

E = 56.1 / 1 = 56.1

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

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

Volume of KOH used = 7.81 ml

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

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

Sample size for Acid Value

2.3 gm and maximum 10 gm for very low acid value

Acid value of Castor Oil

Weight of castor oil sample (W) = 3.39 gm

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

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

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

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

Acid Value of Glycerol

Weight of glycerol sample (W) = 3.225 gm

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

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

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

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

Acid Value of Modified Polyols

Weight of modified polyols sample (W) = 2.324 gm

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

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

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

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

Figure A1.2: Arrangement for Titration

A1.1.4 Determination of Hydroxyl Value

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

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

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

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

Calculations:

Preparation of 1N NaOH Solution

Weight of NaOH (W) = EVN/1000

Where, E = Equivalent weight = molecular weight/ functionality

E=40/1 =40

V= Volume = 1000 ml

N = Normality =1

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

Dissolve 40 gmNaOH in 960 ml of water and make solution.

Standardization of NaOH solution

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

Volume ofNaOH used = 8.72 mL

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

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

Hydroxyl Value of Castor Oil

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

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

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

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

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

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

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

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

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

Hydroxyl Value of Glycerol

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

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

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

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

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

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

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

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

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

Hydroxyl Value of Modified Polyols

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

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

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

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

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

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

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

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

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

A1.1.5 Determination of Water Content

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

Figure A1.4: Karl Fisher Titration

A1.1.6 Determination of Viscosity

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

Figure A1:5: Brookfield Viscometer

A1.1.7 Determination of % of NCO content

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

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

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

Figure A1.6: Water bath with Air Condenser

Calculations:

Preparation of 0.5 N HCl solutions

Weight of HCl (W) = EVN/1000

Where, E = Equivalent weight = molecular weight / functionality

E = 36.5 / 1 = 36.5

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

18.25 gm for 100%

For 36.5 % = 100/35.6= 2.8

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

Normality of HCl

$N_1V_1 = N_2V_2$

N_1 x 16.6 = 0.9449 x 10

N HCl = **0.5692**

% of NCO content of MDI

% of NCO = (B - S) ×N (HCl) ×4.2/W

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

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

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

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

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

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

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

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

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

A1.1.8 Percentage of Solid Contents

Calculations:

Percentage of Solid Contents inModified Polyols (S)

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

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

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

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

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

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

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

$S_1 = D_1 X\ 100 / W_1$ = 3.43 x100 /3.465 = 98.85

$S_2 = D_2 X\ 100 / W_2$ = 3.415 x100 /3.470 = 98.56

$S_3 = D_3 X\ 100 / W_3$ = 3.165 x100 /3.210 = 98.60

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

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

Percentage of Solid Contents in MDI

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

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

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

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

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

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

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

$S_1 = D_1 X\ 100 / W_1$ = 3.207 x100 /3.227 = 99.38

$S_2 = D_2 X\ 100 / W_2$ = 3.269 x100 /3.314 = 98.64

$S_3 = D_3 X\ 100 / W_3$ = 3.089 x100 /3.124 = 98.88

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

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

APPENDIX-2

A2.1 Calculations of the Formulation for Polyurethane Foam Formation

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

NCO Index (KZ)

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

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

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

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

Calculation of the OH value and of α_{OH}:

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

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

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

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

α_{KOH} = Mole KOH

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

Calculation of α_{NCO}:

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

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

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

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

Where, 42 = molecular weight of NCO

and mol is converted simultaneously to mMol, then one obtains

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

Hence, α_{NCO} can be calculated from the transformation

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

Calculation of the Polyisocyanate content of a Formulation:

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

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

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

Transformation gives

$$M_{Polyisocyanite} = \frac{O_{HZ\times}\ M_{Polyol}}{1336\times\%NCO} \times KZ \text{.....................Equation 4}$$

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

CHAPTER 7

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