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Effect of Different Formulations of MDI on Rigid Polyurethane Foams based on Castor Oil

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ABSTRACT

Polyurethane rigid foams are among the most important class of polyurethanes. The scientific interest in using bio-based polyols in the manufacture of polyurethane products has increased significantly in recent years. Accounting for the rising prices of petrochemicals and due to environmental concern, present study has been carried out with an aim to manufacture the rigid polyurethane form from natural and eco-friendly source. As polyols play an important role in the synthesis of polyurethane foams, the castor oil has been modified with glycerol to form the polyol and reacted with MDI in different proportions to achieve rigid polyurethane foam. The prepared (PU) structural rigid foam had been tested for its structure and mechanical properties and was found suitable to be applied in various engineering applications.

KEY WORDS: Rigid polyurethane foam, Castor oil, Glycerol, 4,4'-diphenylmethanediisocyanate (MDI), Mechanical properties

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1. INTRODUCTION

Polyurethane (PU) is one of the most versatile material and are widely used in both industry and everyday life[1]. Its applications includes as material for packaging; furniture; thermal insulation of buildings, refrigerators, deep freeze equipment, pipelines and storage tanks; buoyancy aids in boats and flotation equipment etc. Polyurethanes are included in both thermoplastic and as well as thermosetting polymers. The research and development of all kinds of domestic as well as international in polyurethane material industry have been received in recent years thus showing the current situation of the polyurethane industry in the developing direction. A large selection of polyols and polyisocyanates are available which permits the design of polymers for many applications. PU serves the mankind in its various roles such as flexible foam, rigid foam, elastomers, surface coatings and adhesives. Polyurethane foams represent the most important class and are further classified as flexible polyurethane foam and rigid polyurethane foam. PU foams have a remarkably broad range of applications including thermal insulation, cushioning, buoyancy, energy absorption (packaging) etc. Their low density also allows the design of light, rigid components such as aircraft-interior panels, structural shapes (transom cores, bulkhead core, stringers, motor mounts, etc.) in fiber-reinforced plastic (FRP) boat building, impact-limiters and crash-pads, composite foam cores, mold-patterns and plugs, sports-equipment core material, and composite tooling[2]. Khemani, 1997 and Kumar and Kaur, 2013 reviewed the background and history of urethane foams and elaborates on their potential future utility[3,4,5]. Rigid polyurethane foams are very popular and highly energy-efficient materials of polyurethane product and are good at both through its physical strength and mechanical properties. Rigid polyurethane foams are particularly useful in the construction field and they can be used as polymeric concrete components, insulating materials, sealants and others[6].

The synthesis of vegetable oil based polymeric materials with excellent physical and chemical properties has drawn great interest in the recent times[7]. 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, alkyd, polyester, amide and epoxy resins. The potential for polyols derived from vegetable oils to replace petrochemical- based polyols began garnering attention around 2004, partly due to rising costs of petrochemical feedstock’s and partially due enhanced public desire for environmentally friendly green products. There is a growing worldwide interest in the development of vegetable oil based polyurethane. This interest is economically driven because vegetable oils are relatively inexpensive and a renewable resource[8,9]. Moreover, these are renewable resources.

Vegetable oils are composed of triglycerides of long chain fatty acids. The most common chain lengths in these fatty acids are 18 or 20 carbon atoms which can be either saturated or unsaturated, where unsaturation of the double bonds are located at the 9, 12 and 15 carbon. By using enzymes or chemicals to modify the unsaturated fatty acid and introducing hydroxyl functional groups, vegetable oils could be converted into polyols[10]. 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[11,12]. Lu et al., 2005 used waterborne polyurethane made from rapeseed oil-based polyol to modify glycerol-plasticized starch and develop biodegradable films[13]. 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[14,15]. Rigid polyurethane foams had also been reported to be synthesized from rhodium catalyzed hydroformylated polyols[16]. Petrovic et al, 2000 et al., Zlatanic et al., 2004 investigated the structure and properties of vegetable oil-based polyols, their applications in polyurethane foams, and the foam's biodegradation behavior and thermal stability[9,17].

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[18], 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.

1.1 *Chemistry of the reaction*

a) The gereralized Polyurethane reaction is : $R^{1}\text{-}N{=}C{=}O + R^{2}\text{-}O\text{-}H \longrightarrow R^{1}\text{-}\overset{H}{N}\text{-}\overset{O}{\overset{\parallel}{C}}\text{-}O\text{-}R^{2}$

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

A polyisocyanate is a molecule with two or more isocyanate functional groups, $R\text{-}(N{=}C{=}O)_{n\geq 2}$ and a polyol is a molecule with two or more hydroxyl functional groups, $R'\text{-}(OH)_{n\geq 2}$. The reaction product is a polymer containing the urethane linkage, -RNHCOOR'-. Polyurethane is produced by the polyaddition reaction of a liquid polyisocyanate with liquid blends of polyols in the presence of a catalyst and other additives.

The present work reports the synthesis and characterization of rigid polyurethane foams based on castor oil modified with glycerol (used as crosslinking agent) to form the polyol. N-pentane is used as a blowing agent. The formulated polyol is further used to react with 4, 4’-diphenylmethanediisocyanate (MDI) in different proportions. The reaction is catalyzed by Cobalt octoate and Silicon oil is used as surfactant. The purpose of adding the surfactant is to stabilizing the resulting foam during foaming stage. It is aimed to evaluate the effect of this renewable polyol with different proportions of MDI on the properties of the resulting rigid polyurethane foams and to develop a material for commercial uses that is quite inexpensive and somewhat eco-friendly.

2. EXPERIMENTAL

2.1 Chemicals

Castor oil (99%) and 4,4’-diphenylmethanediisocyanate (AR grade) was obtained from Shivathene Linopack ltd. Parwanoo, Himachal Pardesh. Cobalt octoate (99%), n-Pentane (99%), and Silicon oil, were purchased from Standard Chemicals (ISO 9001:2008 certified), Tilak Bazar, Delhi. Glycerol (99.9%) was supplied by Sisco Industries Pvt. Ltd. All the reagents were of analytical grade and used as they were supplied.

2.2 Preparation of Castor Oil based Rigid Polyurethane Foams

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 and in the subsequent step it was reacted with MDI to obtain the rigid foam.

2.2.1 Modification of Castor Oil

Experimental Setup and Procedure

The properties of the castor oil were studied and are reported in Table: 1. The values obtained are almost similar to that available in literature[19,20]. 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 glass reactor of 500 mL capacity with 180 mm height and 90 mm diameter equipped with a mechanical stirrer. The stirrer was mounted on an overhung shaft, i.e. shaft supported from above, along the axis of the reactor, with a clearance from the bottom equal to one third of the diameter of the reactor. The shaft was driven by a 1/8 H P motor which was controlled through a dimmerstat. Heating was carried out by means of an oil bath. Reactor was supported on a circular copper plate with in the oil bath. Nitrogen 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.

Procedure:

The reaction kettle was charged with castor oil. Glycerol 10% (w/w) was added to it. 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 hydroxyl value. For this purpose, the samples at regular intervals were taken out and checked for hydroxyl value, acid value, viscosity and water content[4]. The heating was carried out till a hydroxyl value of 390-410 mg KOH/g is achieved. The time required to complete the reaction was 3-4 hrs. The resulted polyol was stored in dark bottles away from direct sun light.

2.2.2 Preparation of Foams

The polyol, cobalt octoate 2 %w/w_{Polyol}, n-pentane 20 %w/w_{Polyol} and Silicon oil 3 % w/w_{Polyol} were added in the reaction kettle and thoroughly mixed under controlled temperature conditions at 35 ± 2^0C. Calculated amount of MDI on the basis of NCO/OH ratio was taken and mixed thoroughly by high-speed mechanical stirrer at 1200 rpm. The resulting reaction mixture was poured into a metal mould (100x100x10 mm^3), 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 foam thus produced was left to stand for 24 hours before it was tested. After demoulding, the resulted foam was cut into desired dimensions and tested for its visual colour, tensile strength, compression strength water absorption and morphology.

3. RESULTS AND DISCUSSIONS

The rigid polyurethane foams had been produced by the reaction of MDI with castor oil based modified polyols. The various polyurethane formulations used are as reported in Table:2. Formulation 1 constitutes a conventional polyurethane composition and it contains MDI and Polyol in the ratio 1:1. The product of this formulation has a spongy texture and it is quite weak. Formulation 2 contains MDI : Polyol ratio as 2:1 and consequently found somewhat better in terms of strength and formulation 3, containing MDI : Polyol ratio of 3:1 is very strong and stiff.

Table: 1: Properties of Commercially available Castor Oil

S. No.	Property	Value
1.	Color and Appearance	Clear/ Dark Yellow
2.	Acid Value	2
3	Hydroxyl Value	166-167
4	Water Content	0.5%
5	Solubility in Alcohol	Completely Soluble

Table: 2 : Ratio of MDI:Polyol in Different Formulations

S. No.	Formulation	MDI : Polyol
1.	Formulation 1	1:1
2.	Formulation 2	2:1
3.	Formulation 3	3:1

3.1 Visual Studies for Color

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

3.2Mechanical Properties

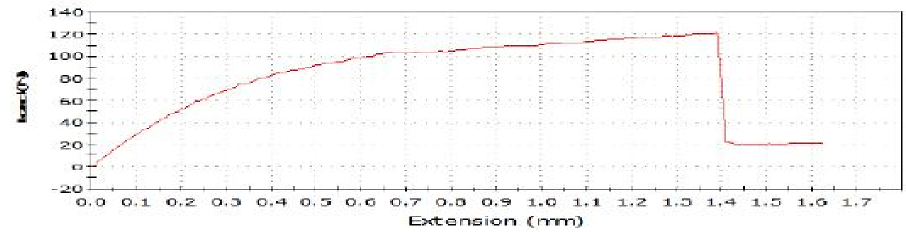
The mechanical properties of the castor oil based rigid polyurethane samples were determined according to the standard procedures. Samples were cut at ambient temperature to the required dimensions. Tensile and compressive properties of the resulted foams were measured at room temperature using Instron (model No.: 3369) universal testing machine tensile as per ASTM D-638 and ASTM D 695 method respectively. The tensile stress at maximum load (MPa) and maximum compressive load (kgf) for different formulations are as given in Table: 3. The tensile stress at maximum load as well as maximum compressive load was observed to be increased with increase in MDI : Polyol ratio, thus indicating a significant improvement in overall mechanical properties of the foamed samples, with MDI.

Table : 3 : Mechanical Properties of Castor oil based Rigid Polyurethane Foams

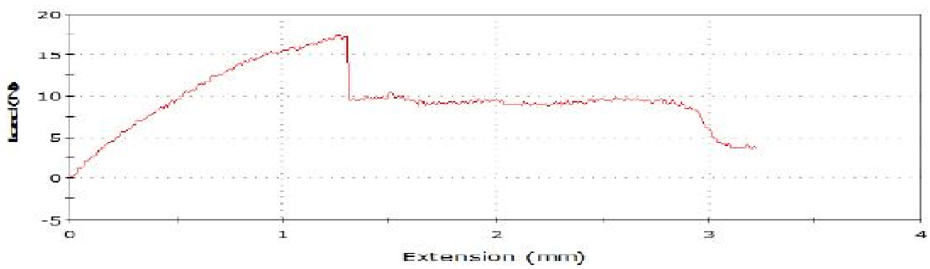
S No.	Tensile stress at Maximum Load (MPa)	Maximum Compressive Load (kgf)
Formulation 1	0.12903	1030.18514
Formulation 2	0.29220	1082.10801
Formulation 3	0.35285	1091.64952

Tensile Strength

The tensile strengths of the resulted foam samples were found good and was found increased with increase in MDI: Polyol ratio. Test results are presented in the form of graph between tensile load and extension, which shows that most of the response is linear, followed by brief nonlinearity before fracture. Tensile strength values as functions of loading direction were derived respectively from the gradient of the linear portion and the maximum stress before failure. The relationship between tensile load and extension for the castor oil based rigid polyurethane rigid foams is as shown in Fig 1 (a) to (c). From Fig 1(a) to (c), the value for tensile modulus for formulation I (i.e. MDI : Polyol::1:1) is seemed to be less as compared to that observed in case of formulation 2 (MDI : Polyol::2:1),which in turn is lesser than for formulation 3. It is very clear from Fig 1(a) that extension is very high in formulation1, before the breaking point arrived and it shows elasticity within the material. As seen from Fig 1(b), the formulation 2 shows elasticity but to a less extent and breaks under the applied load. The formulation 3, as indicated by Fig 1 (c) has not extendibility at all and break under the condition of maximum applied load thus representing that sample is very tough. The load bearing capacity of the resulted castor oil based rigid polyurethane foam increases with increase in MDI: Polyol ratio. From the above discussions, it is clear that the tensile strength and hardness increases whereas, elongation decreases with increasing NCO/OH ratio. High NCO/OH leads to low molecular weight of polymer[21] and higher levels of covalent crosslinking[22], which in turn increases the modulus as per the theory of rubber elasticity. This clearly justifies the higher tensile strength and hardness of formulation 2 as compared to formulation 1 and further increased tensile strength and hardness of formulation 3 as compared to formulation 2. The more load is needed to be applied to break the samples from the formulation 3, probably due to the requirement of cleavage of rigid crosslinks that were formed between castor oil and MDI.



(a)



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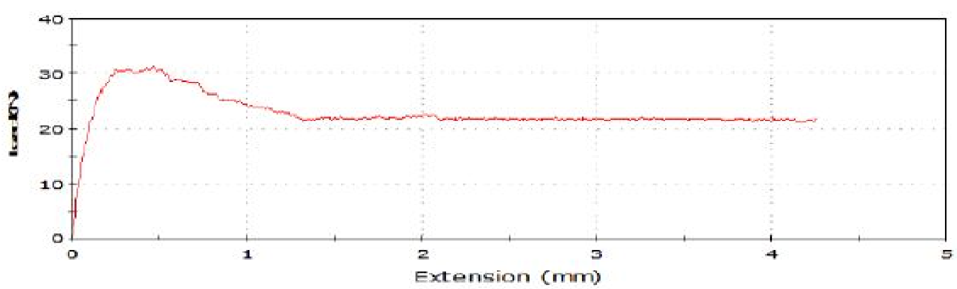
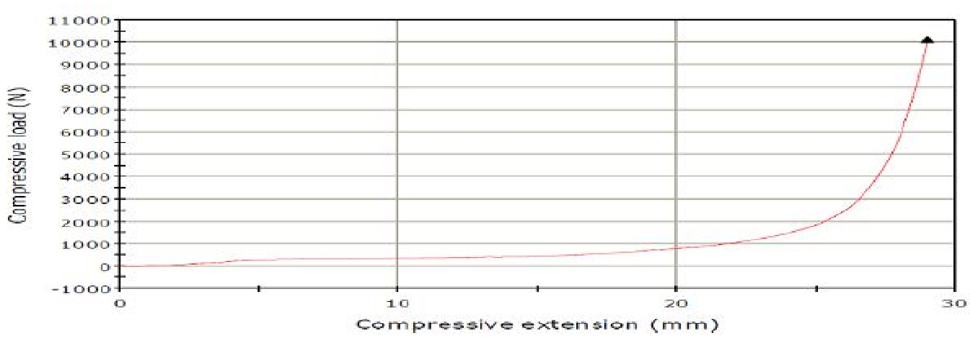


(c)

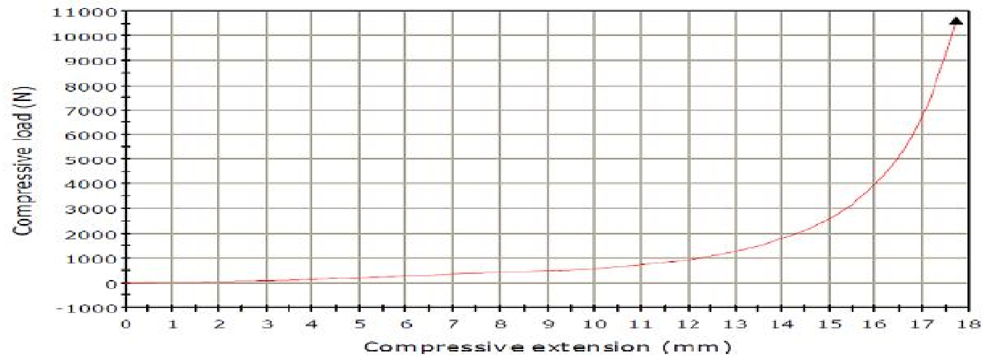
Fig 1. Relationship between load and extension for (a) Formulation 1 (b) Formulation 2 and (c) Formulation 3

Compressive strength

The compressive strengths of the resulted rigid polyurethane samples were found good. The relationship between compressive load and compressive extension for the castor oil based rigid polyurethane rigid foams is as shown in Fig 2 (a) to (c). It is seen from Fig 2 (a), for formulation 1(MDI : Polyol::1:1) for a maximum compressive load of 1030.18514 kgf, an extension up to 26 to 29 mm is there. Similarly for formulation 2 (MDI : Polyol::2:1), for a maximum compressive load of 1082.10801 kgf, an extension up to 17 to 18 mm had been observed. And for formulation 3 (MDI : Polyol::3:1), for maximum compressive load of 1091.64952 kgf, an extension of 15-16 mm is there. Thus it is very clear that with increase in MDI content in polyurethane foams, the load bearing capacity i.e. stiffness was increased and the extension was reduced. This result is in accordance with that reported in literature. Tu et al., 2007 reported that with increase in the isocyanate index or the increase in the isocyanate usage in the polyurethane foam, there is increase in the foam's cross-linking density which leads to a higher compressive strength[23]. The increase in compression strength is also favored by the fact that with increased content of MDI, a more closely packed structure is obtained, as reported under the section for SEM studies of the resulted foams, which may probably be due to formation of rigid crosslinks formed between castor oil and MDI. Because of restricted airflow in a closely packed foams, result in a higher compressive load bearing[24]. Due to rigid crosslinks within the foam structure, elastic recovery (that is more common in case of flexible foams) is restricted thus making foams rigid and stiff. This result is according to the theory of rubber elasticity, which states that higher levels of covalent crosslinking increase the modulus or stiffness of the polymer.



(a)



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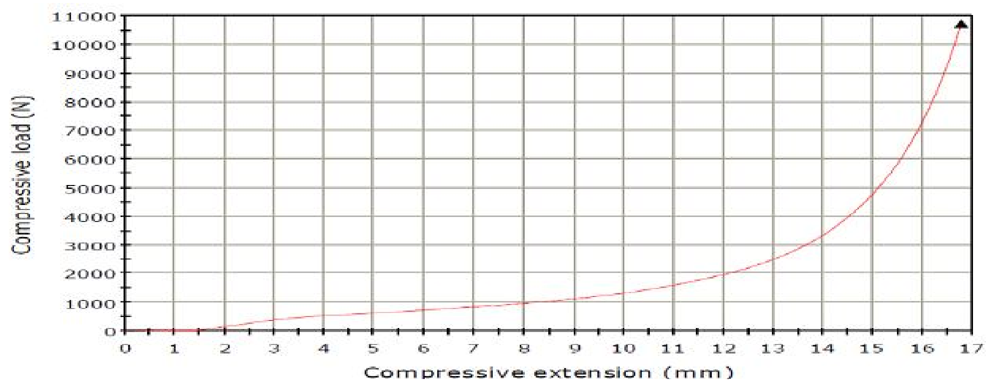


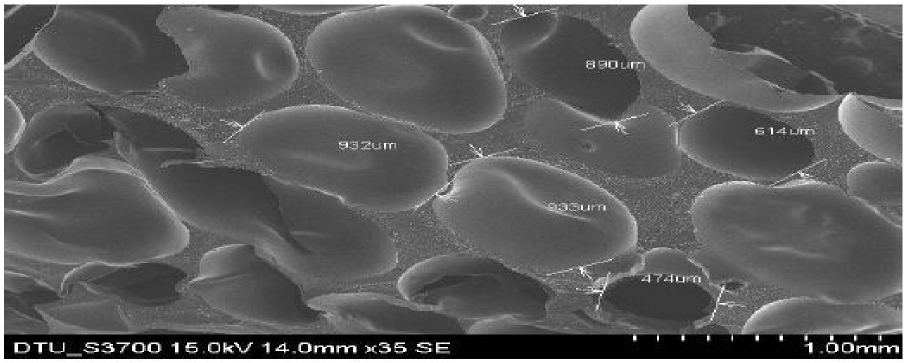
(c)

2. Relationship between compressive load and compressive extension for (a) Formulation 1

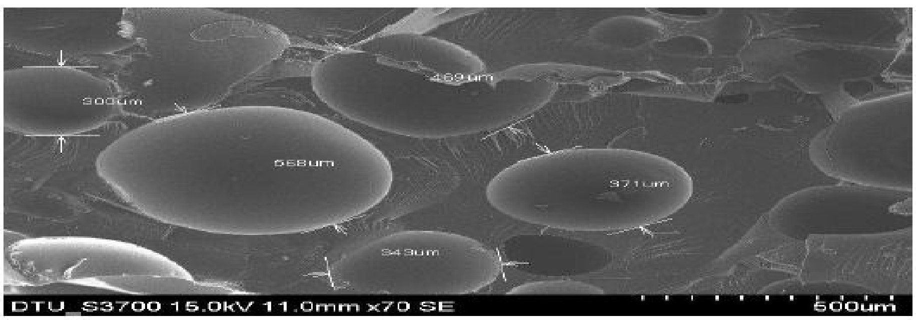
(b) Formulation 2 and (c) Formulation 3

3.3 SEM Images of Castor oil based Rigid Polyurethane Foams

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 srtucture of the foam specimen using SEM. The cell structures of the samples were characterized with a Hitachi S3700 SEM (Scanning Electron Microscope) using an acceleration of 15 kV. Figure 3(a) to (c) show the scanning electron micrographs of the castor oil based rigid polyutrthane rigid foams with different MDI contents. As seen in Fig 3(a), for the formulation 1, i.e for MDI : Polyol ratio 1:1, the foams present a smaller cell density with a higher pore size. The size of pores is mostly in range of 900 µm and a few are in the range of 500-600 µm, with an average pore size equal to 768.6 µm and it subsequently get reduced for other two formulations. For formulation 2 (MDI : Polyol ratio equal to 2:1), it is clearly indicated that pore size is reduced to an average pore size of 410.2 µm. And, with further increase in MDI content, i.e for formulation 3 with ratio of MDI : Polyol equal to 3:1, average pore size was reported to be 232 µm only (Fig 3(c)).



(a)



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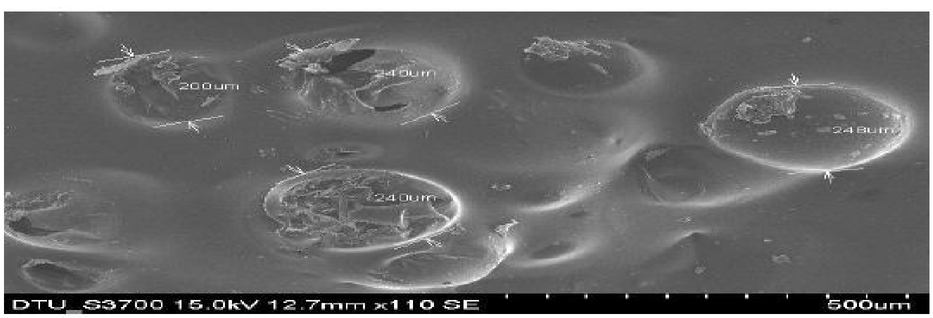

(c)

Fig 3: SEM of Caster oil based Polyurethanes for (a) Formulation 1 (b) Formulation 2 and (c) Formulation 3

Thus, there is nearly 47% reduction in pore size when MDI content is made double and nearly 70% reduction in the case where MDI content is tripled. The reduced pore size, as in case of formulation 2 and formulation 3 indicated that the 3-D structure of foam was more packed and consequently resulted in increased density and increased compressive strength. The same result i.e increased compressive strength was reported in the former section (where results of compression testing are reported).

3.4 Water Absorption in Foams

Results for water absorption tests for castor oil based rigid polyurethane samples are as given in Table: 4. It had been observed that percentage of the water absorbed in the resulted foamed samples was decreased with the increase in MDI concentration. With increase in MDI content, the pore size was found to be decreased (as confirmed by SEM studies) and foamed structure was found to be more closely packed, which in turn reduced the water absorption capacity of the form especially in the formulation 3. The water absorption capacity can be further reduced by adding suitable fillers.

Table: 4: Water Absorption in Different Formulations

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

4 CONCLUSION

The scientific interest in using bio-based polyols in the manufacture of polyurethane products has increased significantly in recent years. In the past, usually petroleum polyols were used for polyurethane production. With the diminishing and non-renewable petroleum resource, vegetable oil based novel polyols have been explored for their potential of replacing the petroleum polyols. Because of lower costs, more environmental friendly and bio-renewable polyols derived from vegetable oils have a great prospective to partially replace the petroleum resource. One of the objectives of this research was to reveal that the bio based polyglycerol may be used for the manufacture of rigid polyurethane foams. Rigid polyurethane foams were produced by reacting modified castor oil and MDI. By varying the MDI: Castor oil ratio, different formulations were obtained. Glycerol modification of castor oil results in more cross-linked and stiffer polymer. The tensile and compressive strength of rigid polyurethane foams were found to be increased with increase in the MDI content. The highest values were obtained for the formulation 3 with MDI: Polyol ratio equal to 3:1. SEM studies had also shown evidence for improved cell morphology and closed packing with increase in MDI content. The resulted castor oil based rigid polyurethane foams, due to their high strength and load bearing capacity are found suitable as a substitute of wood and can be used to make doors and light weight decorating articles.

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CONFLICT OF INTEREST

The studies presented in manuscript had been carried out for research purpose only and there is no involvement of any kind of financial gain.

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