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CORN OIL-BASED HIGHLY FLAME RETARDANT RIGID POLYURETHANE FOAMS FOR INDUSTRIAL APPLICATION

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CORN OIL-BASED HIGHLY FLAME RETARDANT RIGID POLYURETHANE FOAMS FOR INDUSTRIAL APPLICATION

A Thesis Submitted to the Graduate School
in Partial Fulfillment of the Requirements
For the Degree of
Master of Science

Muhammad Rizwan Sulaiman

Pittsburg State University

Pittsburg, Kansas

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CORN OIL-BASED HIGHLY FLAME RETARDANT RIGID POLYURETHANE FOAMS FOR INDUSTRIAL APPLICATION

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CORN OIL-BASED HIGHLY FLAME RETARDANT RIGID POLYURETHANE FOAMS FOR INDUSTRIAL APPLICATION

An Abstract of the Thesis by
Muhammad Rizwan Sulaiman

The synthesis of flame retardant polyurethane (PU) foam was carried out using two different flame retardants, triethyl phosphate (TEP) and triphenyl phosphate (TPP). The thermal and mechanical characteristics of the foam were analyzed. The obtained TGA results confirmed that the flame retardant acts in the gaseous form to stop the fire. All the prepared samples displayed excellent closed cell content, which was above 90 %. The burning time was reduced from 80 s to 7.5 s with the weight loss 3.2% of for sample E-12 (19.29 wt. % TEP) and from 80 s to 11 s with the weight loss of 3% for the sample E-14 (26.4 wt. % TPP). Thus, this study displayed the potential use of corn oil-based polyol for industrial preparation of rigid polyurethane foams. Furthermore, the addition of low amount of TEP and TPP can increase the flame retardancy of the foam. Thus, this study shows that corn oil-based polyol can be substituted for the petrochemical-based polyols for the industrial applications while retaining almost the same thermomechanical properties.

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CHAPTER I

INTRODUCTION

1.1. Green Polyurethane

The dependency of the petroleum feedstocks for different purposes, such as energy generation and different material synthesis, is an ever-increasing concern for the environment [1]. Nowadays, natural gases and crude oil are considered the main sources of energy. However, the demand for petrochemical feedstock as a raw material for thousands of different products and as a chemical building block for industrial purposes is increasing day by day. In the middle of the 20th century, the chemical industry grew remarkably due to the huge availability of petroleum [2]. However, fast depleting fossil fuel reservoirs, fluctuating and increasing oil prices, and the hazardous impact on the environment have forced the researcher to find alternative raw materials which do not affect the environment and must be cheap, readily available, and efficient. Bio feedstocks including plant and animal biomass, agricultural wastes, forestry feedstock, algae and bacterial cellulose can be considered as an alternative for different chemicals and raw materials [3]. Although the utilizations of bio feedstocks are in early stages, it is expected to significantly raise the demand for bio feedstocks with the end of affordable fossil fuel around 2040 [4]. Already, United States Department of Energy has planned strategies to obtain 10% of starting chemicals from plant based renewable resources by 2020 and continue the plan to achieve the target of 50 % on 2050 [5] .

1.2. Current Position of Polyurethane Foams

Since the discovery of polyurethane foam (PU) in 1937, it has been developed into a multipurpose material that has many different physical states for various applications. Polyurethane can be produced as rigid foam, flexible foams, adhesives, elastomers and thermoplastic, that can be utilized in various applications such as construction, furniture, automobile, footwear etc. [6]. Polyurethane is the sixth most employed polymer and makes a 5 % contribution in the total polymer market [7]. Polyurethane can possess a wide range of properties with various physical characteristics, such as rigid, flexible, and elastomer, depending on the type of reactants used. Flexible polyurethane foams (FPF) are employed in furniture, automobiles, etc., while elastomer PUs are used in making shoe soles, etc. Rigid polyurethane foams (RPFs), however, are contributing one fourth of the total PU market after flexible polyurethane foam [8]. RPFs are the mixture of polyurethane matrix and air, which results from the blowing agent. About 96% volume of the total PU is the space filled with gas. Rigid Polyurethane Foams are considered a promising candidate for thermal insulation, filling material in the field of construction because of the features of low thermal conductivity, low density, low moisture permeability, high compression, and the dimension stability. RPFs can also be used as a sealant. Furthermore, they are also used in refrigerators, aircrafts, and boat industries [9]. Other than these, Polyurethanes are also used in other applications, such as adhesive and sealants, coatings, and molded automotive parts, etc.

1.3. Development of Polyurethane

Polyurethane foams are basically produced by the reaction between an isocyanate and polyol. Most commonly, the isocyanates employed for the preparation of PU are bifunctional and, therefore, known as diisocyanate. The physical properties of the PU are influenced by the properties of the isocyanate on the molecular level. For instance, toluene diisocyanate (TDI) produced rigid PU, because of the presence of the benzene structures in the chain that restricts the chain movements. While the hexamethylene diisocyanate (HDMI) gives rise to a flexible PU. The reaction path that these reactions follow is known as a polyaddition reaction. A lot of other chemical ingredients are also required to make foams, such as catalyst, surfactant, and blowing agent.

The catalyst makes the foaming reaction faster, which is mainly helpful for economic reasons. The commonly used catalysts are amine-based or metal complex-based, which can be used separately or even combined. The metals in metal complex-based catalysts are usually zinc, lead, tin, bismuth, etc. However, tin and lead-based catalysts pose great danger to environment and health and more research is required in this area to develop harmless yet efficient catalysts.

Blowing agents are employed to regulate the cell size by releasing gases during the foaming process. A certain amount of blowing agent is required to produce foams with desirable characteristics. Otherwise, the foam mechanical characteristics and cell morphology are highly affected, making it more brittle and fragile. The blowing agent can be chemical or physical. The chemical blowing agent, such as water, reacts chemically with the other ingredients and produces gas in the form of bubbles. It reacts with isocyanate to form carbon dioxide bubbles. Using water as the blowing agent has various economic advantages, such as low cost, high efficiency, and environmental friendliness. The physical type of blowing agents is mostly comprised of gases. These types of blowing agents are introduced into the foaming process by physical methods. The common type of physical blowing agents that are used extensively include, 1,4–diazabicyclo[2.2.2]octane, dimethylethanolamine, ,diethylenetriamine, triethylamine, etc.

Surfactant is used to increase the surface area of the pores arise due to the blowing agent and also provides structural stability to the foam by creating an emulsion, which helps in the adequate mixing of the reactants. In the processes other than foaming, the surfactants ensure the prevention of the bubbles by increasing the surface tension of the mixture to gain a proper mixing. The basic reaction steps for the preparation of polyurethane are displayed in **Figure 1.1** and **Figure 1.2**.

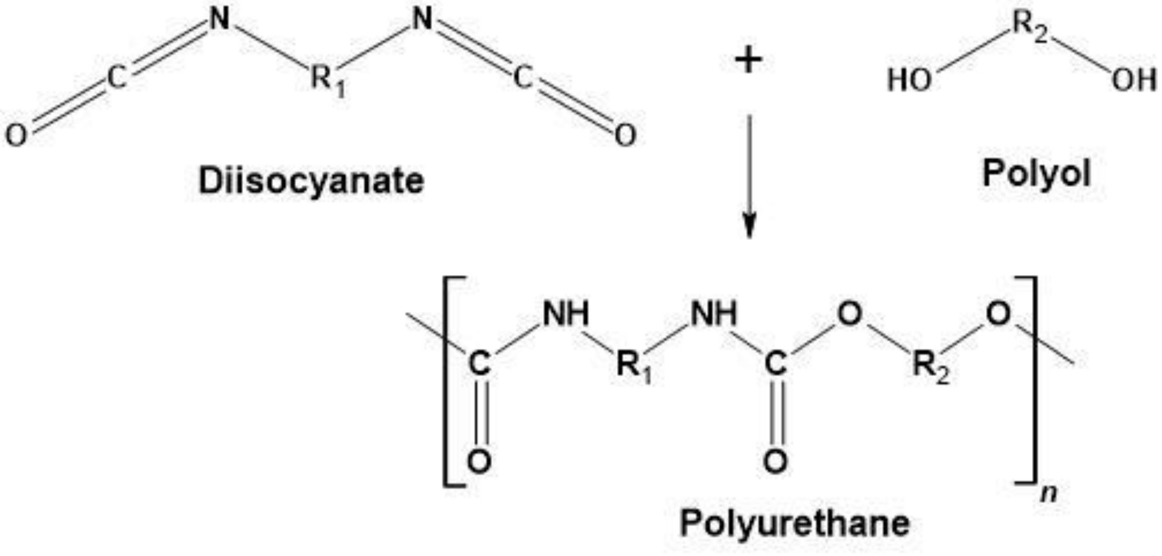


Figure 1.1. Polyol and diisocyanate reaction to produce polyurethane.

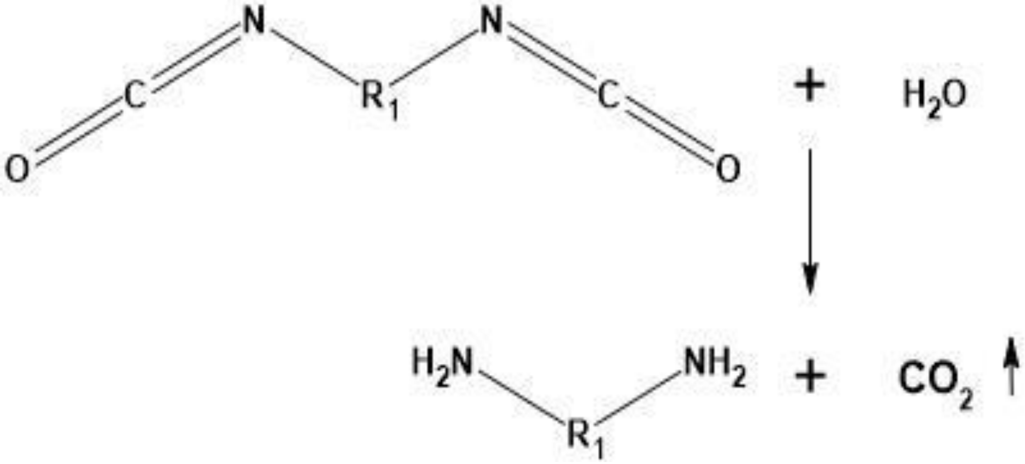


Figure 1.2. Water and diisocyanate reaction to produce CO_2.

1.4. Polyurethane from Bio-Based Materials

In recent times, bio-based polyols, which is the starting material for making polyurethane foams, has interested researchers due to the growing concerns about petrochemical usage. One of the main reasons is environmental pollution. The other reasons to look for the alternative are the deficiency of the petrochemicals, their fluctuating prices and comparatively similar efficiency of the bio-based and the petrochemical raw materials. Large-scale of research is being done to produce efficient bio-based alternative for polyols and diisocyanate, which are the basic raw materials for polyurethane foams production, to limit the use of petrochemical raw material.

Commonly, PU foams are synthesized by using petrochemical-based diisocyanate and many plant-based diisocyanate have been reported in different articles. Plant-based isocyanates are commonly obtained by reacting bromine with the triglyceride of the different plant seed oil and then introducing cyanate group by eliminating bromine by the action of AgNCO [10]. Hojabri and his colleagues successfully synthesized linear saturated diisocyanate from oleic acid and the prepared polyurethane foam sheets which indicated excellent physical properties comparable to the PU foams obtained from petroleum-based diisocyanate [11]. The main advantages of utilizing vegetable oil over conventional petrochemical materials are their reduced price and the voluminous availability.

1.5. Chemistry of Plant-Based Polyol

Oils extracted from different plants such as corn, rapeseed, soybean, castor, palm and so on, have different level of unsaturation present in the triglyceride molecules is an important factor to be considered. The unsaturation provides a path for attaching hydroxyl groups to the unsaturated triglyceride molecules. Different types of vegetable oils have been tested for the purpose of preparation of polyol for PU. These vegetable oils contain unsaturated triglyceride molecules that can be easily transformed into hydroxyl group to get polyol which can later reacts with diisocyanate to produce PU foams. The commonly utilized vegetable oils to produce polyurethane are Soybean oil [12, 14], castor oil [15, 16], rapeseed oil [17, 18], palm oil [19, 20] and corn oil [21].

Previously, vegetable oils have been processed to produce polyols for PU due to their advantages such as commercial competitiveness, viability, availability and to increase value of agricultural products. There are various methods to incorporate hydroxyl groups in the triglyceride to react with diisocyanate. Epoxidation [22]–[24], hydroformylation [25]–[27], ozonolysis [28], [29], and transesterification [30], [31] are the frequent methods to transform triglyceride unsaturation. But one of the main drawbacks of these synthetic routes is requirement of the high-priced catalysts for the reaction. Moreover, these processes are usually completed in several steps. Whereas thiol-ene chemistry provides straightforward, effective, and fast route to introduce hydroxyl group to the unsaturated molecules. In thiol-ene chemistry, thiols undergo free radical addition reaction with the double bonds and require ultraviolet radiation or heat to initiate the reaction [32]. The thiol-ene addition reaction is illustrated in **Figure 1.3**.

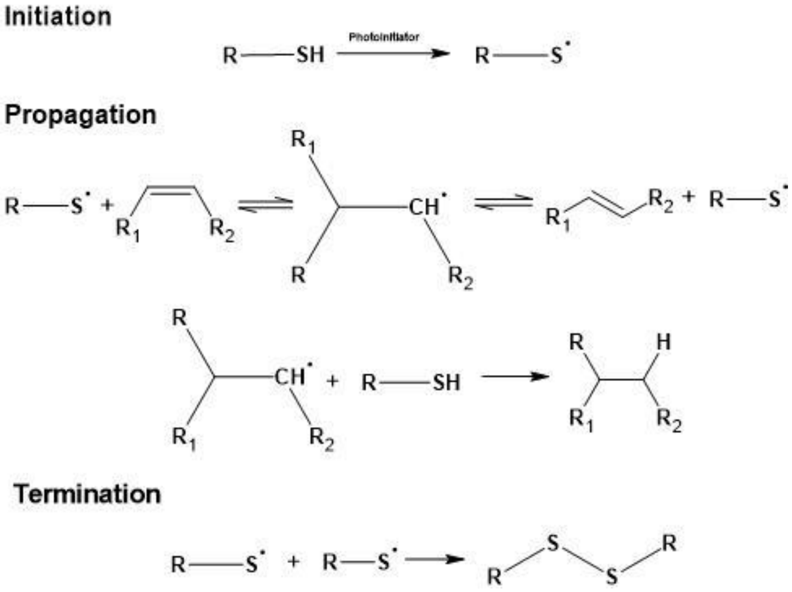


Figure 1.3. Mechanism of thiol-ene reaction.

Apart from the addition reaction to produce polyol, thiol-ene chemistry is employed to transform the chemical structure of the different plant-based oils for different applications. Thiol-ene chemistry is employed to enhance the friction resistivity of the oils [33]–[35]. It is an efficient route for crosslinking and oligomerization of different plant oil under ultraviolet radiation [36]–[38]. Thiol-ene chemistry is also used to produce fatty acid-based renewable monomers. These monomers are utilized to produce polyesters and polyanhydrides which can be degraded at a faster rate. The speedy degradation makes these types of polymers useful in medical applications [39], [40].

The physical properties of the PU depend on the type and characteristics of the polyol employed to prepare the foam. The polyol containing only 2 or 3 hydroxyl group with molecular weight of around 2000 to 10000 g/mol can produce an elastic PU while polyol having large number of hydroxyl group with low molecular mass between 300 to 1000 g/mol can produce considerably more rigid PU due crosslinking [41].

1.6. Flame-Retardant Polyurethane Foams

Polyurethane foams are prone to catch fire and have very low flame retardancy which is the most important disadvantage of the polyurethane foams and restrict most of the possible practical applications in different fields [42]. The low retardancy of flame in PU foams results from the existence of carbon, oxygen, and hydrogen within its structure. Moreover, high porosity of the polyurethane foams increases the burning rate [43]. To overcome these problems, various research has been done to determine the ways to enhance the flame retardancy of the polyurethane. Different elements, such as phosphorus, nitrogen, and aluminum and expandable graphite have been extensively studied by adding compounds comprising these elements in the PU and examining flame retardancy of PU [44]–[47]. Compounds containing phosphorus proved to be a more effective flame retarding agent.

1.7. Flame Retardant Material

The function of flame retardant materials is to make the product less vulnerable to fire. There are typically two classes of flame retardants that are used in the flame retardant polyurethane foams. One is the non-reactive classes, also called additive flame retardants. These types of flame retardants are not added into the material during its preparation but are included as additives at the end of the synthesis process. This class of flame retardants is economical but has drawbacks, which is due to the additive moving out of the polymer structure when included physically [48]. It weakens the structure of the polymer due to the adverse interaction between the additives and the polyurethane structure [49] .

For this reason, the use of a second class of flame retardants, known as reactive flame retardants, has been adapted. In contrast to additive flame retardants, reactive flame retardants are used during the preparation of the polyurethane foams and therefore they get integrated into the structure of polymer. Reactive flame retardants provide mechanical strength to the polymer and make them robust. But there are some restrictions to use these types of flame retardants by the European Union because these materials produce dangerous gases around these halogenated flame retardants. To circumvent with this issue, phosphorus-based flame retardants, which are also called halogen-free reactive flame retardants have been gaining great attention because of their advantage of not emitting any deadly gases and having a high efficiency of controlling fire

[50], [51] . DOPO (9.10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide), phosphine oxide and cyclic phosphates are the flame retardants that are mostly incorporated as phosphorus-based flame retardants [52]–[54].

In recent days, intumescent flame retardants are proving to be a good alternative to the halogenated flame retardants. These types of flame retardants expand and produce char when subjected to fire and do not let the fire to spread and shield the material [55]. Polyolefins are being investigated nowadays as an intumescent flame retardant because they have shown a favorable result to get the desired flame retardancy in polyurethane foams [56].

1.8. Objective of the Thesis

The main goal of this work is to prepare a PU foam from corn oil-based polyol to replace petrochemical-based material on an industrial level. Polyol was synthesized by single step, solvent-free and cost-efficient thiol-ene chemistry. Various important characteristics, such as hydroxyl number, viscosity, molecular structure, and molecular weight were determined by the different experiments to ensure that the desired properties of the polyol have been obtained for the preparation of polyurethane foams. To enhance the flame retardancy of the polyurethane foams two different type of flame retardants, such as TEP and TPP were employed. Different concentrations of these flame retardants were used to compare the effect on their thermal and mechanical properties of the polyurethane foam. Various tests and techniques, such as apparent density, closed cell content, horizontal burning test, scanning electron microscopy, compression test and thermogravimetric analysis were carried out to study structural, mechanical, thermal and flame retardant properties of the polyurethane foam.

CHAPTER II

EXPERIMENTAL DETAILS

2.1. Starting Materials

2.1.1. Polyol

Polyol, as is clear from its name, is actually an organic compound that has various hydroxyl functionalities attached to the main organic chains. It is also known as sugar alcohol. Various types of polyols obtained from different sources can be used for the preparation of PU foam, but the PU properties extensively depend on the type of polyol being used for making PU. In this work, vegetable oil-based polyol was prepared from corn oil and 2-mercaptoethanol. The locally available corn oil was procured from the nearby market. The 2-mercaptoethanol, structure is shown in **Figure 2.1,** is a water soluble, colorless liquid with the molecular mass of 78.13 g/mol. It degrades at the temperature of around 316.5 °F, and has a viscosity of 343 cP, and was procured from Acros Organic. To enhance the properties of the foam, Jeffol 520, which is a sucrose-based polyol, was also used in the synthesis of polyurethane foams. It was procured from Huntsman, USA, and used as it, without any modification. Jeffol 520 has a molecular mass of 539 g/mol and OH content of 520 mg KOH/g. It has the functionality of 5, viscosity of 27000 cps@25°C, and specific gravity of 1.18 @25°C.

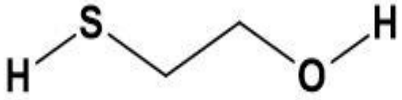


Figure 2.1. Structure of 2-mercaptoethanol.

2.1.2. Isocyanate

Isocyanate is a crucial ingredient for the preparation of polyurethane foams, which significantly affect the characterization of the prepared PU product. It has a functional cyanate group R-N=C=O (-NCO) attached to it. The isocyanate reacts with the -OH group of the polyol to produce a urethane bond by the course of addition reaction. The isocyanate is known to yield the hard domains in the resulting polymer structure due to the development of urethane bonds that can create hydrogen bonding with the surrounding polymeric chains and restrict moveability. Furthermore, the industrial isocyanates used for producing rigid PUs are usually aromatic because they contain a rigid structure in their chemical configuration. Mostly, two types of isocyanates are used, which are Methylene Diphenyl Diisocyanate (MDI) and Toluene Diisocyanate (TDI). In our research, (MDI), also known as Rubinate M diisocyanate, is used, whose chemical structure is displayed in **Figure 2.2**. The content of -NCO in the procured MDI was found to be 31 % with the equivalent wt. of around 135. It has a viscosity of around 210 cp at 25 °C, functionality of 2.7, and was supplied Huntsman, USA.

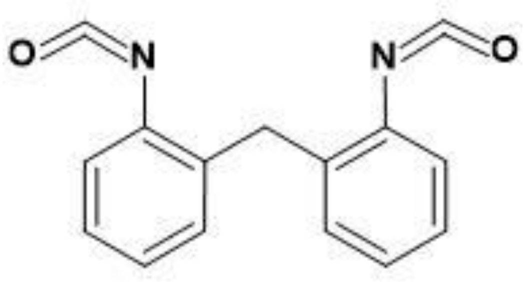


Figure 2.2. Structure of MDI.

2.1.3. Catalyst

The catalyst is the compound that alters the rate of any chemical reaction but does not itself take part in the final product. They do not change the chemical composition of the product and can be taken out of the reaction mixture after the completion of the reaction. Two basic types of catalysts are normally used which are the positive catalyst and the negative catalyst. The positive catalyst is used to accelerate the rate of any chemical reaction, which has low rate of reaction while the negative catalyst is used to slow down the rate of reaction. Catalysts have significant effect on various type of polymerization, such as cationic, anionic, and free radical polymerization. The rate of reaction and the characteristic of the polymer depends on the type of catalyst used. The selection of catalyst plays an important role for the preparation of polyurethane foams as well because the reaction rate between the diisocyanate and the polyol/water is considerably a low. So, the catalyst selection is an essential step and must be done carefully.

The catalysts that are generally used are organometallics and amine-based catalysts. Amine catalysts affect the blowing part of the reaction, while the gelling process in polyurethane preparation is usually performed in the presence of organometallics catalyst.

In this work, Dibutyltin Dilaurate (DABCO® T-12) catalyst was employed. DABCO® T-12 aids in the preparation of flexible and rigid PU foams, adhesive, sealants, and coatings and was obtained from Air products, USA. The other catalyst employed in this study is Niax™ A-1 and was also procured from Air products. The chemical structure for both of the catalysts is displayed in **Figure 2.3**.

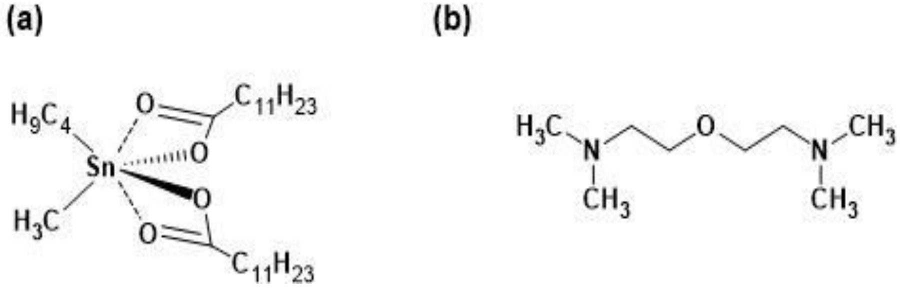


Figure 2.3. Chemical structure of (a) dibutyltin dilaurate (DABCO® T-12) and (b) bis-2-dimethyl-aminoethyl ether (Niax A-1).

2.1.4. Surfactants

Surfactant is the material used for reducing the interfacial tension between non-miscible materials. Surfactants are one of the important compounds for the production of polyurethane foams. There are several reasons of using surfactants in foam production such as enhancing solubility and improving property by increasing uniformity in the PU foam structure. But, most importantly, it is used to promote the compatibility of the immiscible reactants. The study involves the reaction between the hydroxyl group and isocyanate, which produces the heterogeneous form because of less interaction between their molecules. To avoid such a scenario, surfactants are used, which ensures the proper dispersion and hinders the defoaming effect during the foam production, hence, the stability of the PU foams are increased. They provide strength to the foam structure by maintaining size of the pores and closed cell characteristics. The use of surfactants also inhibits flaws in the foams such as generation of pinholes and sink marks.

In this work, B-8404 was used for the foam production. It is a silicon-based surfactant and provides excellent structural stability to the foam. It was procured from Evonik, USA and was utilized as received without any alteration.

2.1.5. Blowing Agent

Blowing or liberation of the gas is considered an important phase during foaming. As already discussed above gas liberations are normally done with the help of two types of blowing agents. One is the chemical gas formation, which is due to the employment of the chemical blowing agent, which chemically reacts and produces gases. The other one is the physical blowing agent that is typically present in gaseous state and injected during the foaming process and does not react chemically. In this experiment, distilled water is employed as the chemical blowing agent because if its high viability, low cost, and environmental friendliness. During the foaming process, the reaction between water and the isocyanate results in the production of unstable carbamic acid, which breaks down into the amine-based compound and CO_2. The produced CO_2 resulted in the creation of pores and provided a porous structure to the foam. The whole reaction is illustrated in **Figure 1.2.** The distilled water was procured from the local market, Pittsburg, KS, USA.

2.1.6. Flame Retardant

Flame retardants are added to the PU foams to minimize the burnability of the foam. There are various types of flame retardants present in the markets. These flame retardants can be classified into two main groups. One is the reactive flame retardant and the other one is the non-reactive flame retardant. Some are available in solid form, such as melamine trihydrate, aluminum trihydrate and graphite. The others are the phosphorus-based compounds in the form of phosphates and phosphonate. The effect of reducing fire through the reactive flame retardant can be divided into three phases, such as gas phase, condensed phase, solid phase. The action of the flame retardant in the gas phase comprises the emission of volatile radicals, such as $PO^\bullet$, $PH_2^\bullet$, $Cl^\bullet$, $Br^\bullet$, etc. These volatile radicals help in neutralizing the highly reactive $H^\bullet$ and $OH^\bullet$ species. These species react with polymeric material by undergoing a highly exothermic reaction, which results in heat and extension of fire. Therefore, the volatile radicals stop the propagation of these species into the unburnt foam by neutralizing these highly reactive species into stable volatile compounds or into other forms of compound with lower reactivity. The condensed phase mechanism undergoes the formation of a char layer that helps in the shielding the unburnt polyurethane from the oxygen and radical species, which eventually helps in stopping the fire. Furthermore, some of the flame retardants work in solid phase, which includes the dripping of the burning part of the material that separates the burning part of the foam from the unburnt foam and stops the propagation of fire.

In this work, two phosphorus-based flame retardants, such as TEP (**Figure 2.4**) and the TPP (**Figure 2.5**), are being used in the polyurethane foams. TEP is a colorless liquid and has a refractive index of 1.405 – 1.407, density of 1.065 – 1.074 g/cm^3 and viscosity of 1.7 mPa.s at 20 °C, While TPP is a colorless solid having a vapor pressure of 1 mmHg (193 °C) and boiling point of 244 °C and a density of 1.184 g/ml at 20 °C.

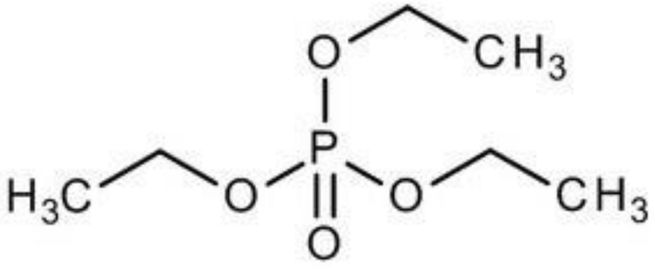


Figure 2.4. Structure of triethyl phosphate (TEP).

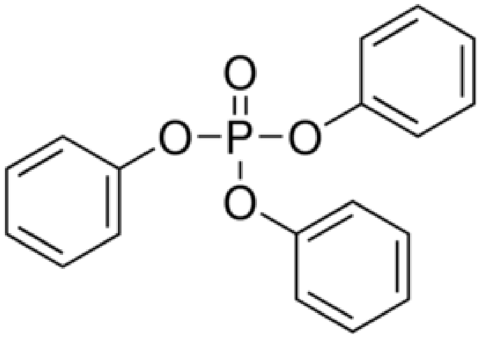


Figure 2.5. Structure of triphenyl phosphate (TPP).

2.1.7. Photo-Initiator

The function of a photo-initiator is to trigger the polymerization reaction by absorbing ultraviolet radiation. When a photo-initiator is radiated with UV radiation, it breaks and produce a reactive species that helps in initiating the polymerization reaction. One main advantage of polyurethane foams formed by using photo-initiators is that it already has little chemical retardancy and has a rigid foam structure. In addition to this advantage, there are a few obstacles like immiscibility concerns, bad smell and discoloration. The rate of polymerization initiated by employing photo-initiator depends on the amount of photo-initiator employed and the intensity of ultraviolet light. These are the two factors that are responsible for the free radical generation that initiate the reaction later. Hydroxy-cyclohexyl phenyl ketone and 2-hydroxyl-2-methyl-1-phenylpropane-1-one are extensively employed as photo-initiator.

In this study, 2-hydroxy-2-methyl propiophenone was employed as a photo-initiator (**Figure 2.6**). It has a boiling point of 102-103 °C at 4 mmHg, density of 1.078 g/ml @ 25°C and has a refractive index of 1.53.

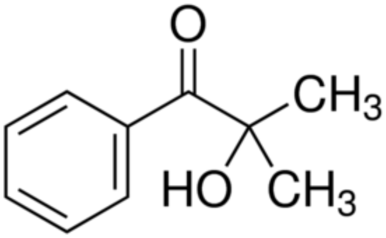


Figure 2.6. Structure of 2-hydroxy-2-methyl propiophenone.

2.2. Production of Corn Oil-Based Polyol

Polyol was produced from corn oil by reacting corn oil (CO) and the 2-merceptoethanol (ME) by a thiol-ene reaction, which took place under ultraviolet radiation, as shown in **Figure 2.7**. Firstly, corn oil (200 g) was mixed with ME (149 g) with double bond molar ratio of 1:4. Then, 2-hydroxy-2-methyl propiophenone 2.5 wt. % was incorporated as a photo-initiator in the reaction mixture. The reaction started as the reactor placed under the ultraviolet radiation of intensity of 365 nm at ambient temperature. The reaction took place under strong stirring with the help of magnetic stirrer at 300 rpm for a period of 6 hours at room temperature. As the reaction completes, surplus amounts of 2-merceptoethanol were recovered by the purification process with the help of rotavapor evaporator.

The reaction between the CO and ME that produces the corn oil-based polyol is illustrated in F**igure 2.8.** The ultraviolet light produced thiol free radical and hydrogen radicals by dissociating 2-mercaptoethanol in the presence of a photo-initiator. The reactive thiol free radical generated by photo-initiation of ME reacted with C=C of corn oil and formed an intermediate carbon-centered species. This carbon centered reactive radical helped in propagating the reaction by getting transferred to another thiol group and form another reactive thiol radical, which can get attached to another C=C bond. As the carbon-centered radical shifted from the intermediate, we got the corn-based polyol (CO-ME). The reaction steps for this reaction are shown in **Figure 2.9.**

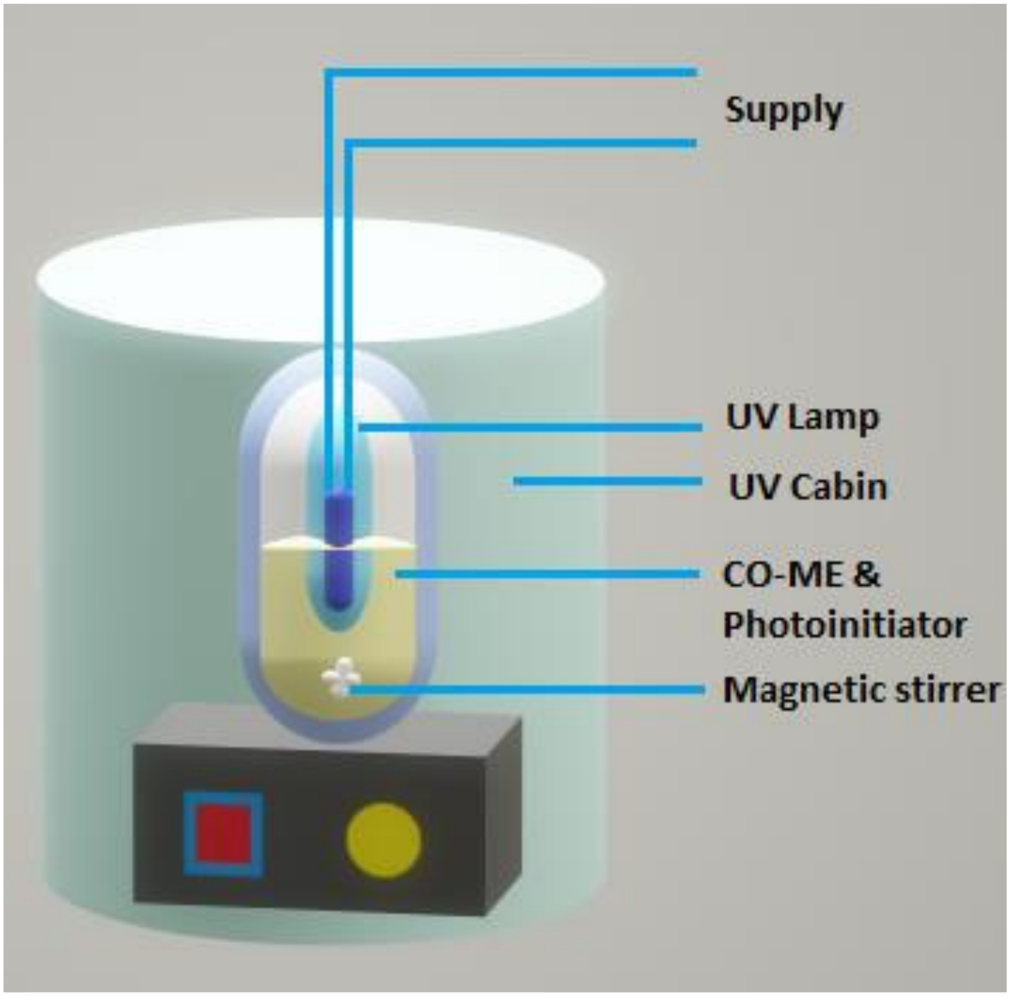


Figure 2.7. Schematic diagram of the reaction design for the production of the polyol. Adopted from [57].

2.3. Characterization of Polyol

The CO-ME polyol obtained from the thiol-ene reaction was characterized by the techniques discussed below.

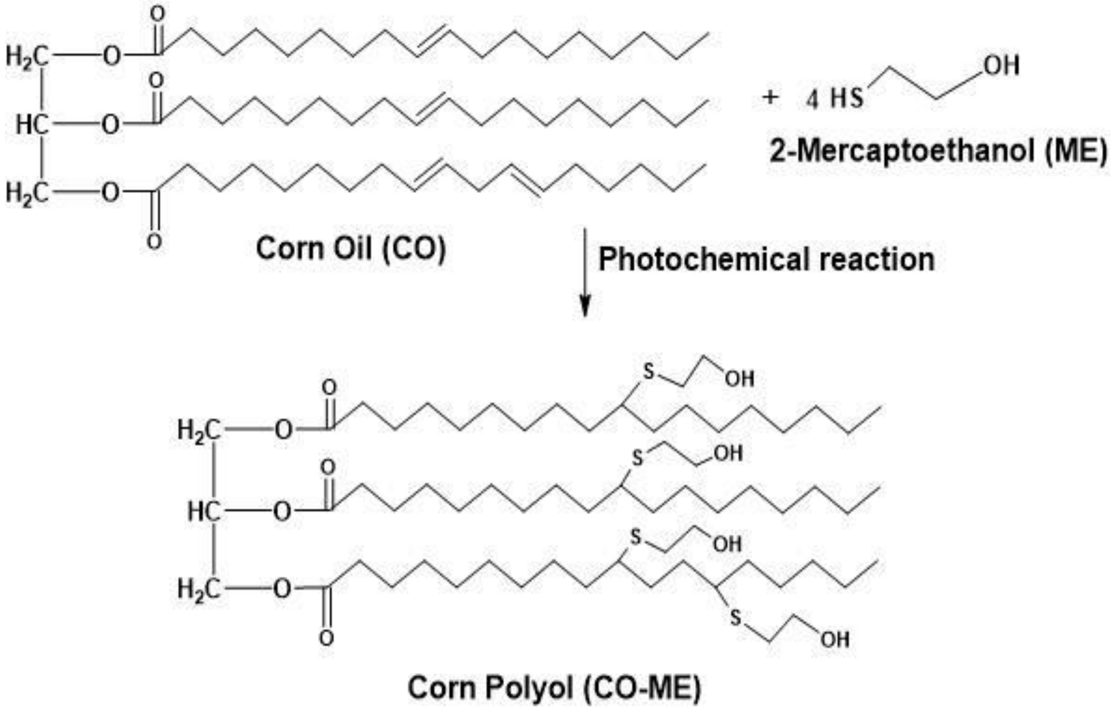


Figure 2.8. The chemical reaction for the production of corn oil-based polyol.

2.3.1. Hydroxyl Number

This procedure is employed to estimate the number of hydroxy groups present in the produced CO-ME polyol by the phthalic anhydride/pyridine (PAP) method. The estimation of the number of hydroxyls attached to the polyol is an essential characterization because this hydroxyl group will further react with isocyanate to produce polyurethane foams. So, it is important to calculate the number of OH groups before the preparation of foams.

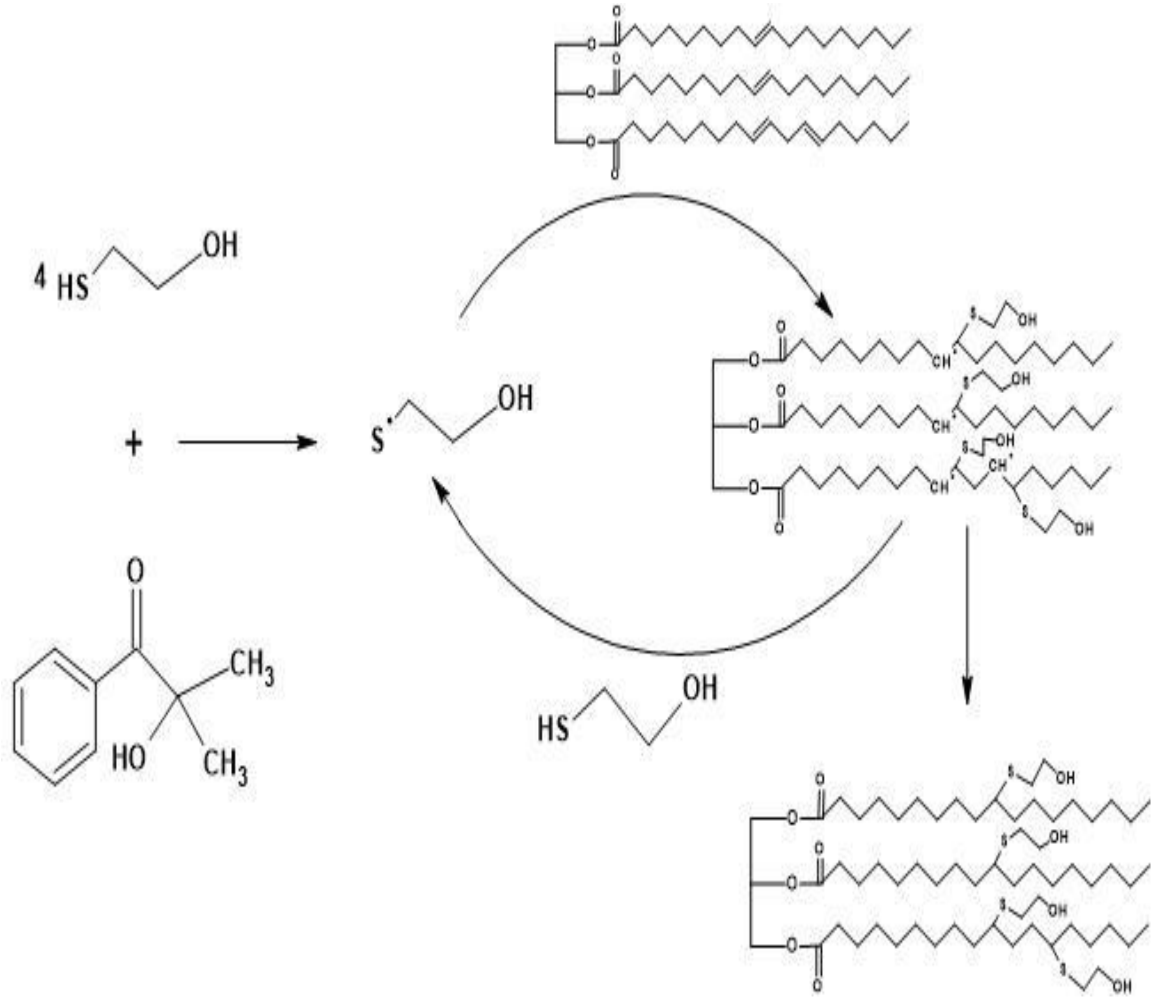


Figure 2.9. Reaction scheme of thiol-ene synthesis of CO-ME polyol.

This PAP method is standardized by the ASTM D 4274 procedure for the calculation of OH number. The OH number is calculated by determining the titration volume of sample in hydroxyl reagent using 1.0 N NaOH solution before (V_0) and after (V) the titration. Then, the calculated volumes are used in the equation:

$$\mathrm{OH\#} = \frac{56.11\mathrm{x}1.00\mathrm{x}(\mathrm{Vo}-\mathrm{V})}{\mathrm{w}}\ (\frac{\mathrm{mgKOH}}{\mathrm{g}}) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The hydroxyl reagent was synthesized by dissolving 148 g of phthalic anhydride and 4 g of imidazole in 1 liter of pyridine. Then, the 0.4 mg of the sample and 10 mL of the reagent was taken in a closed bottle and placed in the oven at 100 °C for about 70 minutes with agitation after every 15 minutes. The sample was then allowed to cool. After cooling, 10 ml of water and 20 ml of isopropanol were added to the solution with few drops of phenolphthalein, which acted as an indicator. The prepared solution was well stirred and was titrated with 1 N solution of NaOH. The initial volume of the solution was noted and denoted as "V_o". As the color of the solution turned light pink, the final volume of the solution was noted and denoted as "V". These two volumes were then used in the equation 1 to calculate the hydroxyl number of the polyol.

2.3.2. Viscosity

The viscosity is the characteristic of the fluid, which is a measure of the resistance faced by the fluid against the direction of its flow. Viscosity is considered as an essential characteristic because it tells the final characteristic of the resulting polymer. Normally, viscosity is evaluated at a range of shear stresses. It is essential for the prepared material to offer high viscosity at low shear rate to provide strength to the structure and to avoid the material collapsing. But the viscosity of the material should be low at high shear stress to provide ease during synthesis of the foams. In this work, viscosity was measured by a AR 2000 dynamic stress rheometer (TA instrument, USA) at 25 °C. It is a cone plate rheometer inclined at an angle of 2° and having a cone diameter of 25 mm. This instrument is capable of increasing the stress from 1 to 2000 Pa. It is evident that the polyol having high viscosity has a higher molecular weight, but less viscous polyol allows appropriate mixing of the polyol with different polymers.

2.3.3. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectroscopy is employed to find out the changes in functional group that occurred during the thiol-ene reaction. In FTIR spectroscopy, the sample is radiated by infrared radiations, which get absorbed by the sample and achieve a excited state and in turn emits the spectrum when coming back to the ground state. These spectrums are the spectral fingerprints of the molecular structure of the sample. Therefore, any modifications in the peaks of the FTIR represents the transformation in the functional group of the corn oil molecules during the thiol-ene process. The FTIR spectroscopy is done before and after the thiol-ene reaction to find out any change in the functional group of the sample. The FTIR spectroscopy is done by a Shimadzu IR affinity-1 spectrophotometer at ambient temperature.

2.3.4. Gel Permeation Chromatography (GPC)

Gel permeation chromatography is normally used to calculate the estimated molecular weight of the polymer. It is also called size exclusive chromatography. In this work, GPC was used to calculate the average molecular weight of the polyol. The GPC used in this work is a product of Waters (Milford, MA, USA). It is comprised of 300 x 7.8 mm phenogel columns with various pore sizes of 50, 102, 103 and 104 Å. Tetrahydrofuran was employed as an effluent solvent, which was controlled at 30 °C and a flow rate of 1 mL/minute.

2.4. Synthesis of Flame Retardant Rigid Polyurethane Foam

Rigid polyurethane with the flame retardant characteristics is prepared by using isocyanate, surfactants, catalyst, water, and the polyol which has already prepared by thiol-ene reaction.

Various compositions of flame retardant material, such as TEP and TPP, were added along with all other ingredients with different compositions to get the best flame retardancy, as shown in the **Table 2.1.** and **Table 2.2.** All the ingredients in the quantity mentioned in the **Table 2.1** were mixed together followed by stirring at 3000 rpm to get a homogenous mixture. Finally, methylene diphenyl diisocyanate (MDI) weighting 28.8 g was added to the homogenous mixture and stirred well at 3000 rpm a few seconds until blowing of the foam is observed. Different samples with different amount of flame retardant were synthesized and labeled, as shown in the **Table 2.1** and **Table 2.2**. The foams were allowed to cool down at ambient temperature until they stopped growing and become rigid. After that, the foams were allowed to cure by placing them at the ambient temperature for about a week.

Table 2.1. Formulation for synthesis of TEP-containing polyurethane foams.

Compound	Jeffol-520 (g)	CO-ME (g)	Niax A-1 (g)	Water (g)	T-12 (g)	Tegostab B-8404 (g)	Diisocyanate (g)	TEP (wt. % to the total weight)
E-0	10	10	0.14	0.8	0.04	0.4	28.8	0
E-1	10	10	0.14	0.8	0.04	0.4	28.8	0.9865
E-2	10	10	0.14	0.8	0.04	0.4	28.8	1.953
E-3	10	10	0.14	0.8	0.04	0.4	28.8	3.832
E-4	10	10	0.14	0.8	0.04	0.4	28.8	5.641
E-5	10	10	0.14	0.8	0.04	0.4	28.8	7.382
E-6	10	10	0.14	0.8	0.04	0.4	28.8	9.061
E-7	10	10	0.14	0.8	0.04	0.4	28.8	10.680
E-8	10	10	0.14	0.8	0.04	0.4	28.8	12.242
E-9	10	10	0.14	0.8	0.04	0.4	28.8	13.750
E-10	10	10	0.14	0.8	0.04	0.4	28.8	15.207
E-11	10	10	0.14	0.8	0.04	0.4	28.8	16.616
E-12	10	10	0.14	0.8	0.04	0.4	28.8	19.298

2.5. Characteristics of Rigid Polyurethane Foam

After the curing process of the foams, all the foams were cut into various size based on the testing. The samples were then characterized by using various methods, which are discussed below.

Table 2.2. Formulation for synthesis of TPP-containing polyurethane foams.

Compound	**Jeffol-520 (g)**	**CO-ME (g)**	**Niax A-1 (g)**	**Water (g)**	**T-12 (g)**	**Tegostab B-8404 (g)**	**Diisocyanate (g)**	**TPP (wt. % to the total weight)**
E-0	10	10	0.14	0.8	0.04	0.4	28.8	0
E-1	10	10	0.14	0.8	0.04	0.4	28.8	0.986
E-2	10	10	0.14	0.8	0.04	0.4	28.8	1.953
E-3	10	10	0.14	0.8	0.04	0.4	28.8	3.832
E-4	10	10	0.14	0.8	0.04	0.4	28.8	5.641
E-5	10	10	0.14	0.8	0.04	0.4	28.8	7.382
E-6	10	10	0.14	0.8	0.04	0.4	28.8	9.061
E-7	10	10	0.14	0.8	0.04	0.4	28.8	10.680
E-8	10	10	0.14	0.8	0.04	0.4	28.8	12.242
E-9	10	10	0.14	0.8	0.04	0.4	28.8	13.750
E-10	10	10	0.14	0.8	0.04	0.4	28.8	15.207
E-11	10	10	0.14	0.8	0.04	0.4	28.8	16.616
E-12	10	10	0.14	0.8	0.04	0.4	28.8	19.298
E-13	10	10	0.14	0.8	0.04	0.4	28.8	23.013
E-14	10	10	0.14	0.8	0.04	0.4	28.8	26.400

2.5.1 Apparent Density

The apparent density of the foams was determined in accordance with the standard ASTM D1622. The density of the foams must be in the range of industrial standard, which is from 30 to 50 kg/m^3. The apparent density is calculated by the taking the average between the top and the middle section of the foam. To determine the density, the cylindrical form of the foams was used.

2.5.2. Closed Cell Content

The determination of the closed-cell content is an important characteristic of the foam because it is used to measure the thermal insulation properties of the foams. To get efficient thermal insulation, the closed-cell content of the foam must be high. The closed-cell content of the synthesized foams was evaluated by using an Ultra pycnometer (Ultra foam 1000) in accordance with the ASTM D 285.

2.5.3. Compressive Test

The compression characteristic is another important parameter, which measures the mechanical strength of the synthesized foam. For compression testing, the foams were cut into a rectangular shape in the dimension of 50 x 50 x 25 mm. The compression property is determined at 10 % strain by using Q-test 2-tensile machine (MTS, USA) in accordance with the ASTM D 1621. The compression force was exerted at a strain rate of 30 mm/min.

2.5.4. Thermogravimetric Analysis (TGA)

TGA is employed to examine the thermal behavior of the foam and is done to find out the approximate temperature which the foam can resist before degradation. It is done by evaluating the reduction in weight of the foam as the temperature changes from room temperature to 600 °C under nitrogen and air. The heating rate was set at 10 °C/min. The thermogravimetric analysis was done with TGA Q500.

2.5.5. Horizontal Burning Test

The flame retardant property is a critical parameter in polyurethane foam and the study of the flame retardancy is significant in this work. For this reason, the horizontal burning test of the foam was conducted in accordance with standard ASTM D 4986-98. The test was conducted by putting the sample on fire for 10 s. The standard sample size for the burning test is 150 x 50 x 12.5 mm (length x width x height). The burning time and the weight loss before and after the exposure of the flame were documented.

2.5.6. Scanning Electron Microscopy

Microstructure of the cells and the cell size distribution of the foam were detected by using a phenom G2 Pro Scanning Electron Microscope (SEM), Netherlands. To prevent the charging effect at the time of imaging, the gold sputtering was carried out on all the samples.

CHAPTER III

RESULTS AND DISCUSSION

3.1. Properties of Polyol

The properties of the polyol, such as hydroxyl number and viscosity are essential in determining the reactiveness of the polyol with the diisocyanate. The chemical properties of the polyol were obtained through FT-IR and GPC. The results obtained from these studies about the polyol are discussed below in detail.

3.1.1. Hydroxyl Number

The produced polyol was tested for the hydroxyl number, which is a measurement of the amount of KOH (in milligrams) equivalent to the number of OH functional group attached to the unit weight of polyol. The higher value of OH number suggests the superior reactiveness of the polyol. In this work, the OH value of the synthesized polyol was found to be 174.61 mg KOH/g, which is close to the previous study [21]. This indicates efficient transformation of the corn oil into polyol.

3.1.2. Viscosity

The polyol production progress can also be associated with the rise in the viscosity of the reactants. At the start of the reaction, the viscosity of the corn oil was noted to be 0.06464 Pa.s and as the reaction proceed towards completion, the viscosity of the resulting polyol increased to 2.054 Pa.s. However, the viscosity of the commercially available (Jeffol 522 polyol), was found to be 26.58 Pa.s. Since there is an obvious increment in the viscosity from the corn oil to the polyol, the final viscosity of the polyol is low from the point of view of processing and blending and hence permitted smooth processing for polyurethane foam.

3.1.3. Fourier Transform Infrared Spectroscopy

The structural characteristics of the prepared polyol were analyzed through FTIR spectra. The FTIR data of the reactant and the product help us understand the reaction, which aids understanding the reaction mechanism by observing the raw materials and the final polyol spectra, as shown in **Figure 3.1.** The peak in the FTIR data of polyol around 3450 cm^{-1} represents -OH group, which is an essential characteristic of the polyol. Another peak in 2-mercaptoethanol spectrum at around 2552 cm^{-1} is related to S-H bond stretching. The absence of this peak in the polyol spectrum shows that the reaction involving 2-mercaptoethanol took place and it completely consumed during the process to produce polyol. All the spectrum data obtained in this study has close resemblance with the previous works. Therefore, through FTIR study, it is confirmed that the reaction took place as expected.

3.1.4. Gel Permeation Chromatograph

GPC was employed to find out the molecular weight of the resulting polymer using separation technique depending on their molecular size. Compounds having higher molecular weight comes out fast from the column as compared to the low molecular weight compounds. The column is filled with porous beads that capture the low molecular weight compound and hence increase its retention time. Similarly, compounds having high molecular weight find less resistance inside the column and comes out fast, hence, their retention time is low. This technique allows investigating the change in the molecular weight of the reactants and help predict the completion of the reaction. In this study, the resulting polyol has higher molecular weight as compared to reactants, such as corn oil and 2-mercaptoethanol. Hence, the retention time of the polyol is low as compared to the other reactants, as shown in **Figure 3.1**.

The corn oil and 2-mercaptoethanol have the retention time of 35 and 40 minutes, respectively. However, polyol took 33 minutes to come out of the column, which is less than the two initial reacting species. The peak noted at around 34 minutes is due to the unutilized double bonds that corn oil exhibited in its interiors. However, no peak for the

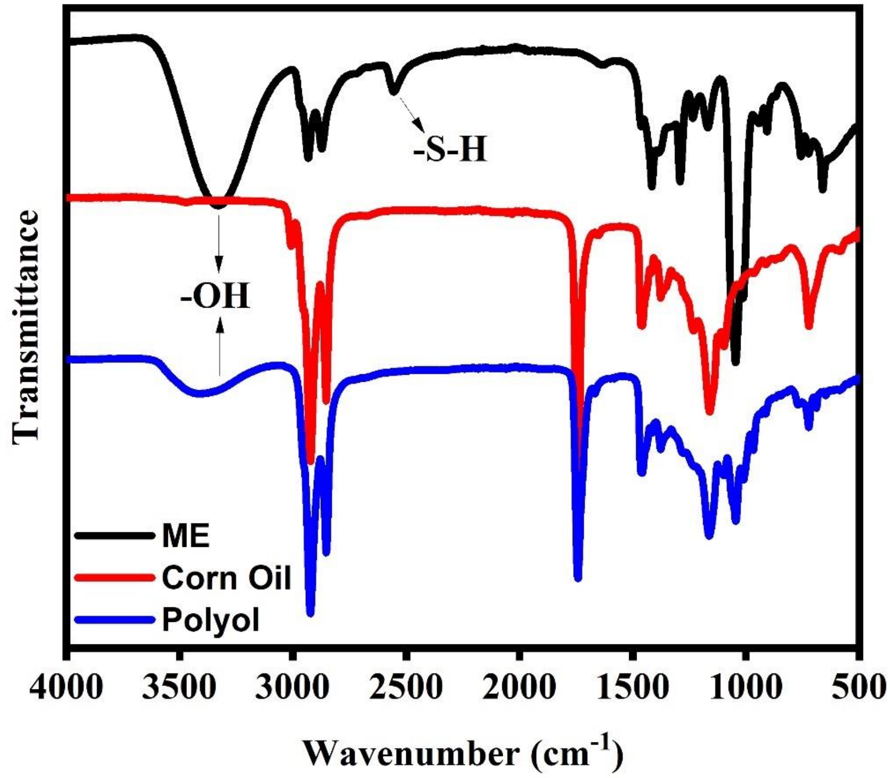


Figure 3.1. FTIR of 2-mercaptoethanol, corn oil, and polyol.

2-merceptoethanol is observed, which indicates that the reaction consumed all the 2-mercaptoethanol and the reaction moved in a forward direction. The GPC analysis also indicates that there are no impurities present in the resulting polyol.

3.2. Properties of Corn Oil-Based Polyurethane Foams

The synthesized polyol with various significantly demanded physical properties are employed to prepare polyurethane foams along with the different quantities of the flame

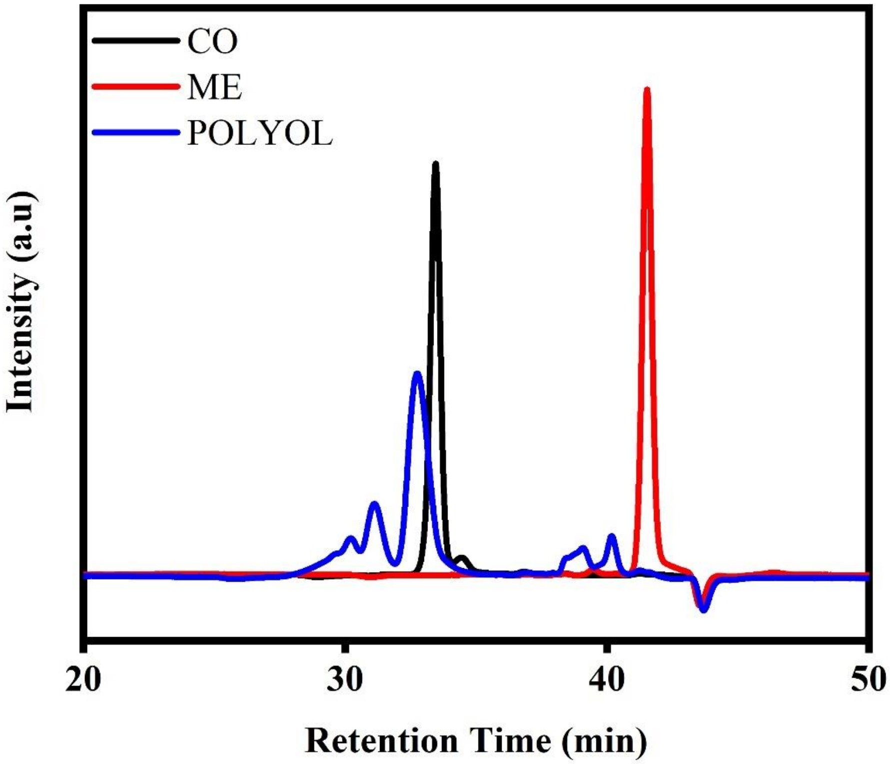
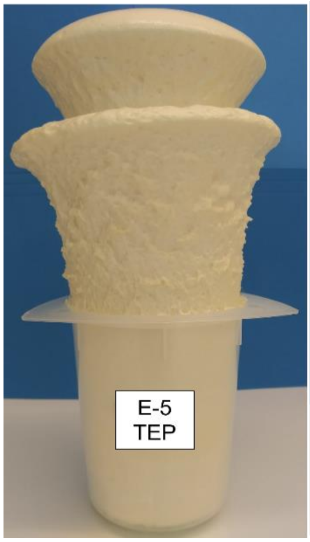
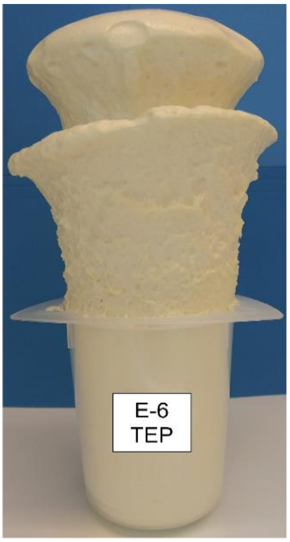


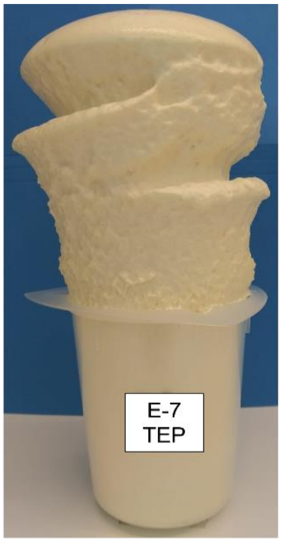
Figure 3.2. GPC of corn oil, 2-mercaptoethanol, and polyol.

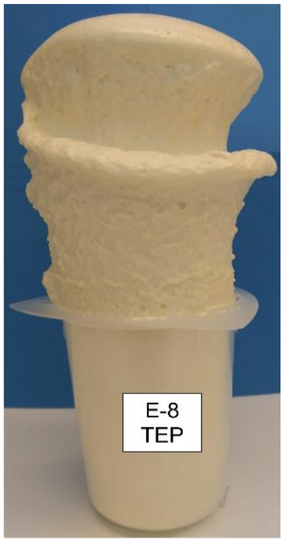
retardant material, such as TEP and TPP. The pictures of the synthesized foams with TEP and TPP are displayed in **Figure 3.3** and **Figure 3.4**. The prepared foams displayed regular growth and possessed clearly defined morphology, which is appropriate for industrial application.

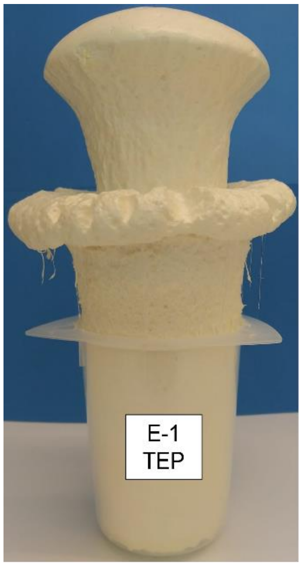
Various studies were carried out for analyzing the physical properties of the foam. These tests include closed cell content, thermogravimetric analysis, apparent density, compression, cell size distribution, horizontal burning study. These characterizations are important in order to analyze the mechanical and thermal properties of the prepared foam. The results acquired from each test are discussed below in detail.

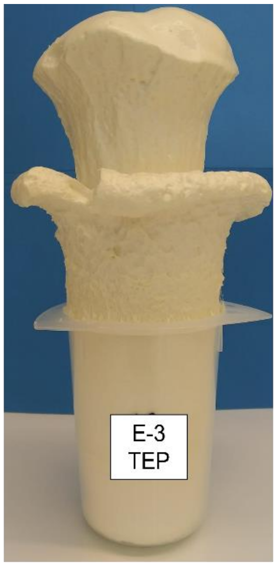












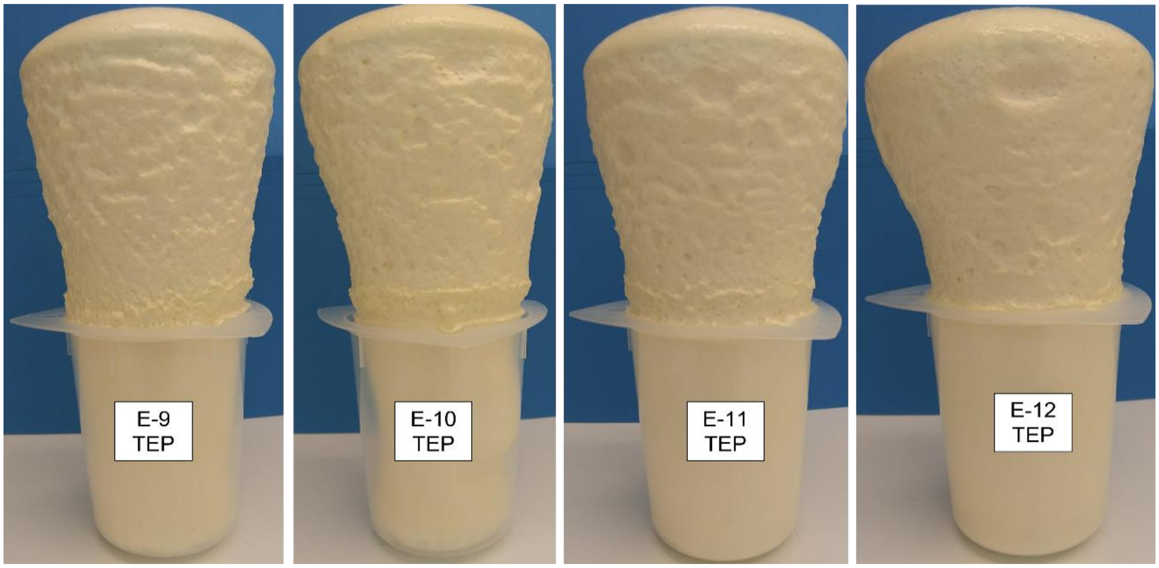
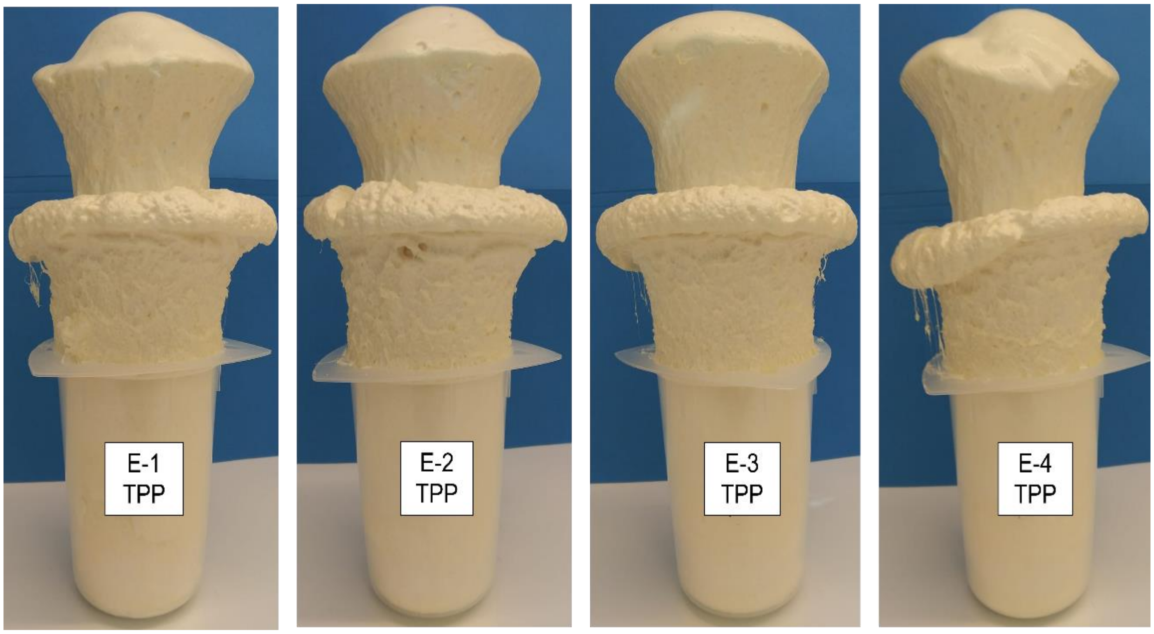


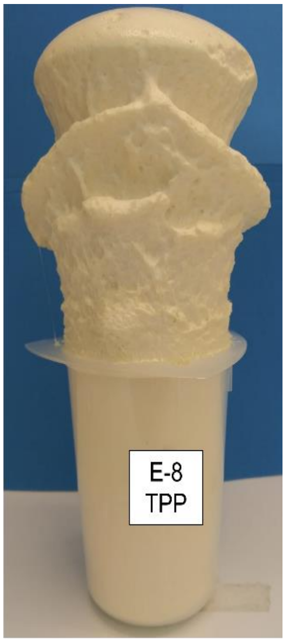
Figure 3.3. Photographs of as synthesized foams with different proportion of TEP.

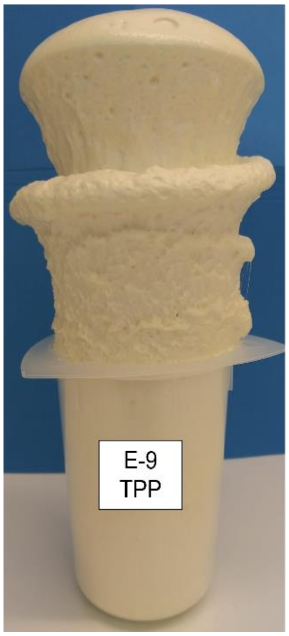


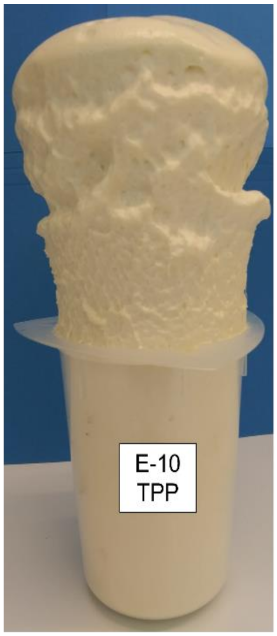

E-5
TPP

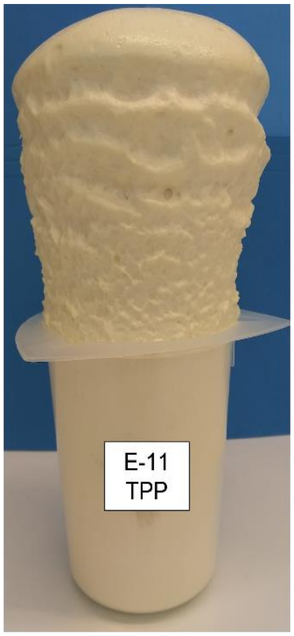

E-6
TPP


E-7
TPP


E-8
TPP


E-9
TPP


E-10
TPP


E-11
TPP


E-12
TPP

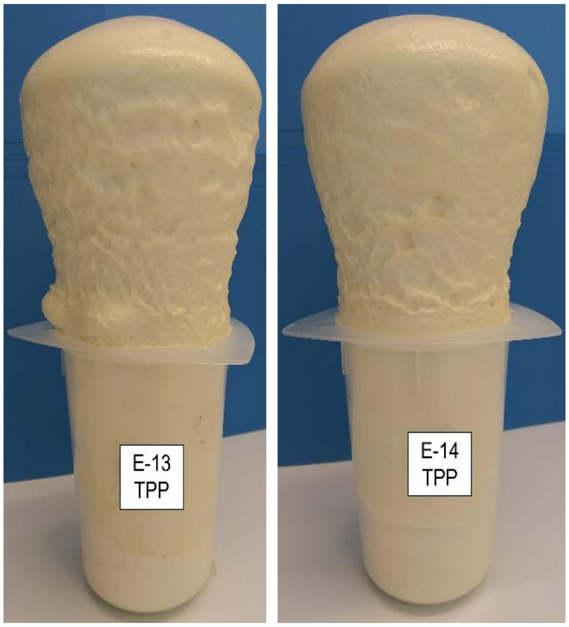


Figure 3.4. Photographs of as synthesized foams with different proportions of TPP.

3.2.1. Apparent Density

The apparent density of the foam is an important parameter, which directly tells the physical and mechanical properties of the synthesized foam. Furthermore, the utilization of the polyurethane foam is decided by its density. The accepted density of the polyurethane foams for commercial purposes is from 30 to 50 kgm^{-3} [90]. In this study, the density of the prepared polyurethane foams was obtained from test samples cut in cylindrical and square shapes. The results of density measurement of all the samples prepared from TEP and TPP are shown in **Figure 3.5** and **Figure 3.6**, respectively. The sample with highest level of TEP (19.29 wt. %) displayed the highest density and the sample with 0.5 wt. % of TEP showed the lowest density. However, the addition of TEP into the formation didn't affect the density of the prepared foam significantly.

Furthermore, samples with 0 and 26.4 wt. % of TPP showed the lowest and the highest densities, respectively. The significantly increasing trend can be seen in **Figure 3.6,** with the addition of TPP into the formulation. The increase in density could be the result of incorporation of the solid TPP which stop the rising of the foam, as can be seen in **Figure 3.6**. The addition of TPP reduced the foam height which ultimately increased the foam density.

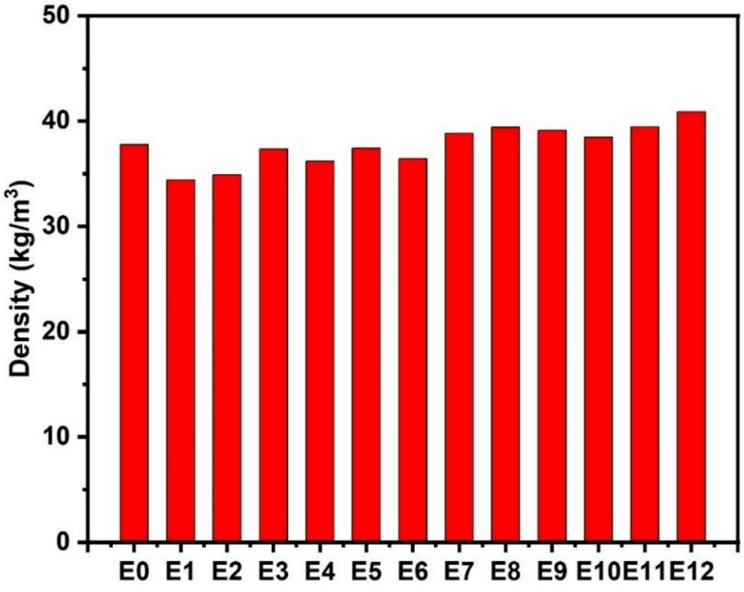


Figure 3.5. Density of corn oil-based foams with different percentage of TEP.

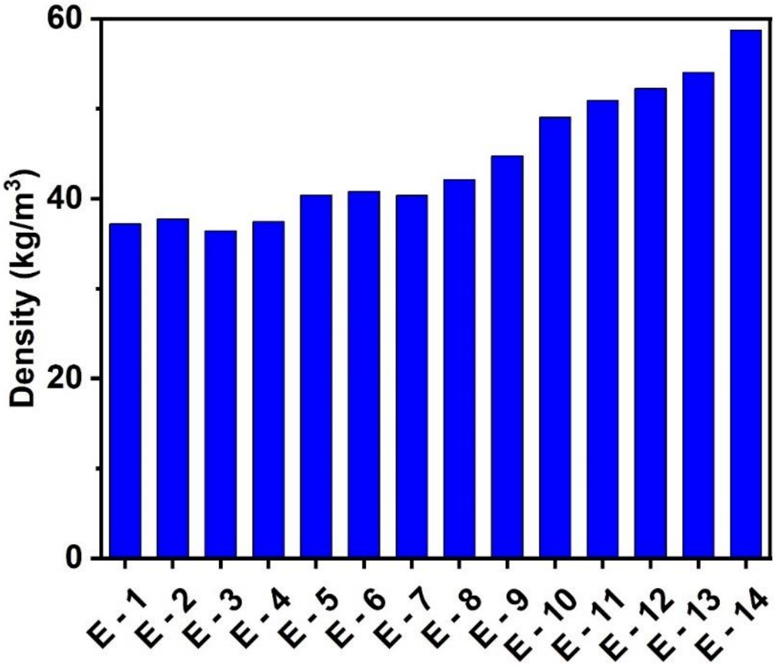


Figure 3.6. Density of the corn oil-based foam with different percentage of TPP.

3.2.2. Closed Cell Content

The closed cell content (CCC) measurement is another significant study that assists in calculating the thermal insulating capabilities of the produced polyurethane foams. It is important for the foam to have higher level of closed cell content in order to procure exceptional thermal stability [89]. The foam having high closed cell content are rigid and have very low thermal conductivity. The calculated percentage of CCC of the produced foams with TEP and TPP are displayed in **Figure 3.7** and **Figure 3.8**, respectively. In **Figure 3.7**., it can be clearly seen that the addition of TEP into the foam slightly decreased the closed cell content of the prepared sample, which can also be seen in the compressive test results because the decrease in the closed cell content decreases the mechanical properties of the foams. All the foams maintained the closed cell content above 90 % which helps in maintaining excellent thermal insulation as well.

Furthermore, In the case of TPP, the addition of flame retardant does not significantly affect the closed cell content of the foam, as shown in **Figure 3.8**. This behavior can also be verified from the compressive tests of the TPP-containing foams. All the samples maintained above 90 % of the closed cell content, which played an important role in maintaining the mechanical strength of the foam.

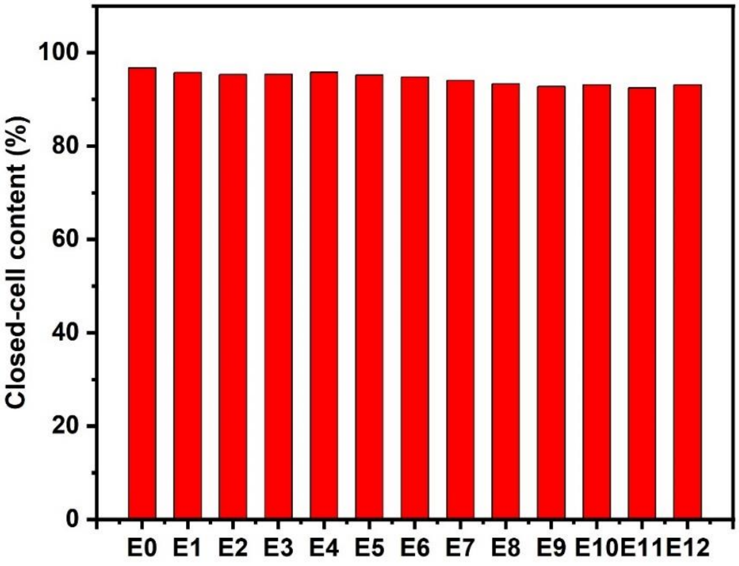


Figure 3.7. Closed-cell content for corn oil-based flame retardant polyurethane foam with increasing concentration of TEP.

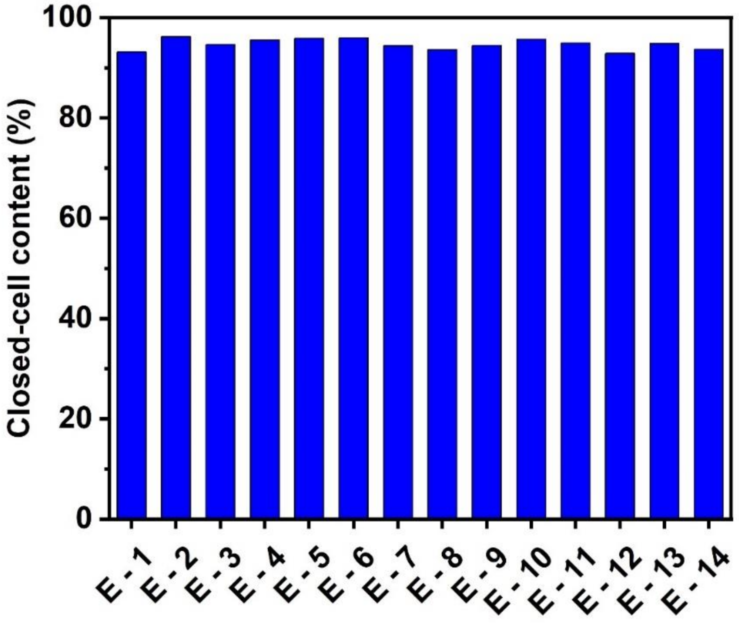


Figure 3.8. Closed-cell content for corn oil-based flame retardant polyurethane foam with increasing concentration of TPP.

3.2.3. Compressive Strength

The mechanical property of the foam is an important characteristic and is examined by compressional testing. The samples with different concentrations of TEP and TPP were tested to understand the effect of these fire retardants on the mechanical properties of the material. The results of the tests were analyzed, which are shown in the **Figure 3.9** and **Figure 3.10**.

3.2.3.1. Effect of TEP

From the results, it can be observed that the compressive strength of the foams decreases with the increasing in TEP content. As it can be seen in **Figure 3.9**, the compressive strength of the foam with 0 % of the fire retardant is around 220 kPa. However, the addition of around 0.5 g of TEP does not significantly affect the mechanical strength of the foam. However, it can also be observed that as the amount of TEP increase in the foam, the mechanical strength of the foam keeps decreasing. The range of compression strength of the foam with different amount of TEP is observed in between 150-220 kPa. The reason for the degradation in the mechanical properties of the foam with the increase in flame retardant material could be due to the plasticizing effect of the TEP, which results in the increase in the cell size, which eventually decrease the compression strength of the foam. This study proves that the addition of TEP significantly decreases the mechanical strength of the synthesized foams.

3.2.3.2. Effect of TPP

Similar to TEP, the addition of TPP into the foam does not significantly affect the mechanical strength of the foam, as can be observed in **Figure 3.10**. The increase in the TPP content result in slightly decreasing the mechanical strength. The range of compressive strength of the foam with different amount of TPP is observed in between 180-220 kPa. The reason for this trend of mechanical strength with the increase in TPP could be the plasticizing effect of the TPP, which eventually increases the cell volume and decreases the compressive strength of the foams, which can also be correlated to the closed cell content study of the foam.

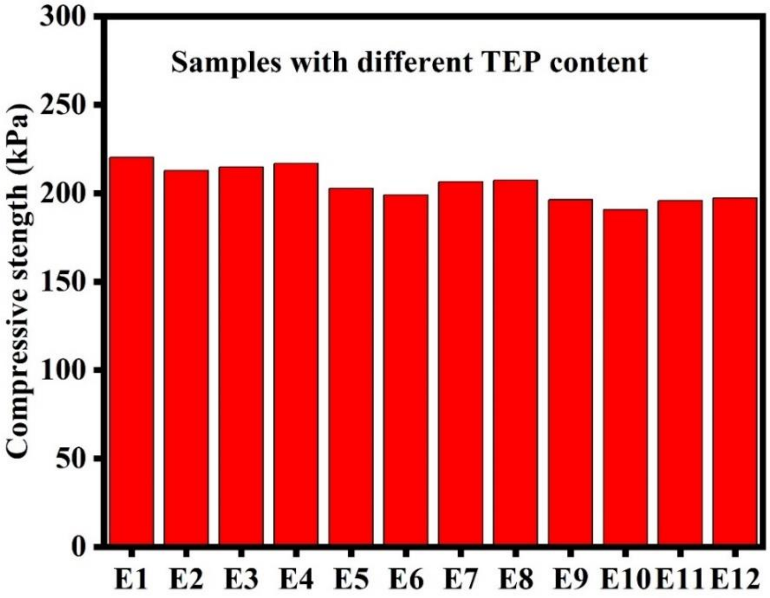


Figure 3.9. Compressive strength for TEP-containing polyurethane foam.

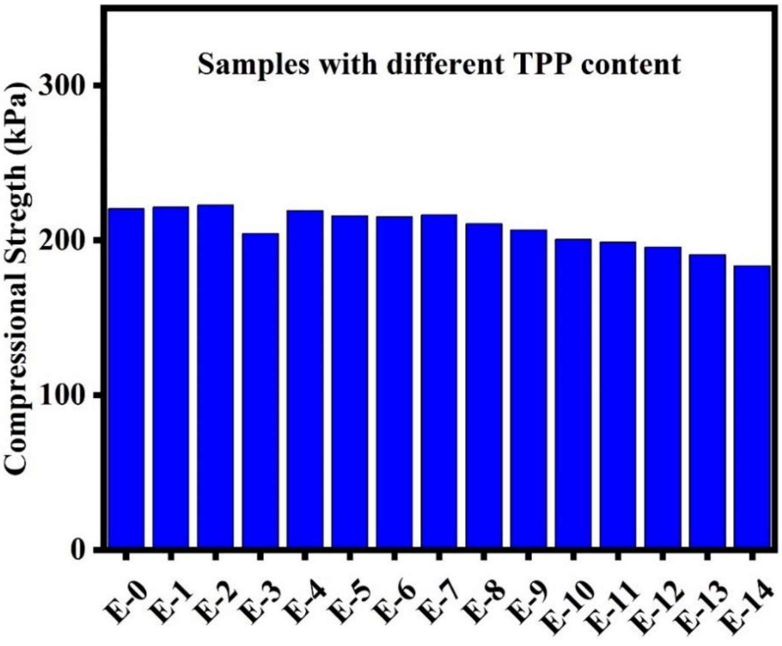


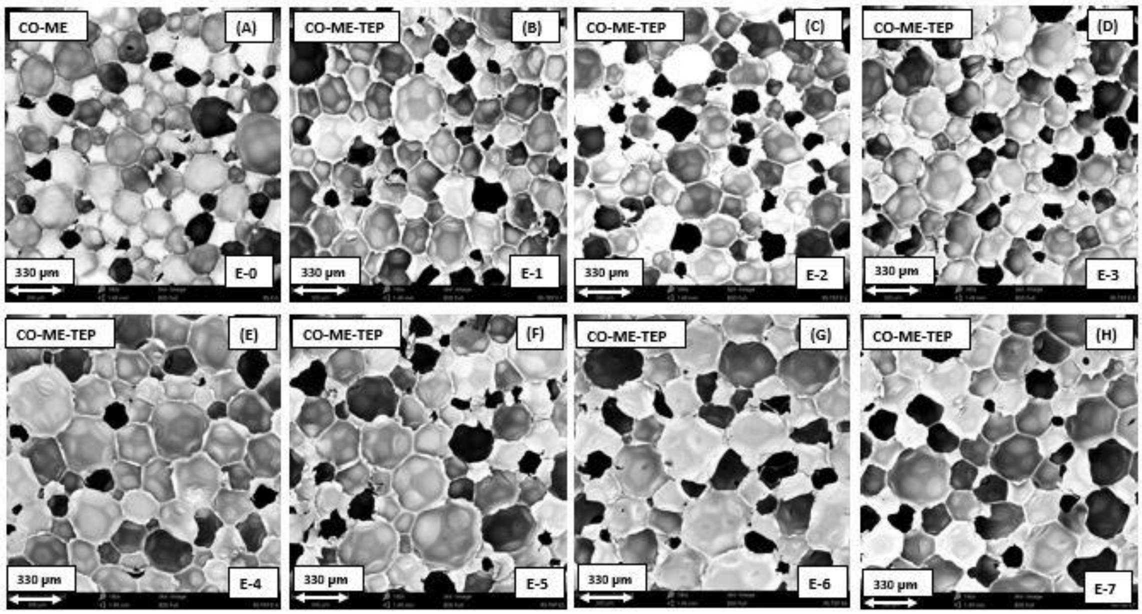
Figure 3.10. Compressive strength of TPP-containing polyurethane foam.

3.2.4. Cell Distribution and Scanning Electron Microscope (SEM)

The study of the cell distribution in the foam structure can be done with the help of a scanning electron microscope. The pictures of different samples of PU foams obtained through a scanning electron microscope with different amount of TEP and TPP are seen in **Figure 3.11** and **Figure 3.2**, respectively.

3.2.4.1. With TEP

In **Figure 3.11 (A)**, it can be clearly seen that the cell size is small. However, as the content of the TEP in the foam formulation increases, a gradual and slow increase in the cell size can be noticed in **Figure 3.11 (B-D)**. After further increasing the TEP content into the formulation, a clear increase in the cell size can be seen from **Figure 3.11 (E-M)**. Furthermore, the increase in TEP content also disturb the cell uniformity, which can be clearly seen in **Figure 3.11 (M)**. However, all the prepared sample of the foams showed excellent physical and mechanical properties. Furthermore, these results also verify the previous results for closed cell content and compressive testing.



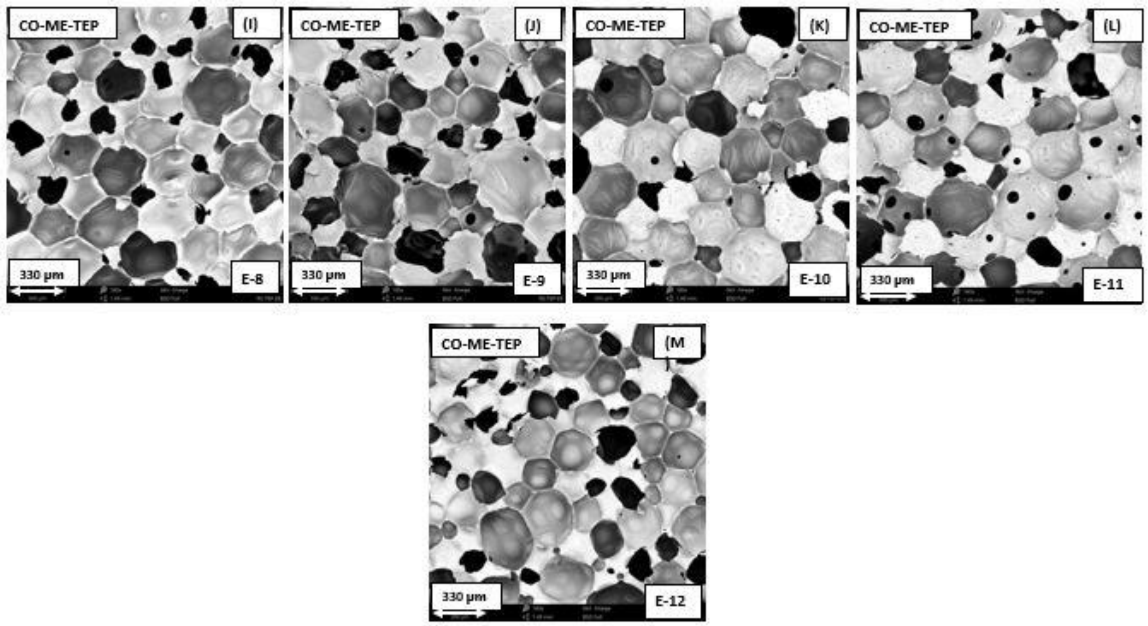


Figure 3.11. SEM images of foams produced with different amount of TEP.

3.2.4.2. With TPP

Just like TEP, TPP showed almost the same results. The SEM images of foams containing TPP are presented in **Figure 3.12**. It can be clearly seen that the cellular size of the foam keeps increasing as the TPP content increases. The major increase in the cell size can be clearly seen from **Figure 3.12 (J-N)**, where the percentage of TPP increased from 15.2 wt. % to 26.4 wt. %. Furthermore, the addition of TPP into the formulation also disturbs the cell uniformity, which led to decreases in mechanical properties and the closed cell content of foam. The obtained results are almost similar to the past study [58].

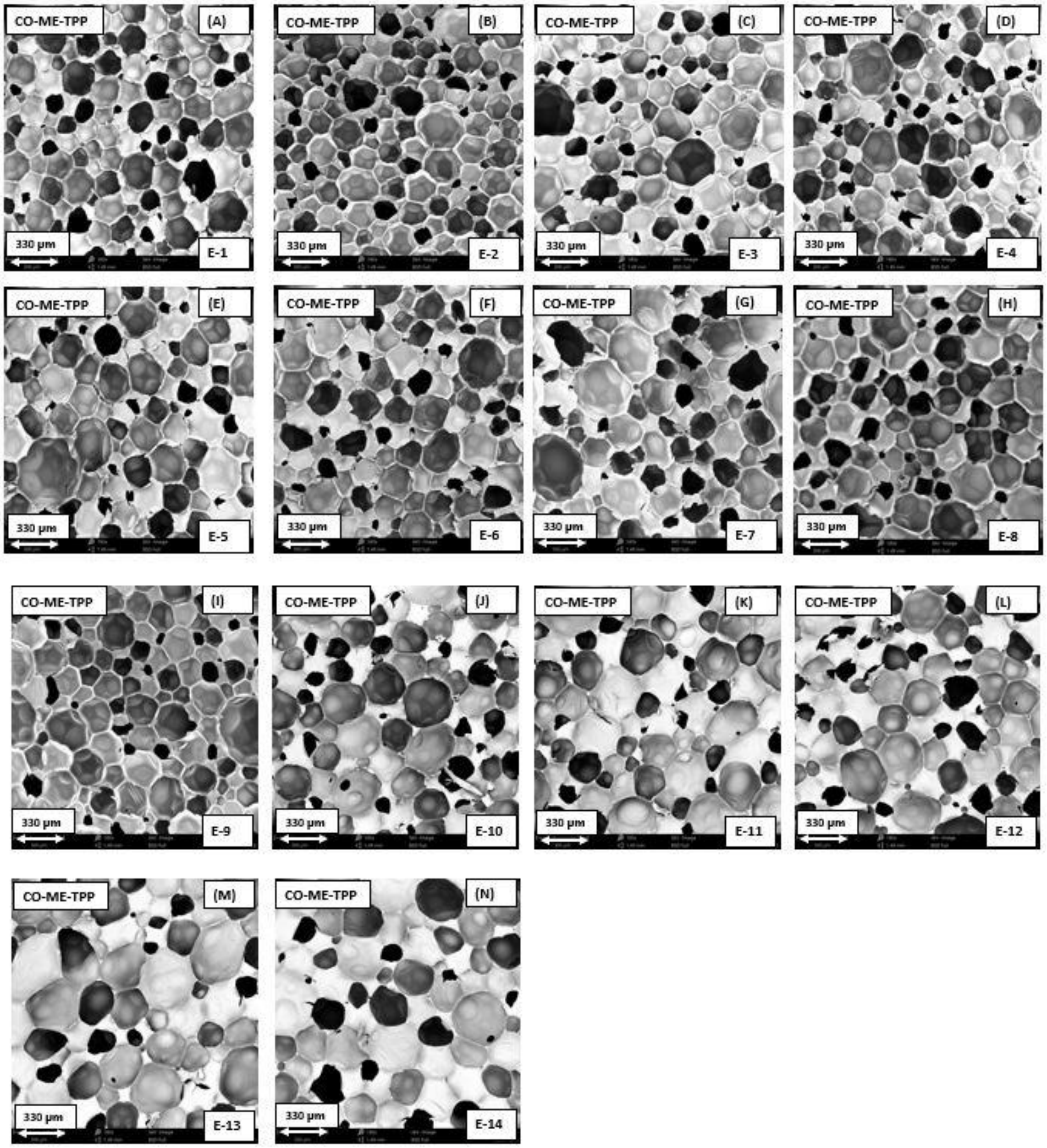


Figure 3.12. SEM images of PU foams with different amount of TPP.

3.2.5. Thermogravimetric Analysis

In rigid polyurethane foams, the thermal property is an important parameter and is tested through thermogravimetric analysis. The results obtained through TGA help understand the thermal stability of the prepared foams through the transitional behavior of the foam under high temperature. In this study, the loss in the weight of the samples containing TEP was observed with increasing temperature. The obtained TGA results for the samples having TEP in nitrogen and air environment can be observed in **Figure 3.13** and **Figure 3.14**, respectively. The observed results showed that the addition of flame retardant induced a new decomposition curve at the beginning of the decomposition of the foam. This peak can be observed at around 150 to 215 °C, which is due to the evaporation of water and TEP (having a boiling point of 215 °C). It can be clearly seen in **Figure 3.13** that the increase in the TEP content increase the decomposition curve, which is responsible the more weight loss due to evaporation of TEP. The major decomposition curve can be observed at around 300-380 °C, which is due to the pyrolysis of the urethane bond involving the breakage of isocyanate and polyols. The plateau observed after that is due to the slow degradation of char layer.

Furthermore, in air, the TGA analysis showed almost the same behavior as in N_2, as shown in **Figure 3.14**. In both of the environments, it can be observed that the material with flame retardant has more increased char decomposition curve than the sample without flame retardant, which reflects that the flame retardant acts in the gaseous phase to stop the fire.

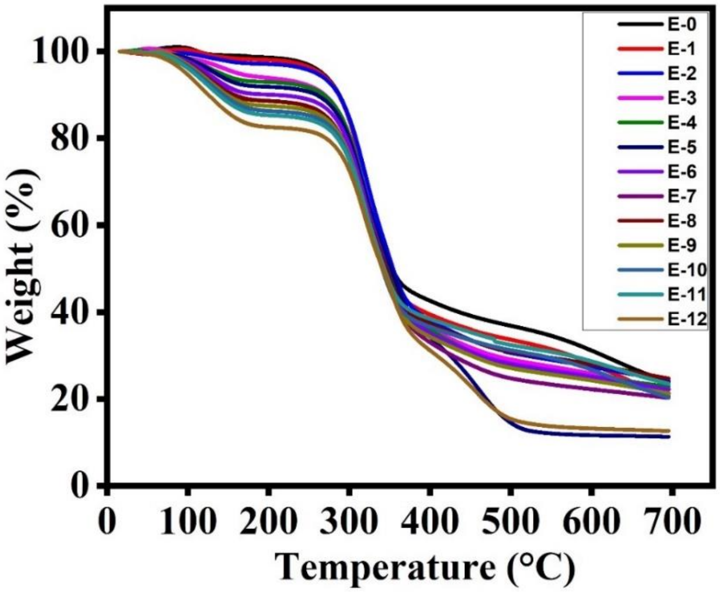


Figure 3.13. TGA of TEP-containing polyurethane foams with different content of TEP in N_2.

Similarly, for TPP, the TGA data displayed early decomposition curves at around 250 °C due to the evaporation of TPP, as shown in **Figure 3.15** and **Figure 3.16**. These early decomposition curves and the low char production after increasing the TPP contents indicate that most of the early weight loss in the foam convert the TPP into gaseous form to stop the fire at an early stage by acting in a gaseous phase. The TGA analysis of the TPP samples in N_2 environment showed higher char stability but showed the same early decomposition curve, which resulted in converting large amounts of foam weight into the gaseous phase at the initial stage that eventually prevent the fire from spreading.

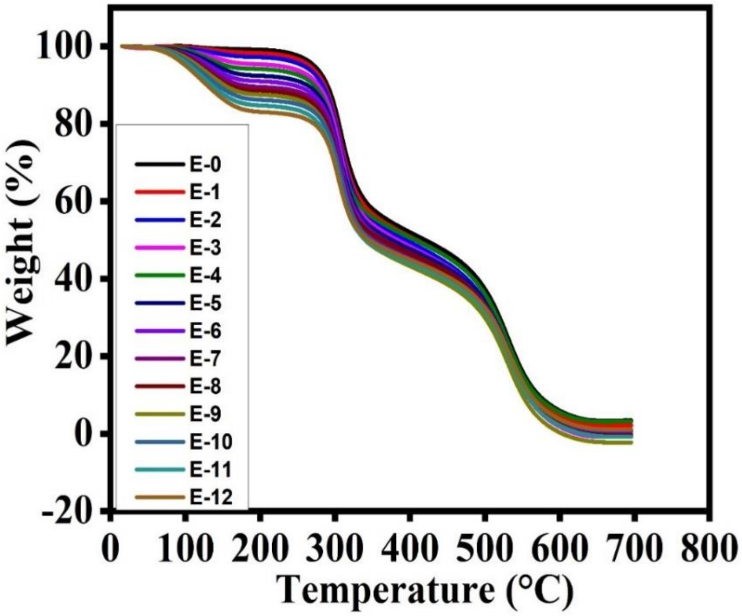


Figure 3.14. TGA of TEP-containing polyurethane foams with different content of TEP in air.

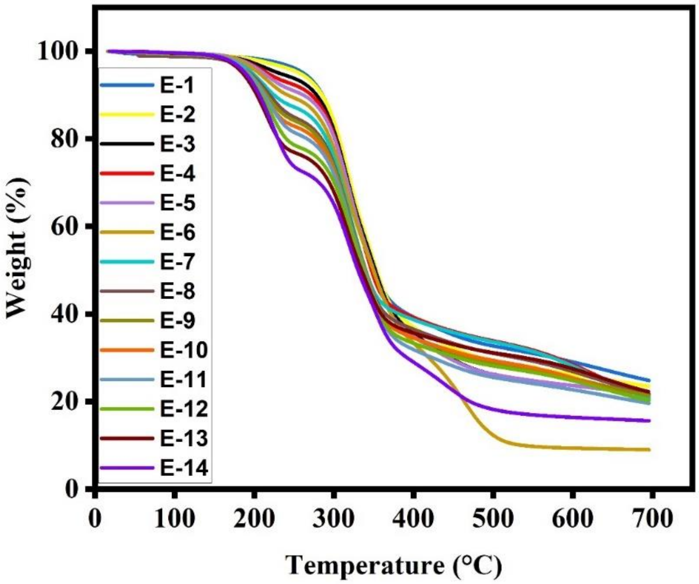


Figure 3.15. TGA of TPP-containing polyurethane foams with different content of TPP in N_2.

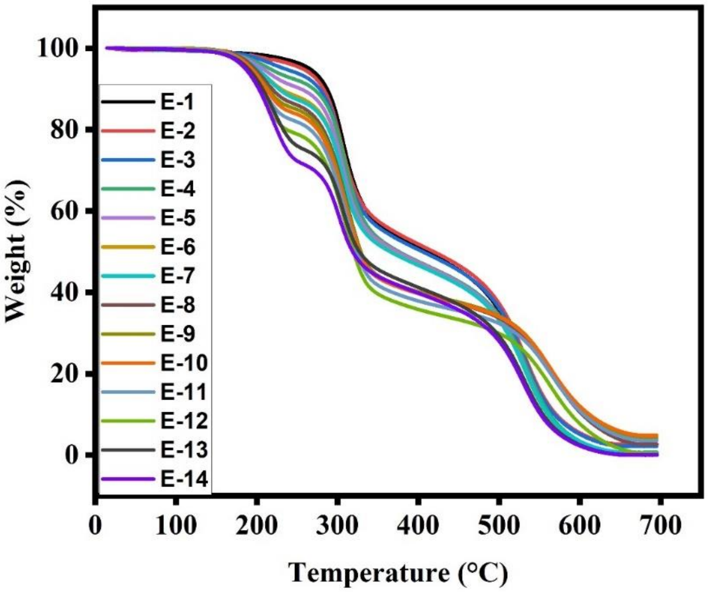


Figure 3.16. TGA of TPP-containing polyurethane foams with different content of TPP in air.

3.2.6. Horizontal Burning Test

The burning tests were performed to analyze the on-field flame retardant characteristics of the prepared foam. For this reason, the foams were burnt horizontally in the accordance with ASTM D 4986-98. The flames were introduced to the foams for 10 seconds, which is placed horizontally. The burning time for all the TEP samples and their weight loss during that time were noted, as displayed in **Figure 3.17** and **Figure 3.18**, respectively.

The foam with zero percent of TEP showed a burning time of almost 80 s with the weight loss of almost 44 wt. %. The burning time and the weight loss percent significantly dropped to 32 s and around 10 percent with the addition of 0.986 wt. % of TEP into the foam. The minimum weight loss of 3.2 wt. % was noted for the sample with 16.616 wt. % of TEP with the total burning time of 7.5 s. Furthermore, it is also observed that the addition of more TEP into foam resulted in the constant burning time and weight loss, as displayed in **Figure 3.17** and **Figure 3.18**.

Moreover, the burning test of the samples with the TPP as the flame retardant also showed significant decrease in the flammability of the foam. **Figure 3.19** and **Figure 3.20** display the burning time and the % weight loss of the foam having TPP as the flame retardant. It can be clearly seen that the addition of TPP into the formulation significantly reduced the burning time and weight loss % of the sample. The minimum weight loss of around 3 % was observed for the sample having 26.4 wt. % of TPP with the burning time of around 11 s.

The images of the burnt foams with TEP and TPP can be seen in the **Figure 3.21** and **Figure 3.22**, respectively. The induced flame retardant behavior in the foam could be due to the contribution of phosphorus present in TEP and TPP, which act in the vapor phase and condensed phase to extinguish fire. The burning of TEP and TPP produce phosphorus-based free radicals, such as PO_2*, PO*, and OHPO*, which significantly assist in restricting H* and OH* [58]. Also, the increased stability of the char layer shielded the unburnt foam and help extinguish the fire. Therefore, adding small amount of TEP and TPP can considerably improve the flame retardancy of the PU foams.

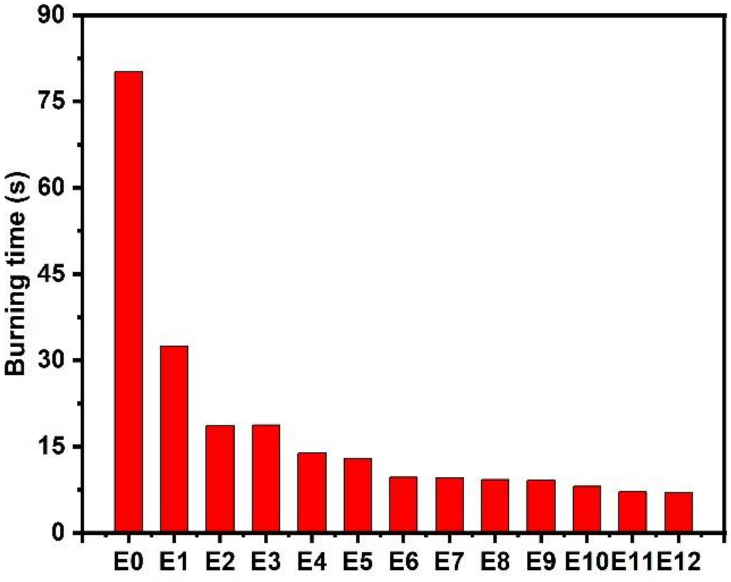


Figure 3.17. Burning time of foam samples with TEP.

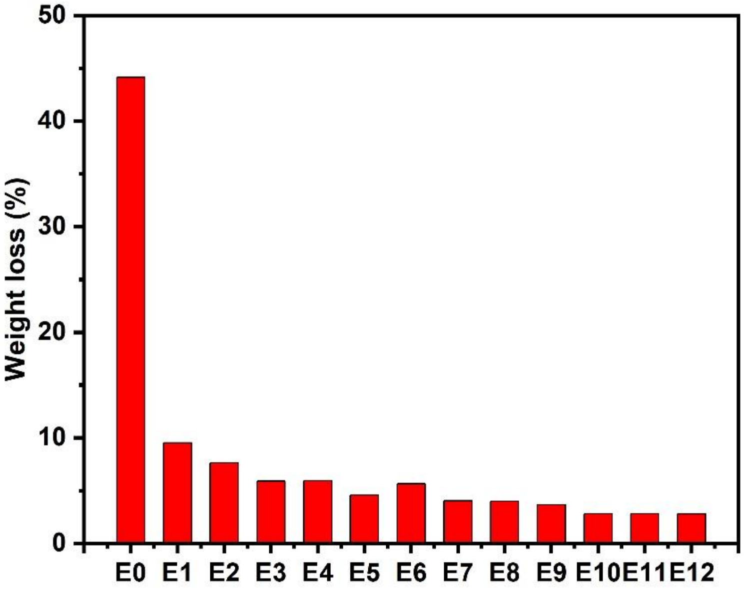


Figure 3.18. Weight loss percentage of foam samples with TEP.

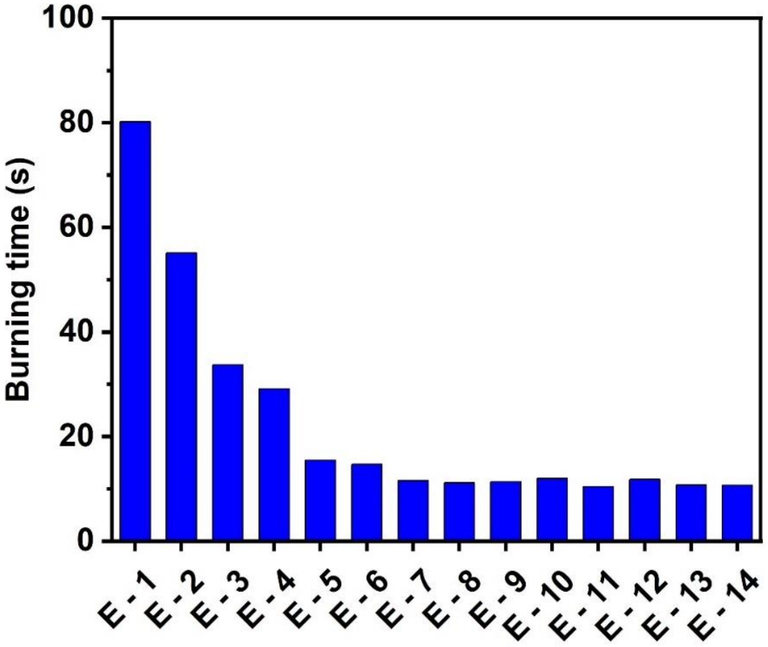


Figure 3.19. Burning time of foam samples with TPP.

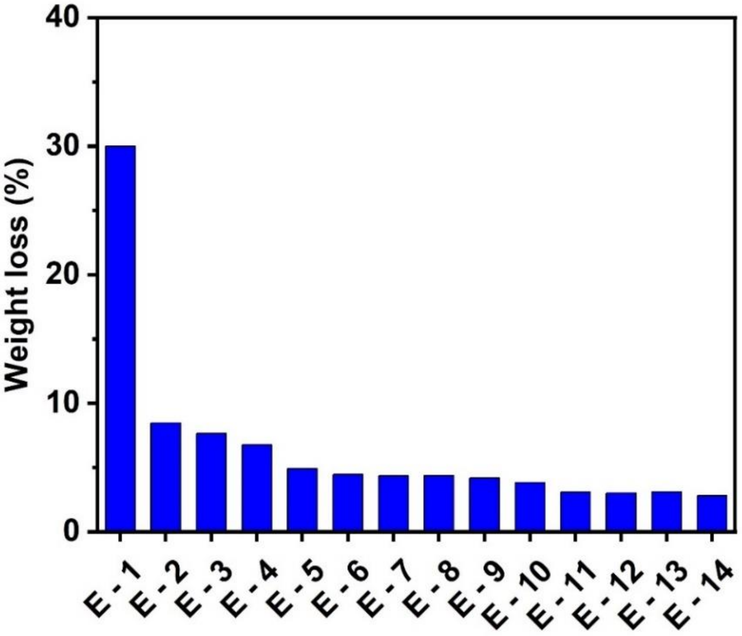
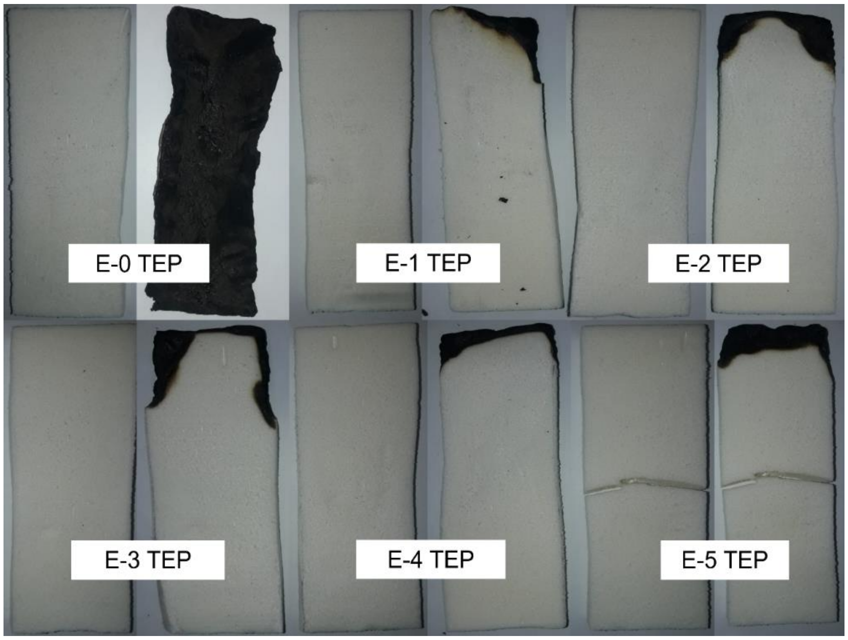


Figure 3.20. Weight loss percentage of foam samples with TPP.



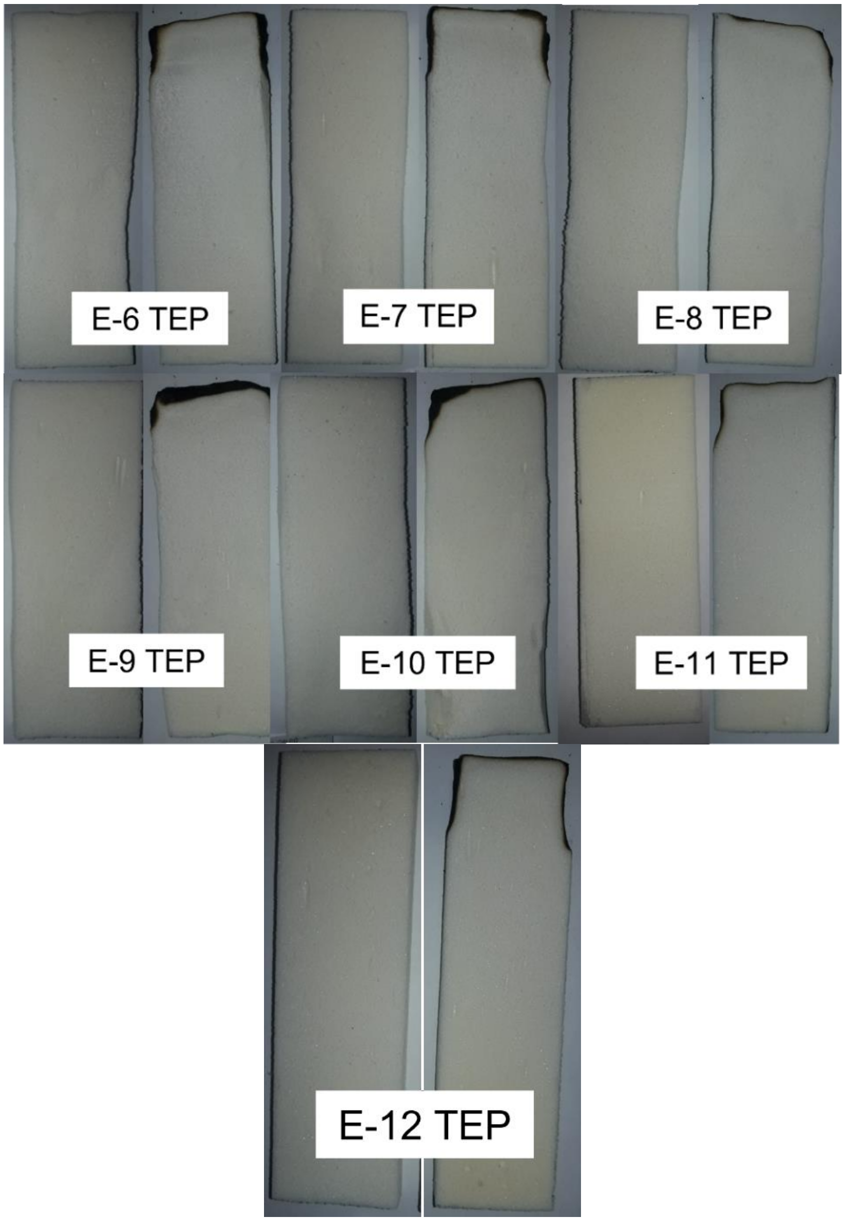
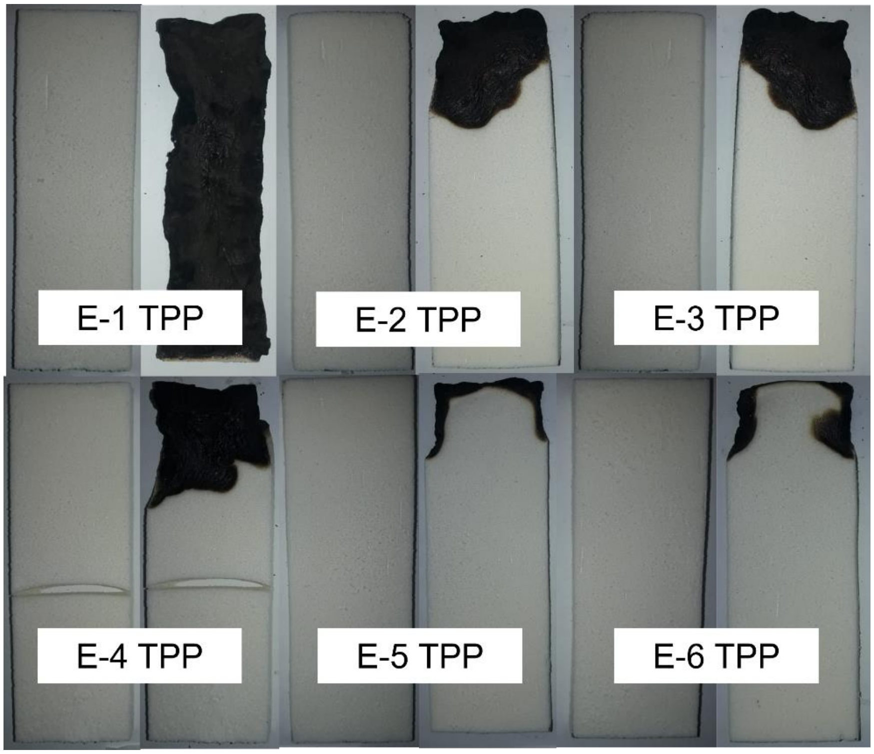
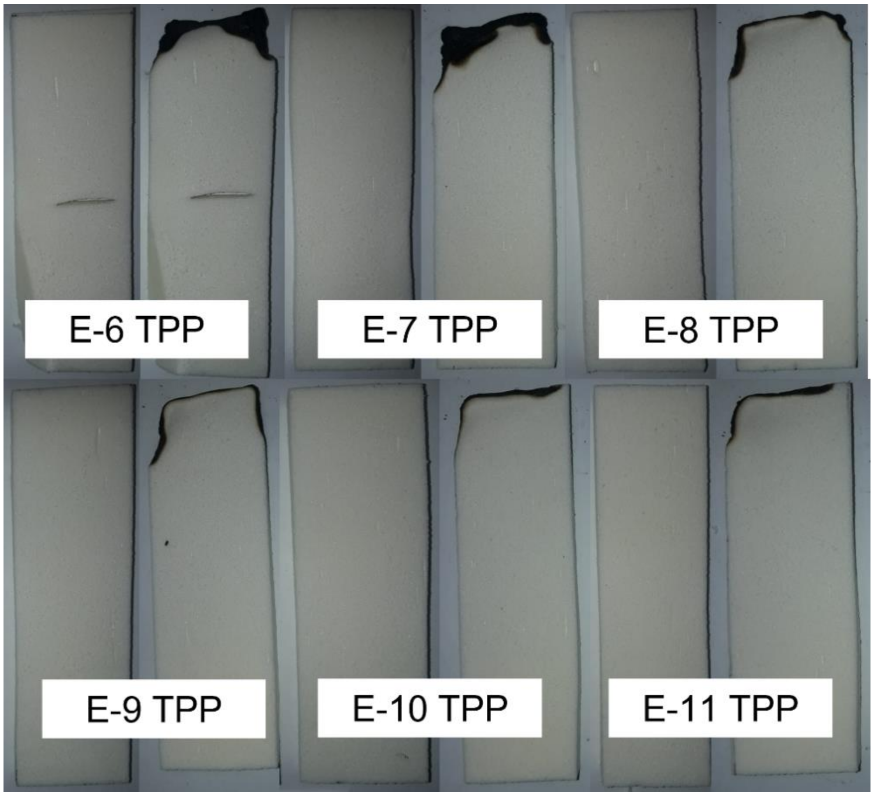


Figure 3.21. Images of the burnt polyurethane sample containing TEP as flame retardant.


E-1 TPP
E-2 TPP
E-3 TPP
E-4 TPP
E-5 TPP
E-6 TPP


E-6 TPP
E-7 TPP
E-8 TPP
E-9 TPP
E-10 TPP
E-11 TPP

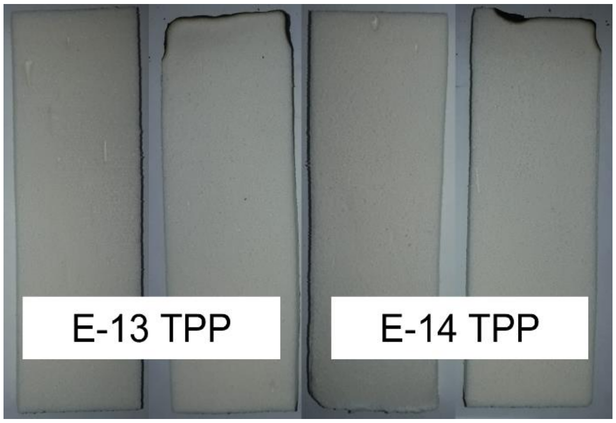


Figure 3.22. Images of the Burnt polyurethane foam containing TPP as flame retardant.

CHAPTER IV

CONCLUSION

In this study, polyurethane foams from corn oil-based polyol were produced with the addition of two different flame retardants, triethyl phosphate and triphenyl phosphate. For this reason, the polyol was produced using the corn oil through thiol-ene reaction. The synthesized polyol was employed along with the flame retardants to prepare the rigid polyurethane foams. The OH number of the prepared polyol was found to be 174.61 mg KOH/g with the viscosity of 2.06 Pa.s. The polyol was characterized using FTIR and GPC to ensure that the reaction occurred and completed. The S-H bond stretching peak of 2-mercaptoethanol was found to be absent in the polyol FTIR data, which proves all the 2-mercaptoethanol was completely utilized in the reaction and the reaction was completed. Similarly, the retention peak of 2-mercaptoethanol was not found in the polyol during the GPC characterization, which is another proof of the completion of reaction. Furthermore, the synthesized foams displayed excellent cellular structure with closed cell content of higher than 90 % and compressive strength of around 150-220 kPa for both TEP and TPP samples along with the appropriate density.

Moreover, it was observed that the addition of both flame retardants, TEP and TPP, increase the flame retardancy of the foams as the burning time for the foams reduced significantly. The burning time of the foam containing TEP reduced to 7.5 s from 80 s with the reduction of weight loss from 44 % to 3.2 %. Similarly, the foams with the TPP as the flame retardant showed a burning time of 11 s with a minimum weight loss of only 3 %. These results prove that corn oil can be used as a substitute to the traditional petrochemical based polyol for the synthesis of polyurethane foams. Also, the TEP and TPP can be used as the flame retardant materials for the industrial application of corn oil-based polyurethane foams to achieve excellent flame retardancy.

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