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HIGHLY FLAME-RETARDANT BIO-BASED FOAMS USING CASTOR OIL AND MELAMINE-BASED INTUMESCENT FLAME RETARDANTS

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

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Pittsburg State University

Pittsburg, Kansas

May 2024

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HIGHLY FLAME-RETARDANT BIO-BASED FOAMS USING CASTOR OIL AND MELAMINE-BASED INTUMESCENT FLAME RETARDANTS

An Abstract of the Thesis by
Niyati Chaudhary

One of the considerable forms of polyurethanes (PUs) with significant potential for insulation and energy efficiency is rigid foam, which is mostly utilized in the construction, refrigeration, and automobile sectors. However, RPUFs are quite combustible and may ignite and spread flames rapidly. As an economical, environmentally friendly, and effective alternative to non-halogenated flame retardants (FRs), nitrogen-based chemical substances are used to reduce the flammability of PU foam. It is demonstrated by research that the ideal choice for incorporating flame-retardant compounds with rigid polyurethane foams is based on melamine derivatives, which majorly contain nitrogen in their structure. Adding melamine and its derivatives to rigid foam enhances its thermal stability and efficiency to prevent fire spread. This thesis aims to incorporate environmentally friendly components into the castor oil polyol, which is utilized to make rigid polyurethane foams. In addition to these, castor oil is inedible and has many functionalized chemical groups that can be used to create polyurethane even without modification. The limited load-bearing capability and lack of thermal stability of RPUFs derived from castor oil restrict their industrial application. These limitations were addressed in two ways: (i) by adding additional hydroxyl groups using standard chemistry methods - the crosslinking density was increased; and (ii) by adding three environmentally friendly FRs - the thermal stability of polyurethane foams was improved. Based on test conclusions, 210 kPa of compression strength, 95% closed cell content, and an apparent density of 37.50 kg/m^3 were observed in the manufactured castor oil-based polyurethane foams without FRs. Even after the addition of FRs, the structural integrity of the foam remains the same indicating the better compatibility of FRs and the castor oil-based PU matrix. As the flame-retardant proportion increased, it also raised flame-retardancy and thermal stability. While rigid polyurethane foams based on castor oil and FRs based on nitrogen showed good mechanical properties and relatively poor thermal stabilities, rigid polyurethane foams based on castor oil and FRs based on phosphorus and nitrogen demonstrated good thermal qualities but relatively poor mechanical characteristics. Nitrogen and phosphorous-based rigid polyurethane foams containing castor oil perform better flame retardancy. This work illustrated that FRs based on nitrogen and phosphorus can lower the flammability of polyurethanes derived from castor oil without significantly altering their physical properties.

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LIST OF ABBREVIATION

ASTM	American Society for Testing and Materials
CCC	Closed Cell Content
CO	Castor Oil
DTGA	Derivative Thermogravimetric Analysis
ECO	Epoxide Castor Oil
FTIR	Fourier Transformed Infrared
FR	Flame Retardant
MA	Melamine
MC	Melamine Cyanurate
MDI	Methylene Diphenyl Diisocyanate
MO	Melamine Phosphate
PU	Polyurethane
RPUF	Rigid Polyurethane Foam
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis

CHAPTER I

INTRODUCTION

1.1. Polyurethane

Polymers are found in many applications that have improved society's standard of living and made science and technology more accessible. Polymers are used in several industries, including construction, furniture, biomedical, automotive, aerospace, electronic devices, and packaging materials [1]. This research describes the synthesis processes, different kinds, applications of polyurethane (PU), manufacturing limitations, and elements that might improve PU performance. PUs films, coatings, adhesives, sealants, and elastomers have greater demand worldwide. Moreover, they find usage in a wide range of sectors, including the medical field, home furnishings, interior design, apparel, electronics, and manufacturing [2].

PU is composed of repeating urethane units (**Figure 1**). Under moderate circumstances, isocyanates and polyols undergo polyaddition reactions to produce PUs with the help of appropriate catalysts and stabilizers [3]. PU is typically produced by reacting a polyol with an isocyanate molecule [4,5]. A urethane linkage's formation during the process is linked to the word "polyurethane". The structure of PUs is divided into two parts: a hard segment created by isocyanates and a soft segment associated with polyol [6]. The rigid domains of PUs may interact with other chains through hydrogen bonding [7].

The soft domains usually have longer chain lengths. The global PUs market is expected to reach USD 78.90 billion in 2024 and is projected to increase at a compound annual growth rate (CAGR) of 3.9% up to 2030. The PUs marketplace is expanding gradually because of the fast expansion of thermal insulation and engineering applications, as well as their high demand in the building, packaging, and automotive industries [8].

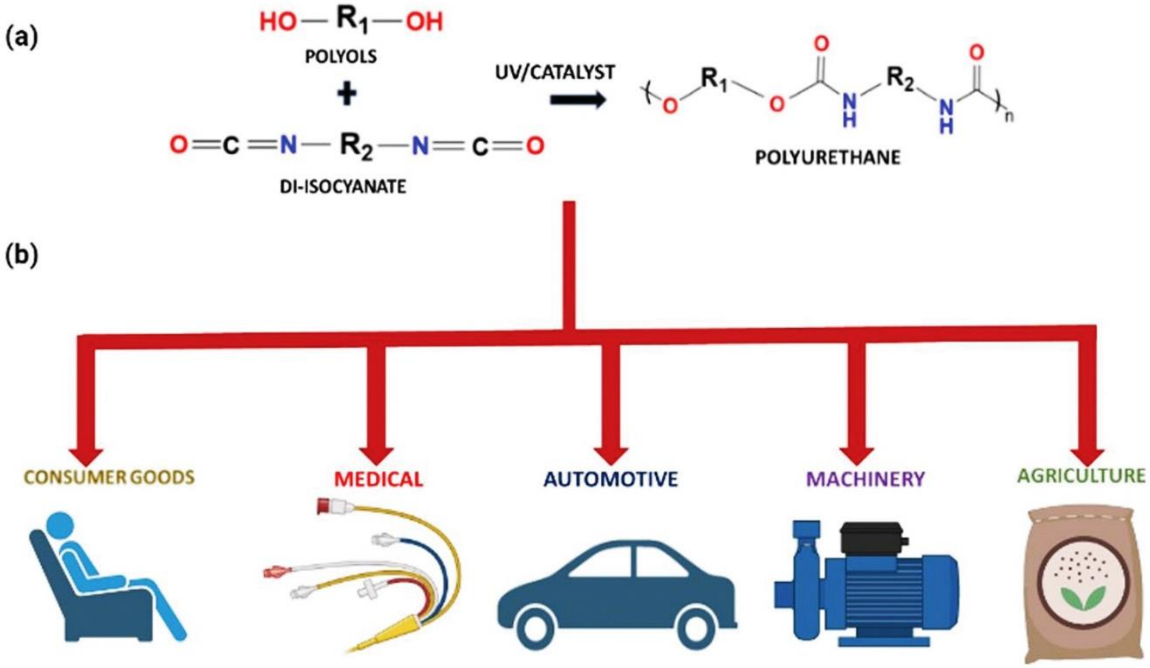


Figure 1. (a) Reaction schematics for PU synthesis. (b) Application of PU in different sectors. Reproduced with permission [9]. Copyright 2023, American Chemical Society.

1.2. Applications of polyurethane

PUs are widely used in many industries due to their ability to adapt different chemistries for synthesis and use of a range of starting materials [10]. Rigid and flexible PUs have unique features such as low density, high thermal insulation, and good mechanical strength which make them very suitable for applications in building and construction [11]. Rigid PUs are also used for thermal and acoustic insulation in automobiles, whereas flexible PUs are used for vehicle seats [12]. Lightweight and strong mechanical properties are some of the important characteristics of PUs that make them very suitable for use in automobiles as they enhance fuel economy and vehicle safety against crashes. **Figure 2** shows various applications of PUs. One of the major drawbacks of PUs is their high flammability. Flame retardants (FRs) based on halogen, nitrogen, and phosphorus are commonly added to reduce PU flammability [13]. However, many FRs particularly, halogen-based are very hazardous due to the emission of carcinogenic gases [14]. Dimethyl methyl phosphonate, expandable graphite, melamine, melamine cyanurate, and melamine phosphate are a few examples of environmentally friendly FRs [15]. However, not all FRs are compatible with PUs, therefore, it is crucial to continue researching and developing FRs that are compatible with PUs.

1.3. Types of polyurethane foam and issues

A chemical reaction between polyols and isocyanates, with blowing agents yields PU foam that could be flexible or rigid forms. The insulation properties and other uses of PU foam make it a highly specialized material [16]. PU foams have many desirable and contemporary qualities. Because of their low thermal resistance, porosity, and cellular structure, they are very combustible, therefore FRs need to be added to make them non-flammable.

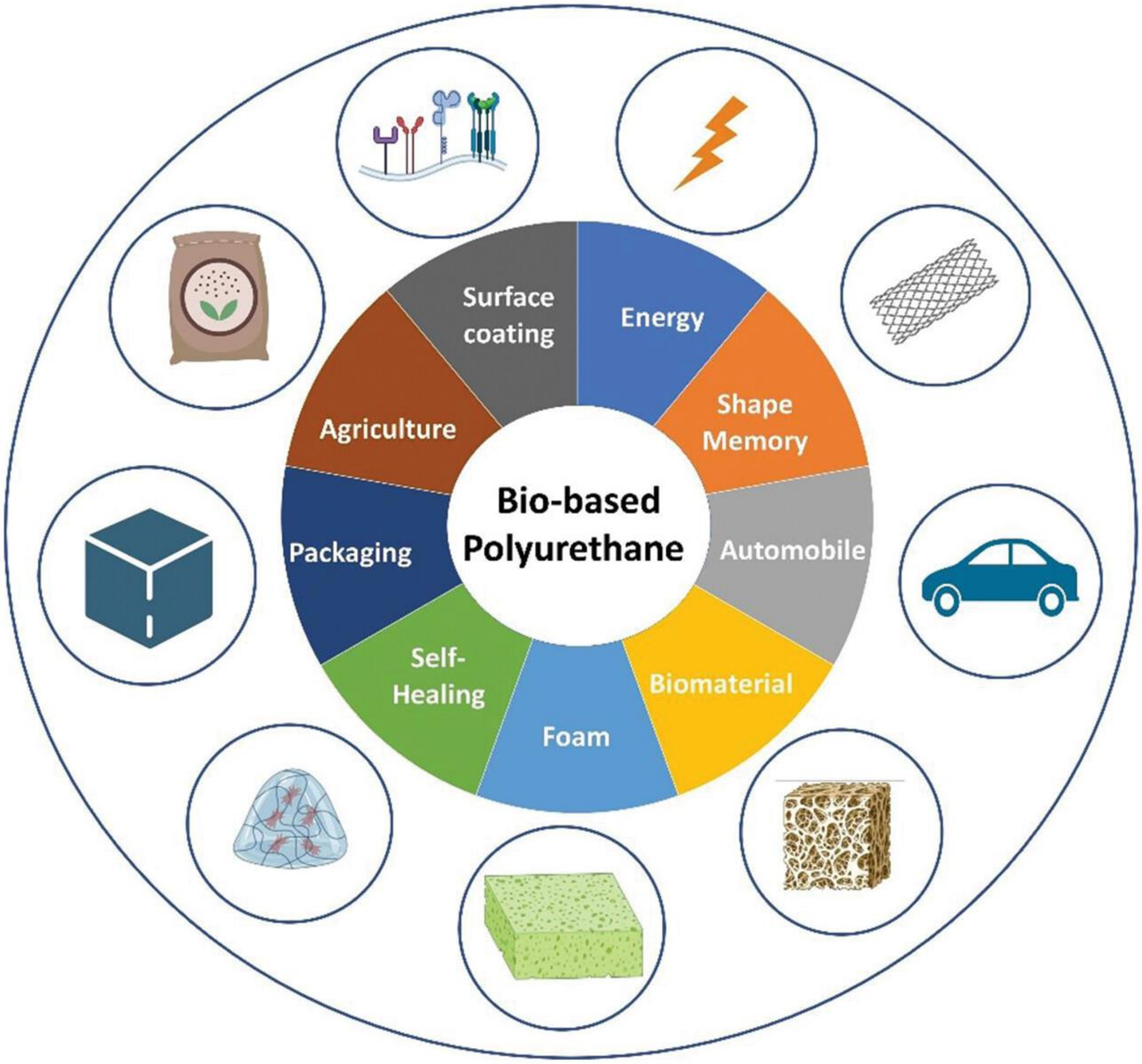


Figure 2. Applications of bio-based polyurethane. Reproduced with permission [9]. Copyright 2023, American Chemical Society.

1.3.1. Flexible PU foams

Flexible polyurethane foam provides a range of features, including lightweight, high surface flexibility, and durability. Flexible polyurethane foams have gained popularity in recent years for their versatility in many commercial and consumer uses [17]. It also has applications for sound insulation and filtering. Furthermore, different formulation and processing methods will most likely result in the continued development of materials with enhanced characteristics [18]. Its low density and open cell structure make it combustible and during the combustion process, it produces a lot of smoke and harmful gases (such as CO and HCN). As a result, FRs must be used to reduce the release of harmful gases [19].

1.3.2 Rigid PU foams

In both commercial and residential settings, rigid foams have demonstrated outstanding efficacy in reducing energy expenses [20]. They are utilized in structural applications in vehicles, aircraft, and construction. Due to their numerous advantageous qualities, RPUs are being used more often in a variety of demanding applications [21]. One of its beneficial qualities as an insulator is its limited ability to transfer heat. In addition, it has significant dimensional consistency and a low density compared to metals and other substances. Estimated at US$ 37.8 billion in 2020, the rigid PU foam market is expected to increase at a compound annual growth rate (CAGR) of 7.59% from 2021 to 2028 to reach US$ 67.8 billion. As with many applications, there's been a shift toward substituting conventional (petrochemical-based polyols) with renewable resources for manufacturing PU foams with reduced flammability [22]. Many efforts have been undertaken to create halogen-free FRs for rigid PU foam (RPUF) to reduce their inherent flammability.

1.4. Polyurethane from renewable sources

To prepare environmentally friendly PUs, biomass derived from sugars, lipids, polyphenols, and other renewable resources are utilized as sources of polyols [23]. Starch is being investigated as a biobased polyol for PU foams, taking advantage of its cheap, biodegradable, and plentiful OH-based groups [24]. Research on using vegetable oils in PU production has been conducted on canola, soybean, corn, and castor oils [25]. Non-edible oils such as castor oil can be also used for the preparation of PU [26,27]. Furthermore, castor oil and other oils naturally contain OH groups, they are utilized as polyols directly. Chemical modifications such as ozonolysis, hydroformylation, transesterification, and thiol-ene are used in the chemical modification of vegetable oils for the synthesis of polyols [28–30].

Castor oil which is produced from the Ricinus communis plant is not used commercially because it contains the lethal protein ricin and is not suitable for consumption [31]. Additionally, farmers frequently find it unattractive to raise castor since it spreads readily among other harvests. However, castor plant production has gained popularity, especially in India, because of its economic importance for the manufacture of PU [32]. The hydroxyl groups in castor oil enable its use as a polyol without chemical alteration (**Figure 3**). Approximately 89% of a single triglyceride from castor oil comes from double bonds and a secondary hydroxyl group present in glycerin and ricinolein acid [33]. However, the extent of unsaturation creates many opportunities for synthetic methods that can yield a wide variety of characteristics. Due to its easy production, extraction, affordability, and desirable qualities, castor oil is currently widely utilized for lubricants, hard foams, flexible PU foams, and elastic materials [34].

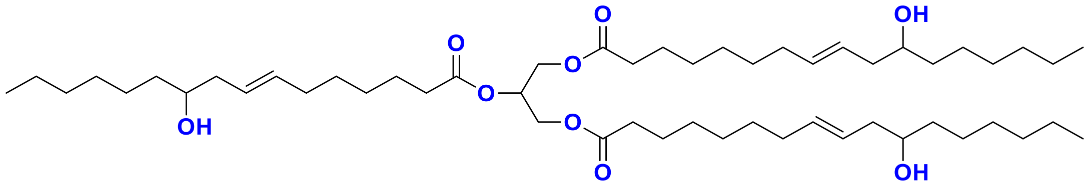


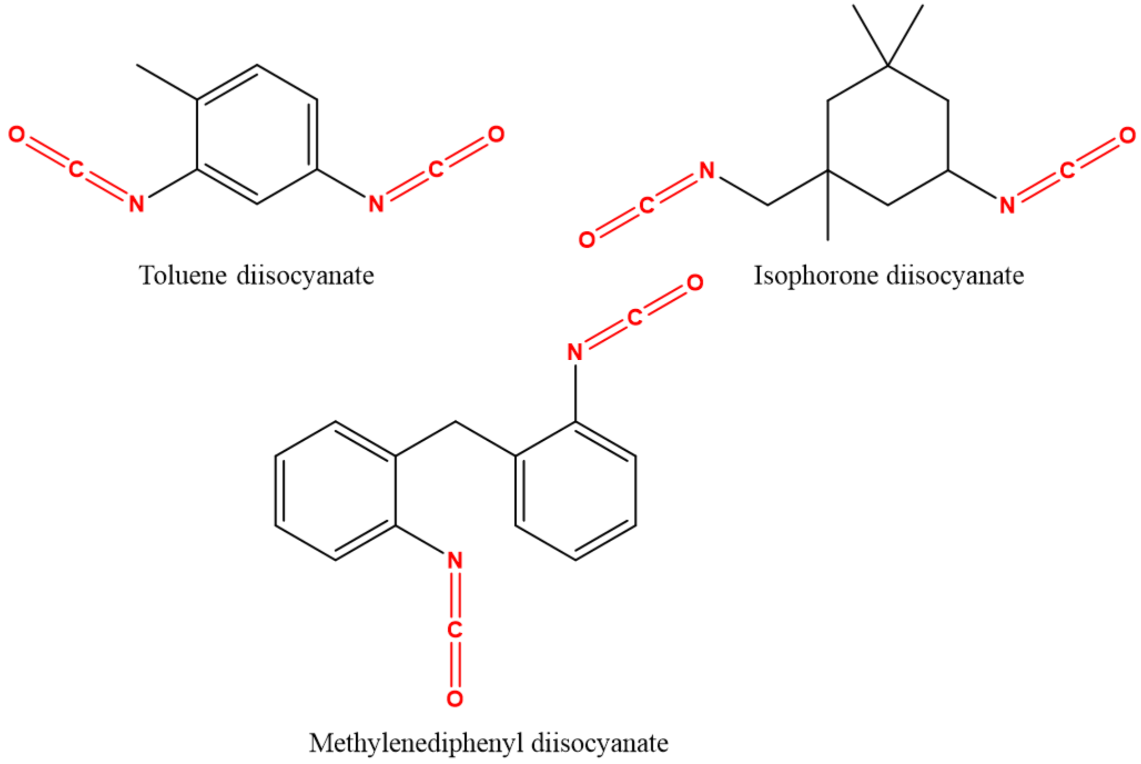
Figure 3. The chemical structure of castor oil.

1.5. Types of isocyanates

One of the characteristics of isocyanates is the existence of reactive groups with a chemical structure of -N=C=O (**Figure 4**). This is a reactive group that reacts with the hydroxyl group (-OH) of polyols to produce PUs [35]. In contrast to polyols, there are only a few commercial isocyanates are available [36]. PUs are typically made using two main types of isocyanates: Aromatic and Aliphatic. Aromatic isocyanates provide a rigidity segment to PU [37]. Toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI) are a few examples of aromatic isocyanates. These substances mostly generate rigid and thermoset PU. Low UV-light stability is one of the limitations of aromatic isocyanates, therefore, they are mostly used for indoor applications. They tend to become brown or yellowish after extended exposure to UV light. In general, PUs with groups ending in isocyanate are stiffer, hydrophobic, and chemically stable [38]. In contrast, those with groups ending in hydroxyl are more flexible, hydrophilic in nature, and chemically unstable [39].

1.6. Flame retardants in rigid polyurethane foam

FRs are added to reduce the flammability of PU foams. They function by reducing or stopping the initiation and spread of fires [40]. The State of California established a flammability standard (Technical Bulletin 117) at the beginning of the 1970s, requiring various home items, including electronics, furniture, and fabrics, to be flame-resistant. Several classifications may be used to classify FRs.


Toluene diisocyanate

Isophorone diisocyanate

Methylenediphenyl diisocyanate

Figure 4. Isocyanates for polyurethane.

1.6.1. Halogenated flame retardants

Halogenated FRs are compounds that contain halogen such as bromine, chlorine, fluorine, and iodine. Halogenated FRs are very effective but due to the release of toxic gases during the burning process, they are banned in many countries.

1.6.2 Phosphorus-based flame retardants

Most of the phosphorus based FRs function by creating a char layer on the surface of foams, and thus prevent further burning. In addition to creating a char layer, some of the phosphorus based FRs also function in the gas phase. Phosphorus-based FRs can be additive or reactive. Additive FRs are added during the foaming process but they don't participate in any chemical bonding with PU. On the other hand, reactive FRs have reactive functional groups that can make chemical bonding during the foaming process [41].

1.6.3. Nitrogen-based flame retardants

During combustion, nitrogen FRs release non-flammable gases that can obstruct gas phase ignition and generate a flame-retardant reaction [42]. Melamine for PUs flexible foams, MA cyanurate for nylons, MA phosphates for polyolefines, dicyandiamide or MA and phosphates for intumescent colors, a substance called phosphates for clothing and textiles, and guanidine sulfamate for backgrounds are among the principal uses of these substances [43].

1.6.4. Inorganic flame retardants

Inorganic FRs produce water vapor when exposed to heat such as magnesium hydroxide and aluminum hydroxide. They function as an FR by cooling the substance and preventing PU from burning [44].

1.7. Flame retardant used in this research

The use of nitrogen based FRs has started as a result of environmental regulations. Nitrogen-based FRs are environmentally friendly. As a result, nitrogen-based FRs such as MA and its derivatives are gaining popularity [42].

The substantial nitrogen content in MA makes it a commonly used FR in PU foams. When heated, MA can produce non-flammable gases such as nitrogen, which helps to reduce the release of combustible gases. Melem can arise from the self-condensation of MA at high temperatures, making the carbon-based layer denser [45]. The chemical structure of MA and melam is shown in **Figure 5** [46].

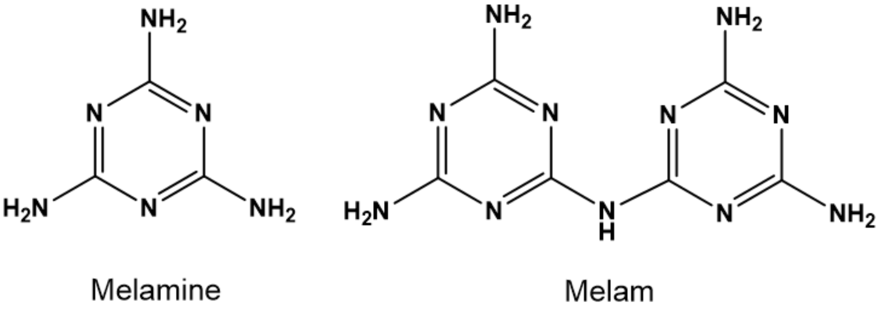


Figure 5. Melamine and its derivatives.

In this research, melamine phosphate (MP) was synthesized by reacting MA and phosphoric acid to produce an FR that contains both N and P (**Figure 6**) [47]. MP provides duel actions: (i) nitrogen that is attached to the triazine rings in MP passes to the gaseous phase and insulates the material from fire, (ii) MP can burn and release phosphorus acids that carbonize and create a stable and dense charring barrier in the condensed phase of the material [48].

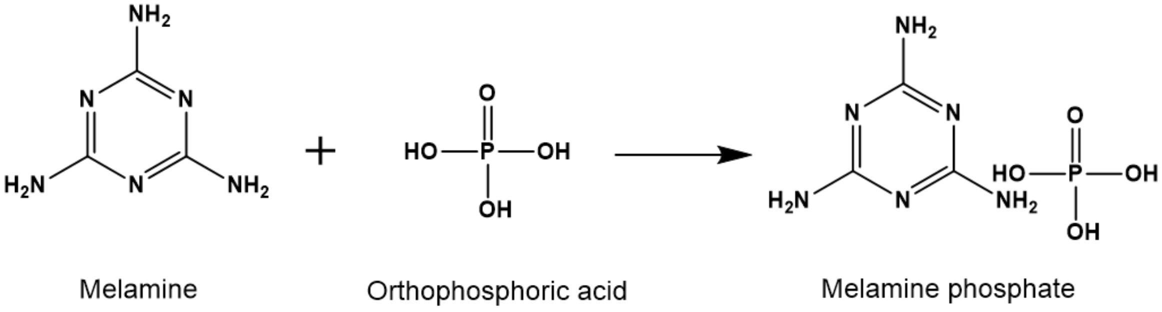


Figure 6. Synthesis of melamine phosphate using MA and phosphoric acid.

Melamine cyanurate (MC) has also demonstrated superior resistance to flame because of its distinctive composition and various mechanisms of activity. It contains a unique hydrogen bonding structure that links cyanuric acid with melamine, improving MC's overall volatility and thermal stability while also providing appropriate protection against fire for combustible polymers and other applications. It undergoes endothermic reactions. After removing cyanuric acid and melamine, it breaks down into NH_3, CO_2, and H_2O at high pressure. Based on particle sizes for MC, MC is divided into two categories: micro and nano. Since a smaller MC particle enables greater contact and the creation of strong hydrogen bonds between MC and matrix polymers, the decomposition temperature and thermal conductivity improve as the particle size decreases. MC protects polymers from combustion in both the condensed phase by forming an insulation char layer and the gas phase by releasing inert gases into the environment (**Figure 7**) [49].

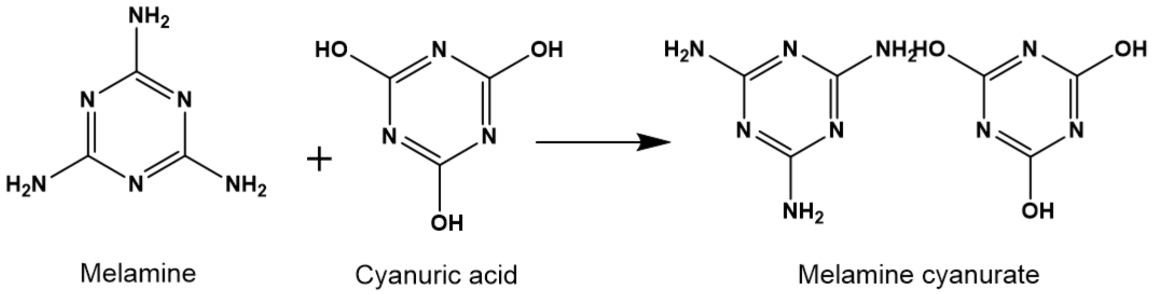


Figure 7. Synthesis of melamine cyanurate using MA and cyanuric acid.

1.8. Materials for polyurethanes

The primary ingredients in the synthesis of PUs are polyols and isocyanates. The characteristics of PUs are anticipated to be influenced by the nature and functions of polyols and isocyanates. The density, porosity, morphology, mechanical strength, and phase of reaction of PUs, among other attributes, can be transformed by changing materials [50]. Industries and academics have conducted several investigations to identify alternatives for petroleum-based polyols. Examples of substances from nature that are utilized in the production of RPUF include glycerol, sucrose, sorbitol, carbohydrate starch glucose, oils from vegetables, animal fat, isosorbide, and lignin [51]. Due to their accessibility, simplicity in the extraction method, cost-effectiveness, diversity of reactive sites, renewability, and biodegradable properties, vegetable oils, and fats are among the most important sources of polyol [52]. A variety of vegetable oils, such as soybean, sunflower, palm, castor, rapeseed, olive, and linseed, can be utilized to produce RPUFs. Their chemical structure includes many double bonds, which, through a variety of processes, can be converted into polyols [27,29,30,53–57]. Ester and double-bonded molecules found in triglycerides can be used in general reactions to convert vegetable oils into polyols [58].

Additional compounds, including blowing agents, surfactants, cross-linkers, catalysts, and chain extenders, can also alter the physical properties of PU foams. Catalysts can minimize a reaction's activation energy and, hence, speed up the process [59]. Minimal molecular weight additions called chain extensions and cross-linkers are employed in PUs to modify their shape, structure, mechanical, and thermal characteristics. The flexibility of the PUs materials can be changed to a desirable degree by using link extension elements such as higher functioning cross-linkers to form covalent connections between two polymeric chains, resulting in a network that is densely connected. Because PUs have chemical bonds in addition to interactions between molecules, cross-linked PUs have a mechanical strength that is greater than that of analogous linear chain-based PU substances [60]. Cross-linking has an impact on the thermal characteristics as well. To provide adequate mixing of the polyol and isocyanate, surfactants are elements introduced throughout the PUs production process [61]. The stability of PU cellular structures is provided by surfactants. Based on their characteristics, surfactants are divided into two groups: cationic and nonionic. Blowing agents are added during the foaming process to create foam structures by raising porosity and lowering density [62]. Foams with high closed-cell content, low density, excellent thermal and electrical insulating behavior, and strong mechanical qualities can be produced by using water as a blowing agent.

1.9. Purpose of this research

Academics and industry have been more interested in bio-based components for PU production in recent decades because of increasing environmental concerns. In this research, nitrogen and phosphorus containing FRs were used to reduce the inherent flammability of PU foams. The purpose of this research was to use melamine and its derivatives such as melamine phosphate and melamine cyanurate to enhance the fire-resistant characteristics of biobased RPUFs. The effects of the addition of FRs on the physicomechanical properties, thermal stability, cell morphology, and flame retardancy of rigid PUs foams were examined [45]. The foams were synthesized using castor oil. Castor oil was first converted into a polyol to provide its functionalities through epoxidation and ring-opening reactions.

CHAPTER II

MATERIALS AND EXPERIMENTS

2.1 Materials

Castor oil (CO), with a hydroxyl number of 122 mg KOH/g and an iodine value of 82.79, was purchased from Alfa Aesar (Haverhill, MA, USA) and used without any further purification. The catalysts NIAX A-1 and DABCO T-12 (> 95%) were acquired from Air Products (Allentown, PA, USA). The silicon surfactant Tegostab B-8404 from Evonik (Parsippany, NJ, USA). Methylene diphenyl diisocyanate (Rubinate M isocyanate) and Jeffol-522 were gifted by Huntsman (The Woodlands, TX, USA). Distilled water as a blowing agent was purchased from Walmart (Pittsburg, KS, USA). MA and MC as FRs were ordered from Sigma-Aldrich, (St. Louis, MO, USA) and (JLS Chemical Inc., Pomona, CA, USA), respectively, while o-phosphoric acid, (85%) was purchased from Fisher Scientific (Hampton, NH, USA). Acetic acid, hydrogen peroxide, toluene, Amberlite IR 120H, sodium chloride, sodium sulfate, tetrafluoro boric acid, Lewitt MP64, and methanol were bought from Fisher Scientific (Allentown, PA, USA) to be used in the manufacture of castor oil-based polyol (COP).

2.2 Synthesis of castor oil-based polyol

A facile approach was used to epoxidize CO (ECO) using peracetic acid that was produced in situ using glacial acetic acid and H_2O_2. Toluene and Amber lite IR-120 were employed as solid heterogeneous catalytic agents and solvents, respectively. In a three-necked round-bottom flask, 500 g of CO, 125 g of amber-lite IR-120 resin, and 250 ml of toluene were added. The hot plate, water bath, mechanical stirrer, and reflux condenser were connected as depicted in **Figure 8**. The mixture was first cooled to about 5°C while being stirred constantly. Then, using a dropping funnel, 48.88 ml of acetic acid (0.5 mol) and 277 ml of 30% aqueous H_2O_2 (1.5 mol) were gradually added. By adding acetic acid and H_2O_2, the reaction mixture's temperature was kept about at 5°C. Once all the ingredients had been added, the temperature gradually rose to 70 °C. At this temperature, the reaction was continuously stirred for 7 hours. Before filtering the mixture to remove the resin from the oil, it was allowed to cool to room temperature. After that, the mixture was rinsed 7 or 8 times in the separating funnel using a 10% brine solution. The mixture was allowed to settle for about 30 minutes throughout the washing process to ensure that the layers of water and oil separated properly. After that, the oil was stirred for a further 15 minutes while around 3 g of anhydrous sodium sulfate was added to extract any moisture. To extract the solvents from the oil, the rotary evaporation process was then carried out at low and high vacuums, respectively [63].

In the ring-opening process, methanol was utilized to speed up the epoxide's ring-opening process, which led to the synthesis of hydroxyl functional groups. Tetrafluoroboric acid (0.05 wt.% of the combined weight of methanol and epoxidized oil) was used as a catalyst, with methanol acting as a nucleophile. 7:1 molar ratio of ECO and methanol were used. Methanol and tetra fluoroboric acid were added in a three-necked flask that was attached to a condenser and dropping funnel. The reaction mixture was prepared at a temperature of around 70 °C. ECO was added dropwise using the dropping funnel to the flask, and the mixture was stirred for one further hour. To neutralize the acid, the mixture was stirred for another 35 to 40 minutes after cooling to room temperature. This was done by adding the Lewitt MP 64 ion exchange resin to the oil. After confirming neutral pH, the resin was removed by filtering, and the remaining solvents were removed using rotary evaporation. **Figure 9** shows the general structural and bonding changes that take place throughout the epoxidation and ring-opening processes.

Figure 8. The setup for epoxidation reaction and polyol synthesis.

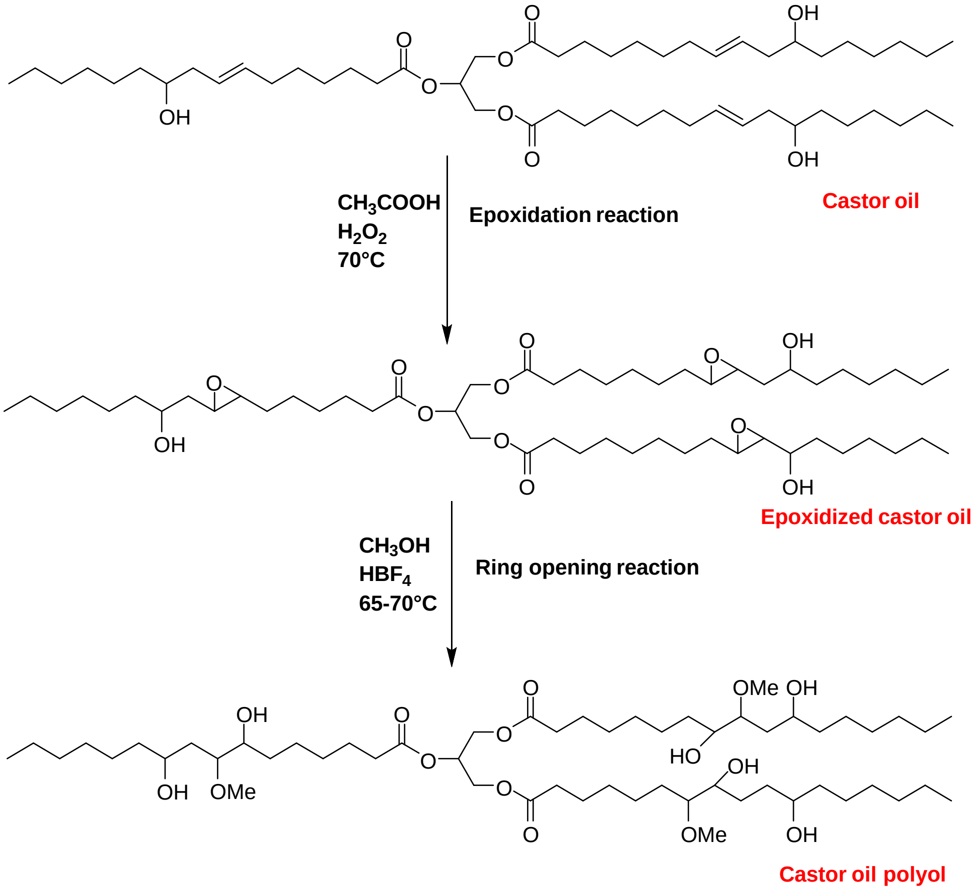


Figure 9. Reaction scheme for the synthesis of castor oil-based polyol.

2.2.1. Preparation of rigid polyurethane foams

Bio-based RPUFs were made using a one-shot free-forming process that includes flame retardant, surfactant, blowing agent, catalyst, and polyol and isocyanate. **Figure 10** displays the process for the preparation of RPUF. A plastic cup was filled with the calculated quantity of SG-522, synthesized COP, FRs, and other components (**Table 1**). The mixture was then stirred for a minute using a mechanical stirrer to ensure its homogeneity. After this, the required amount of isocyanates was added and stirred for a few seconds. The resultant polyurethane foams were allowed to cure for seven days at room temperature before conducting any tests.

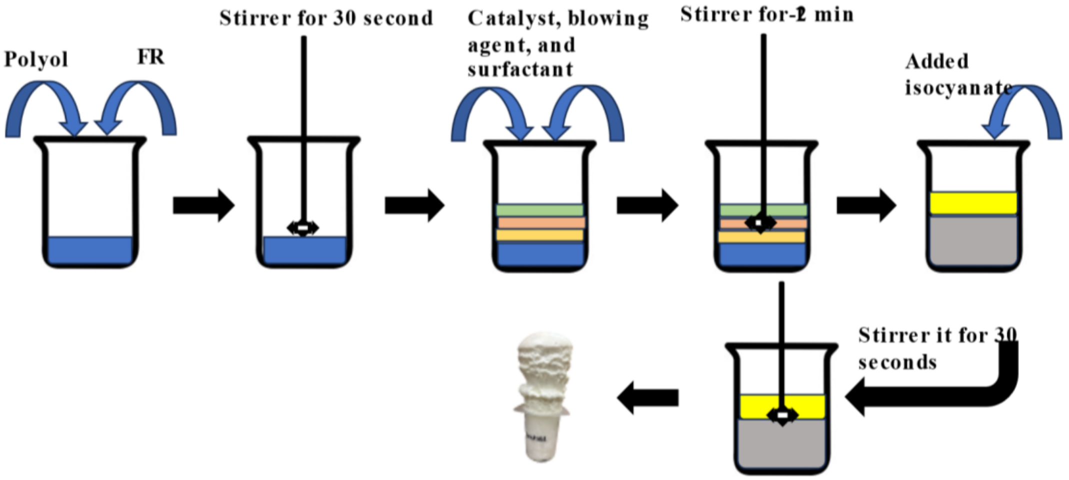


Figure 10. Schematic of making foam.

Table 1. Formulation for RPUF using FRs. All numbers are in grams except wt.% of FR.

Compound	**CONTROL**	**CO-MA-1**	**CO-MA-2**	**CO-MA-3**	**CO-MA-4**	**CO-MA-5**	**CO-MA-6**	**CO-MA-7**
CO-polyol	10	10	10	10	10	10	10	10
SG-522	10	10	10	10	10	10	10	10
A-1 JEFFCAT -ZF22	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18
Water	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
T-12-Dibutyltin dilaurate	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
TEGOSTAB® B 8404	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Isocyanate -MDI	31.1	31.1	31.1	31.1	31.1	31.1	31.1	31.1
Flame retardant	0	1	2	5	7	10	12	15
% of FR	0	1.90	3.80	9.52	13.32	19.04	22.84	28.56

2.3 Characterization of castor oil-based polyol and RPUF

The synthesized polyol along with starting materials were examined using conventional characterization procedures and methods (**Figure 11**).

Figure 11. The titration devices used for the determination of hydroxyl number, acid value, epoxy-oxirane oxygen content, and iodine value.

2.3.1 Iodine value

The amount of unsaturation in the oil was determined by measuring the iodine value (IV). A high iodine value suggests the presence of a significant degree of unsaturation. To determine the number of double bonds in the castor oil, the Hanus technique was applied. Approximately 0.2–0.3 g of castor oil was mixed in 10 ml of chloroform ($CHCl_3$) in a 250 ml Erlenmeyer flask. Once the solution had been gently shaken, 20 ml of Hanus reagent

(BrI) was added, and it was left in the dark for an hour. The glass flask was then filled with 20 ml of a 10% potassium iodide solution and 50 ml of HPLC-grade water, which were combined and mixed to create a solution that was uniform in consistency. After adding six drops of starch indicator, sodium thiosulfate ($Na_2S_2O_3$) was added to the blue solution and titrated until a colorless solution appeared. The amount of reagent needed for the epoxidation reaction was determined by calculating the average value of the triple tests performed for this experiment.

2.3.2 Epoxide oxygen content

Using glacial acetic acid and tetraethylammonium bromide, the epoxy oxygen content (EOC%) was determined. The % of epoxide group produced from the double bonds was examined and confirmed using this assay. In 50 ml of tetraethylammonium bromide (TEAB) solution, 0.3–0.5 g of epoxidized castor oil was dissolved. Before titrating with 0.1 N perchloric acid ($HClO_4$), a drop of crystal violet indicator was added. Epoxidized castor oil's epoxy content was determined by measuring the volume recorded during the titration process, which was marked by a color shift from blue to green. The test was calculated 3 times, and an average value was reported.

2.3.3 Hydroxyl value

The hydroxyl value (-OH number) indicates the functionality of a polyol and is used to calculate the amount of isocyanate needed for the PU preparation. ASTM-D 4274 standard using phthalic anhydride pyridine (PAP) was used to calculate the -OH number for the COP. Here, 10 ml of a hydroxyl solution was added to a glass container containing 0.5 g of the synthesized COP. The glass container was heated to 100 °C for 70 minutes with intermediate shaking of the bottle. After that, it was cooled down to room temperature, and 10 ml of HPLC-grade water and 20 ml of isopropanol were added. 1 N sodium (NaOH) was added and titrated until a pink hue was seen. The hydroxyl number was calculated using volume. This test was conducted three times, and an average value was reported.

2.3.4 Acid value

The acid value of CO, ECO, and COP was determined. The process used for this identification was the IUPAC 2.201. 30 ml of a solvent combination consisting of isopropanol, toluene, and phenolphthalein indicator were used to dissolve around 1 g of the testing material. After that, 0.1N potassium hydroxide was added and titrated until a pink color was noticed. The volume was noted and utilized to get the acid value.

2.3.5 Viscosity

The fluid's viscosity indicates the resistance to flow. A low viscosity might indicate a low molecular weight, whereas a substance with a high viscosity can indicate a high molecular weight. Some other parameters such as hydrogen bonding may affect the viscosity of a material. An AR 2000 dynamic stress rheometer (TA instruments, USA) was used to measure the viscosity of starting and prepared chemicals. (**Figure 12**). At 25 °C, the viscosity was determined as the shear stress increased linearly from 1 to 2000 Pa. The cone plate provided with the dynamic rheometer had a 2° angle and a 25 mm cone-diameter.

Figure 12. AR 2000 dynamic stress rheometer.

2.3.6 Fourier-transform infrared spectroscopy

Fourier Transfer Infrared (FT-IR) spectroscopy is an analytical technique used for analyzing the chemical structures and presence of functional groups in both organic and inorganic. Furthermore, FT-IR can be used to study materials in solid, liquid, and gas phases. To confirm the functional groups and conversion of bonds, a PerkinElmer Spectrum Two spectrophotometer (**Figure 13**) was utilized.

Figure 13. FT-IR analysis instruments.

2.3.7 Gel permeation chromatography

Chromatography is recognized as the most accurate and adaptable technique for studying polymeric compounds. To separate polymers according to their size, gel permeation chromatography is a dependable analytical method. The molecular weight distributions of a complex polymer, for example, can be ascertained using the size-exclusion method in GPC. As shown in **Figure 14**, the experiment made use of the Waters GPC equipment from Milford, Massachusetts, USA. A Phenogel 5 µm LC column 300 × 7.8 mm with four distinct pores measuring 50, 102, 103, and 104 Å was used. Tetrahydrofuran (THF) was used as the fluid phase, with a flow rate of 1 ml/min at 30 °C. After dissolving the sample (20 mg) in 1 ml of 0.888 g/mL THF, 20 µL of the mixture was injected into the column.

Figure 14. Gel permission chromatography instrument.

2.3.8 Characterization of rigid polyurethane foam

The foams were dried for a week before being cut into different shapes and sizes. The apparent density, burning time, and weight loss were measured. All the measurements were performed three times and an average of three was reported. Compression strength, thermal stability, closed cell content, and cell morphology were also studied.

2.3.1.1 Apparent density

ASTM D1622 standard was used to calculate foam density. Vernier was used to precisely measure the samples' dimensions at two randomly chosen sites to calculate their geometric volume and a balance to measure the weight of the foam.

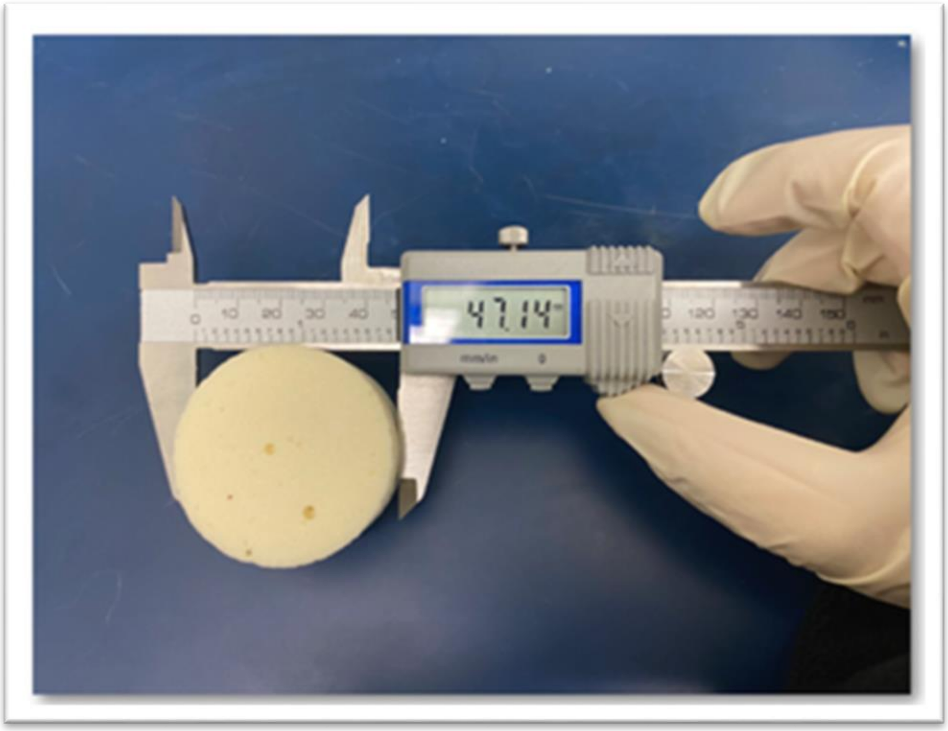


Figure 15. A digital photo of the foam used to measure apparent density.

2.3.1.2 Closed cell content

Foams are classified according to their cell structure, which can be closed or open. The pore structure of PU foams defined the amount of air entrapment. ASTM D2856 was used to estimate the closed-cell content of the foams using an ultra-pycnometer (Ultra foam 1000), as seen in **Figure 16**.

Figure 16. A closed-cell content-measuring ultra pycnometer.

2.3.1.3 Scanning electron microscope

Figure 17 (upper) illustrates a scanning electron microscope which was used to study the cell morphology of the foams. The cell size and pore distribution were studied using the SEM images of the foams. Since foams are insulating in nature, a thin film of gold was coated to improve their electrical conductivity. **Figure 17** (lower) shows the photo of a sputtering unit (Kurt J. Lesker Company) used to coat a thin film of gold on the surface of the foams before taking SEM images. A Thermo Scientific Phenom Pure desktop SEM purchased from Sioux in the Netherlands was used.

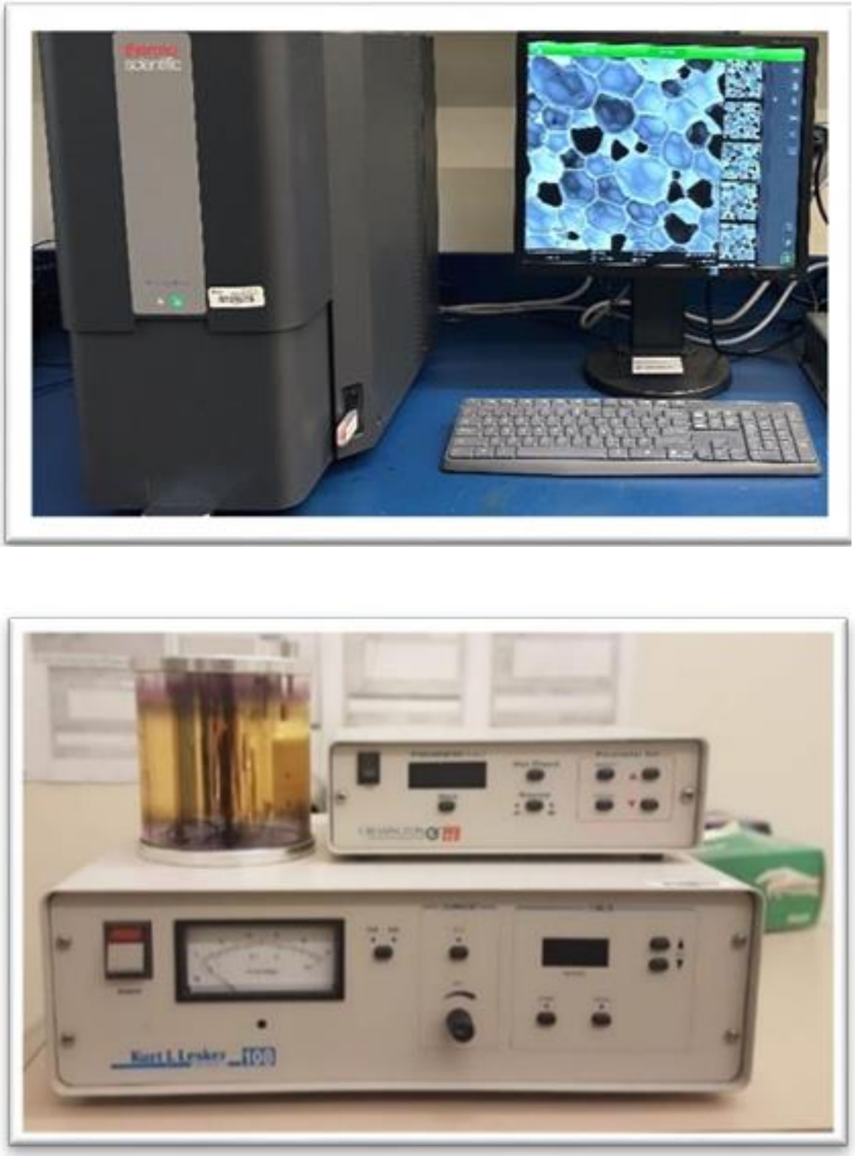


Figure 17. SEM (upper) and sputtering (lower) units.

2.3.1.4 Thermogravimetric analysis

TGA was used to examine the thermal stability of bio-based PU foams and the effect of FRs on the thermal properties of PU foams. In TGA, the change in the weight of the samples as a function of temperature was recorded. TGA Q-500 from TA Instruments was used for this study (**Figure 18**). A sample of about 6 mg was used under a nitrogen environment at a ramp rate of 10 ºC/min.

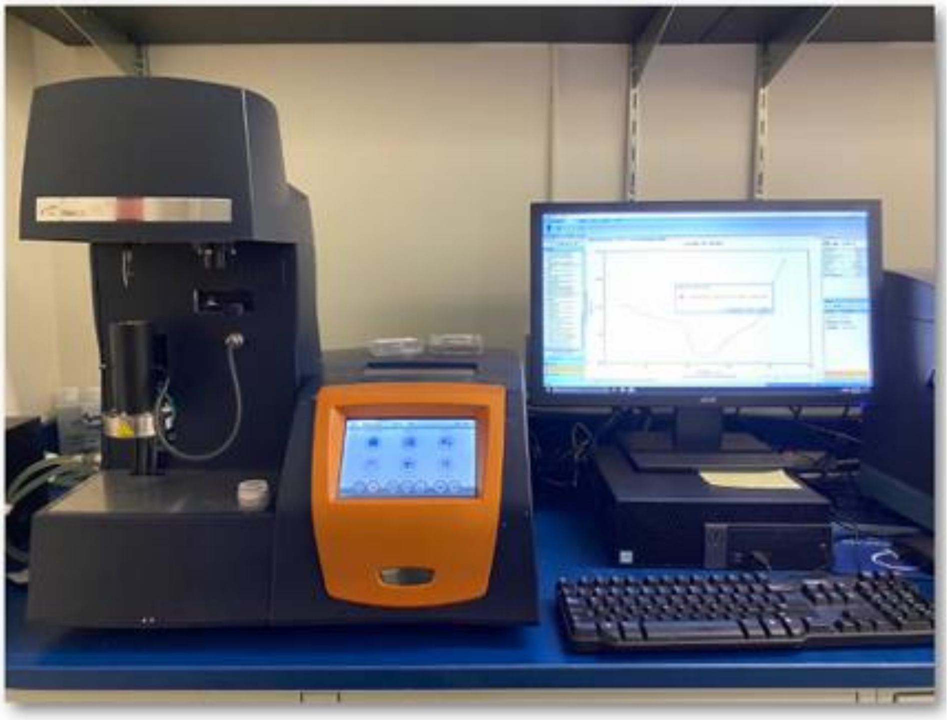


Figure 18. Thermogravimetric analysis instrument.

2.3.1.5 Compression strength test

The compressive strength of a material was determined based on using ASTM D 1621 using "Q test 2-tensile machine" (**Figure 19**). The foams were cut into rectangles of 50 × 50 × 25 mm3 (width × length × height) for a compressive strength examination.

Figure 19. An instrument for determining compressive strength.

2.3.1.6 Horizontal burning test

The RPUFs' horizontal burning test was determined using the ASTM D4986-98 standard. Rectangular specimens of 150 mm in length, 50 mm in breadth, and 12.5 mm in thickness were cut from castor oil-based PUs foams. According to ASTM D 4986-18, the foams were arranged horizontally in a fume hood-equipped room, as shown in **Figure 20**. The burning time and weight loss were determined after applying a flame to the foam for ten seconds.

Figure 20. Horizontal burning test under the fume hood.

CHAPTER III

RESULTS AND DISCUSSION

3.1 Properties of CO, ECO and CO-polyol

In this work, the Prilezhaev, reaction was applied to it to convert CO's double bonds into epoxy groups by in-situ generation of peroxy acid [64]. A molar ratio of 1:0.5:1.5 for C=C: CH_3COOH: H_2O_2 was used. H_2O_2 was employed as the oxidation reagent and acetic acid as the oxygen transporter [65]. Both organic and aqueous chemicals are used in this epoxidation process, as a result, it is critical to pay consideration to the temperature of the reaction. The research determined that 70 °C was the appropriate temperature since double bonds have poor selectivity and higher temperatures tend to increase side reactions. Because of this, ion exchange Amberlite resin IR-120, a catalyst was utilized to speed up the process.

The ring-opening reaction produces different products depending on the reactants. Water, hydrogen peroxide, carboxylic acids, alcohols, and amines are commonly utilized as ring-opening agents, whereas strong acids, Lewis bases, and Lewis acids serve as catalysts [66]. This work utilized methanol as a ring-opening solvent to match the hydrophobic nature of the ECO. HBF_4 was used as the catalyst due to its ability to produce polyols with high OH content. [67]. During ring-opening in an acidic environment, a nucleophilic substitution event occurs on the epoxide ring [68]. The iodine value, oxygen content of epoxy-oxirane, hydroxyl number, acid value, and viscosity of CO, ECO, and COP are listed in **Table 2**.

Table 2. Characterization of castor oil, epoxidized castor oil, and castor oil polyol.

Tests	**Units**	**Castor oil**	**Epoxidized castor oil**	**Castor oil polyol**
Iodine value	g I_2/ 100g	82.79	0.2	0.74
Epoxy – oxirane oxygen value	%	-----	4.88	2.70
Hydroxyl number	Mg KOH/ g	122	------	270
Acid value	Mg KOH/ g	3.67	-----	0.73
Viscosity @ 25°C	Pa.s	0.41	2.06	8.83

3.1.1 Iodine value

The Hanus technique was used to calculate the iodine value (amount of unsaturation) of CO, ECO, and COP. The iodine value of CO was 82.79 g I_2/100 g, indicating that 0.32 molecules of double bonds were present in 100 g of the CO. Following the epoxidation and ring-opening reactions, the epoxide and castor oil polyol showed iodine values of 0.2 g I_2/100 g and 0.74 g I_2/100 g, respectively.

3.1.2 Epoxide number

The percentage of oxirane value illustrates the number of epoxide groups present in a substance. In this investigation, the epoxide number was measured after the epoxidation process of CO, which was around 4.88%. This reaction was carried out with hydrogen peroxide and acetic acid in the presence of a catalyst. Following the ring-opening procedure, the epoxide dropped for polyol by 2.70%.

3.1.3 Hydroxyl Value

The hydroxyl number is one of the most significant parameters for polyol, as it defines the level of reactivity and isocyanate concentration required for the creation of PUs. The OH number of the castor oil-based polyol was determined to be 270 mg KOH/g. The amount of MDI needed to synthesize the rigid PU foams was calculated based on this number.

3.1.4 Acid Value

The CO-derived polyurethane foams were made using an amine-based catalyst. Therefore, using a castor oil polyol with a high acid value will reduce foam volume and reactivity. The acid values of CO and COP were calculated to be 3.67 mg KOH/g and 0.73 mg KOH/g, respectively.

3.1.5 Viscosity measurement

At room temperature, the viscosity of castor oil was 0.41 Pa.s. On the other hand, the produced polyol's viscosity was found to be 8.83 Pa.s, suggesting its higher viscous nature which could be due to the presence of hydrogen bonding between hydroxyl groups.

3.1.6 Fourier-transform infrared spectroscopy

Fourier spectroscopy was used to identify the chemical bonds. The FT-IR spectra for CO, ECO, and COP are shown in **Figure 21.** FT-IR spectrum of CO shows a peak at 3400 cm^{-1} which represents OH stretching vibrations, which clearly illustrate the hydroxyl groups that are found naturally. CO contains unsaturated bonds, as seen by the peaks at 3008 cm^{-1}, which correspond to C-H stretching. Despite this, the peak disappeared after the epoxidation reaction, and a new peak appeared at 843 cm^{-1} which is due to the presence of epoxy oxirane groups (C-O-C) [69]. The presence of a broad peak at 3451 cm^{-1} indicates OH groups of COP [70]. The FT-IR spectra confirm the formation of ECO and COP.

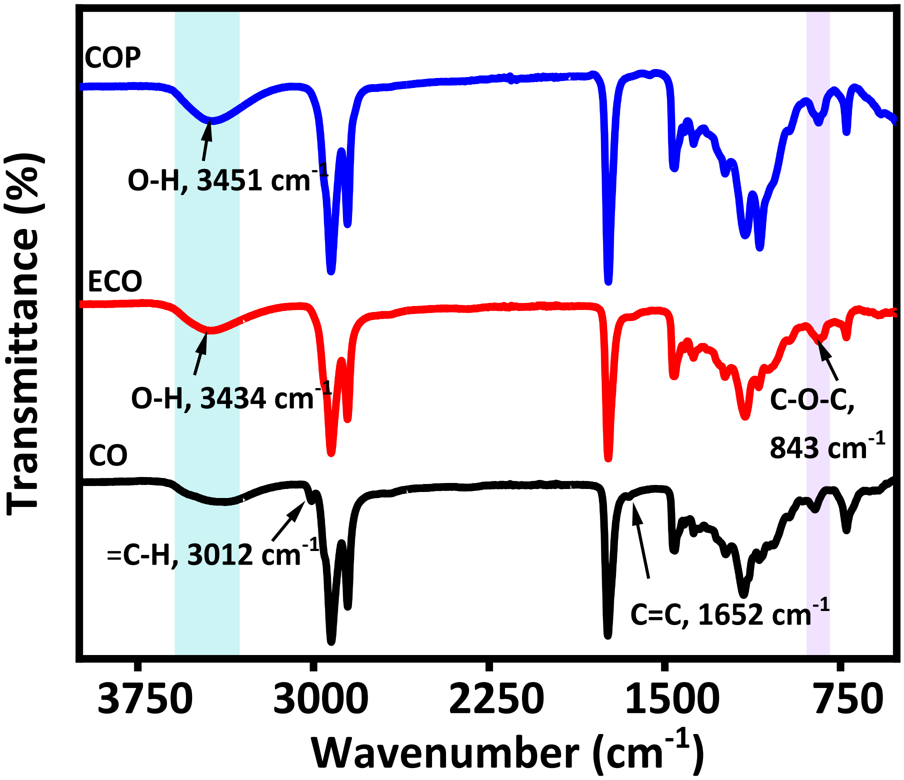


Figure 21. The FTIR spectra of CO, ECO, and COP.

3.1.7 Gel permeation chromatography

Figure 14 displays the GPC of CO, ECO, and COP. COP's retention time was found to be 32.12 minutes. ECO and CO showed a retention time of 32.19 and 32.11 minutes, respectively. In the castor oil polyol, a small peak is seen at 30.40 minutes which could be due to the formation of dimers and trimers [71].

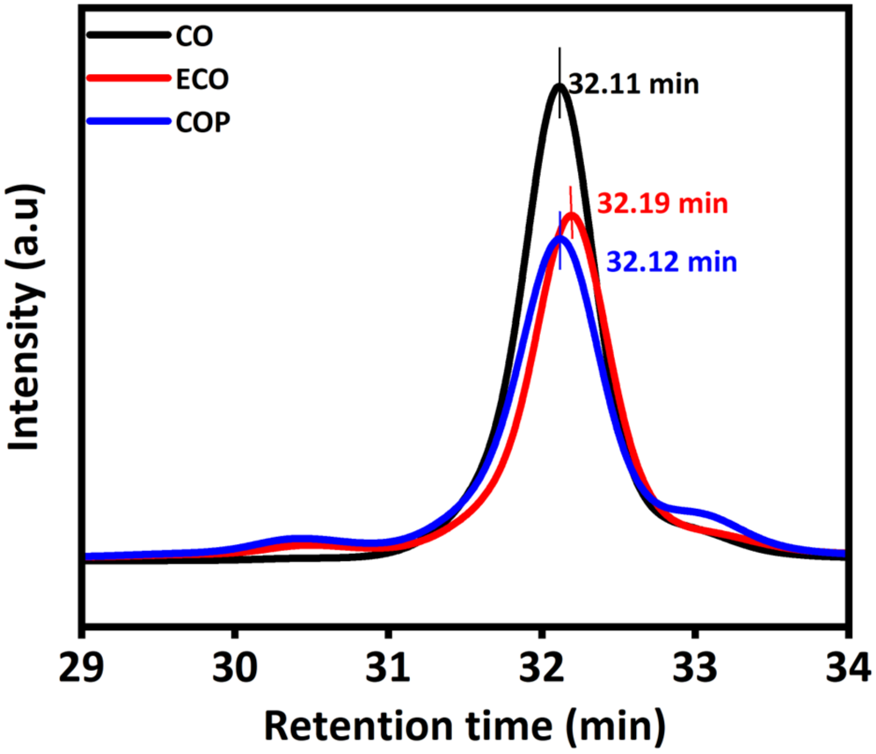


Figure 22. GPC of CO, ECO, and COP.

3.2 Characterization of Flame-Retardant Rigid Polyurethane Foam

Once the proper characteristics of the castor oil polyol were performed, rigid PU foams with different concentrations of FRs were created. The foams were cut into circular and rectangular shapes for further testing.

3.2.1 Apparent density

A detailed examination of the physical properties of biobased rigid PU foams was performed to identify the impact of castor oil-based polyol and flame retardants. The density of the RPUFs was measured and presented in **Figure 23**. Foams having MA as FR showed apparent density in the range of 37–52 kg/m^3 while foams with MC as FR displayed apparent density in the range of 33–51 kg/m^3. On the other hand, foams with MP showed higher density (40–54 kg/m^3) compared to foams with MA and MC. This could be due to the acidic nature of MP which reduced the foam height and thus increased the density.

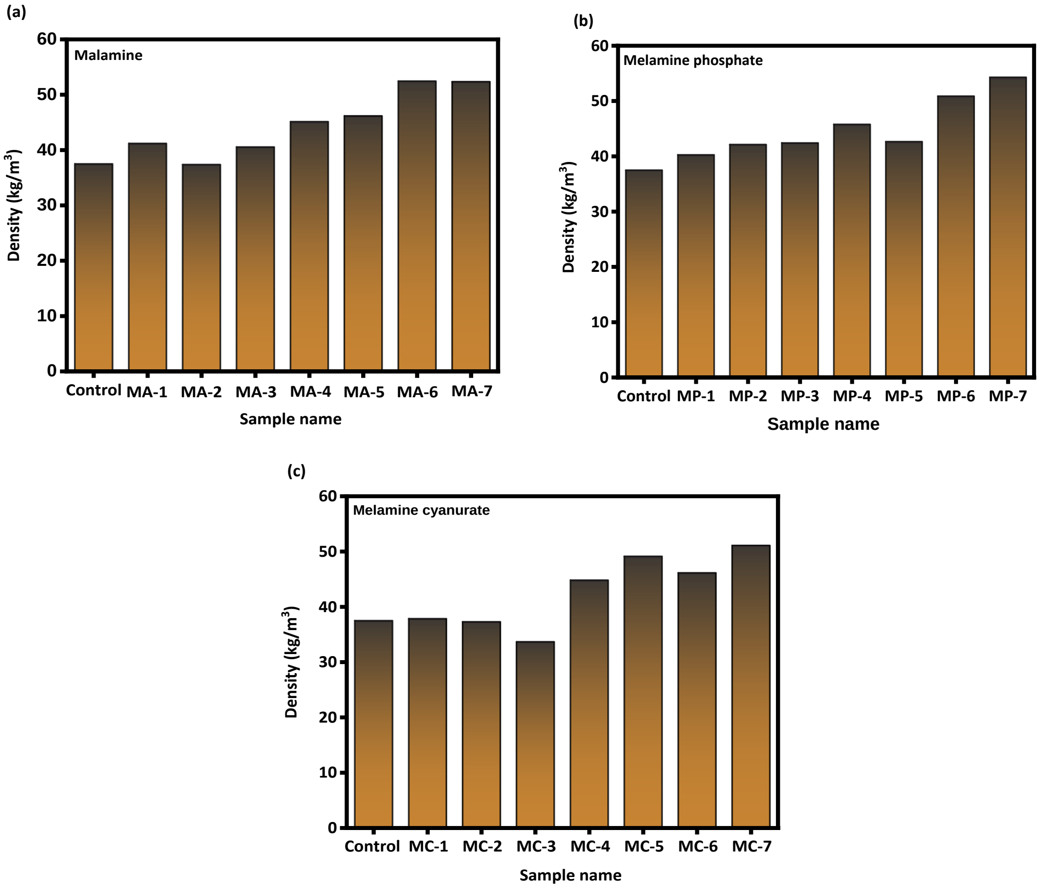


Figure 23. The apparent density of RPUF with (a) MA, (b) MP, and (c) MC as FR.

3.2.2 Close cell content

Figure 24 shows the closed cell content of RPUFs containing different amounts MA, MP, and MC as FRs. The RPUFs without FRs showed a closed cell content of 95% which was the same after the addition of FRs. The research suggests that adding MA, MP, and MC to rigid polyurethane foams results in high closed-cell content which can provide good insulating properties.

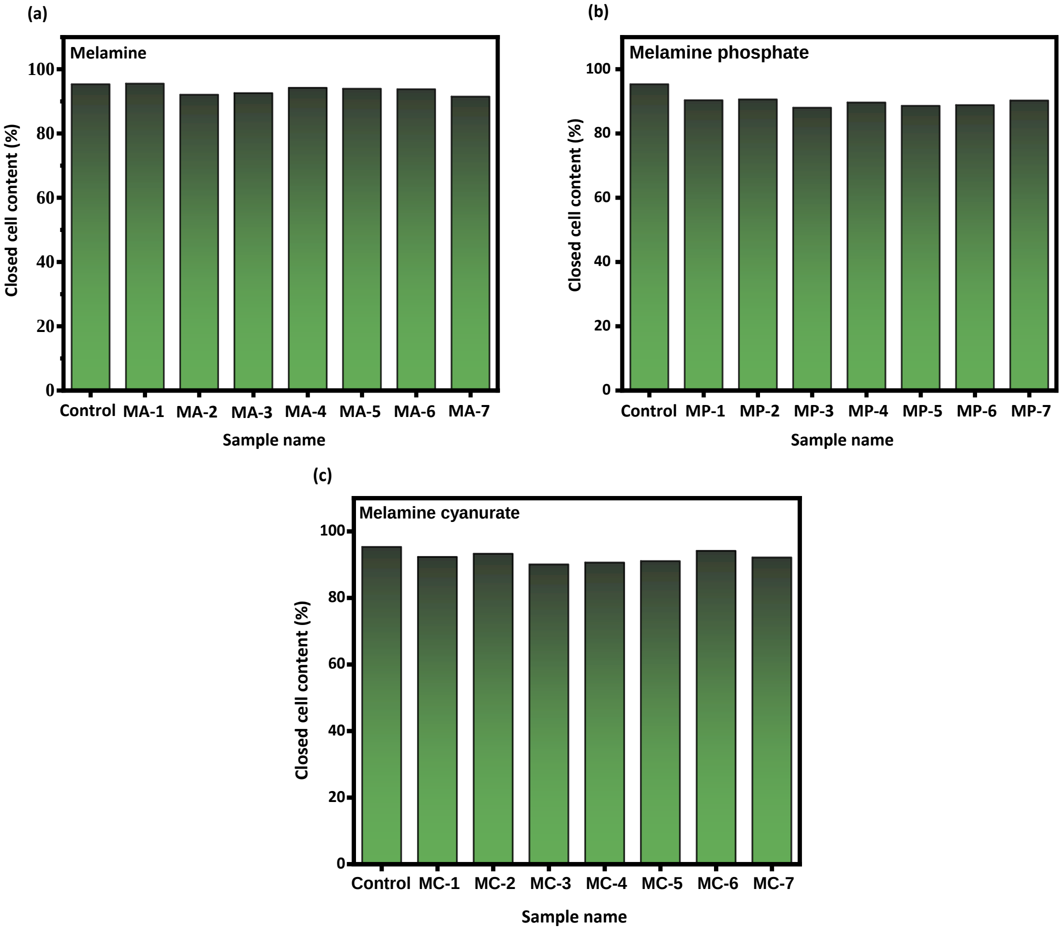


Figure 24. Closed cell content of RPUF with (a) MA, (b) MP, and (c) MC as FR.

3.2.3 Compression strength of RPUFs

The compressive strengths of RPUFs are influenced by their cellular morphology such as cell size [72]. The compressive strength of RPUFs containing MA, MP, and MC FRs is shown in **Figure 25**. The compressive strength of the control foam is approximately 210 kPa. MA-3 showed the lowest compressive strength (180 kPa) and MA-6 displayed the maximum compressive strength of 290 kPa.

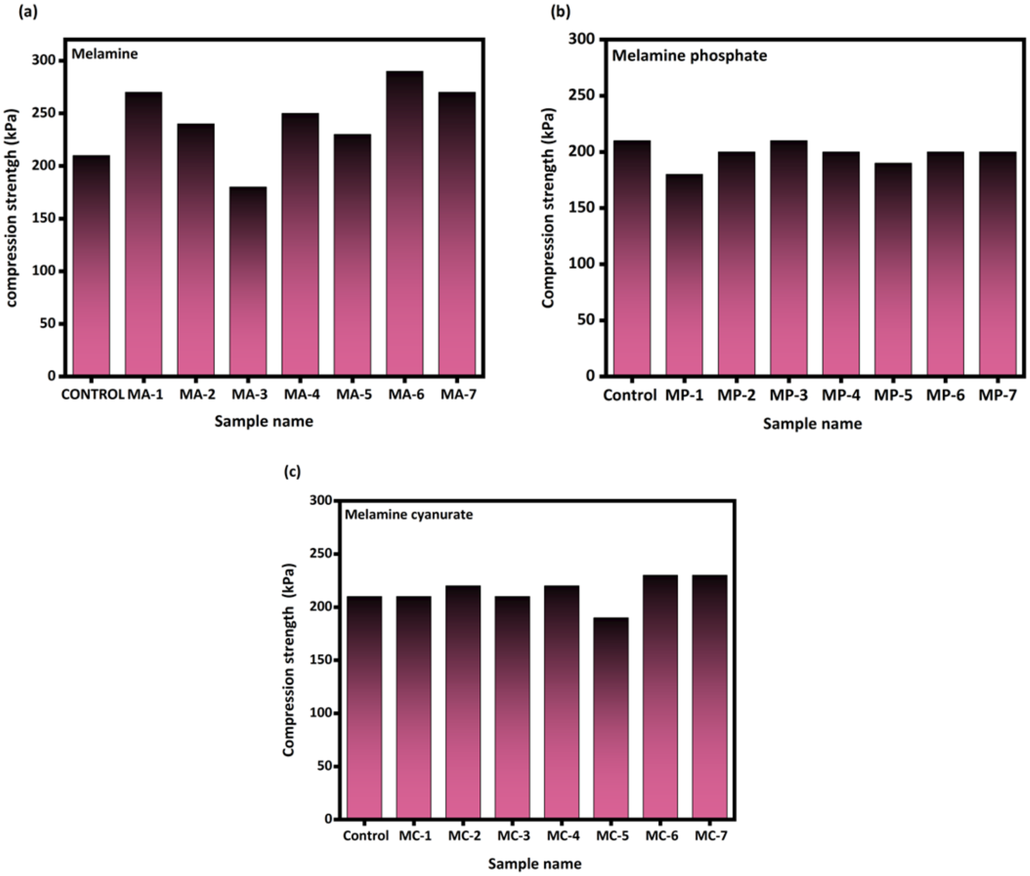


Figure 25. Compressive strength of RPUF with (a) MA, (b) MP, and (c) MC as FR.

3.2.4 Thermogravimetric analysis

TGA and DTGA data were used to examine the thermal properties of foam with different amounts of FRs. **Figure 26** depicts the TGA and DTGA for RPUFs with different amounts of MA. The thermal degradation of RPUFs without FRs occurs in two phases. In general, the first and second degradation phases of rigid foam were seen around 250–300°C and 310–500°C [73]. The addition of flame retardants to foams helps to improve thermal stability. Melamine inhibits fire and absorbs heat, releasing ammonia and nitrogen gas during the condensation reaction. This technique prevents burning by reducing the substance's temperature and diluting flammable gases and oxygen. The average degradation temperature range for MA foams was ~234 °C to ~310 °C [74]. While both MA and MC undergo endothermic reactions, MC exhibits greater thermal stability due to its network structure and hydrogen bonding. **Figure 28** shows MC decomposes around 300–450 °C, producing a small amount behind. MC degrades to melamine and cyanuric acid, which usually evaporates during burning. Melamine releases ammonia when heated, resulting in stable compounds such as melam, melem, and melon at temperatures of 300, 420, and 440 °C, respectively. As the proportion of MC increased, rigid polyurethane foams became more heat resistant. In the case of MP-based foams, the second transition occurred between 420 and 500 °C, resulting in considerable improvement in the thermal behavior. Nitrogen and phosphorus synergistically formed char residue on the foam's surface. Burning foam forms a carbonaceous layer, which improves its thermal stability. Higher concentrations of MP resulted in increased residue formation, preventing subsequent ignition. The TGA curve may have additional peaks because these residues degrade at different temperatures.

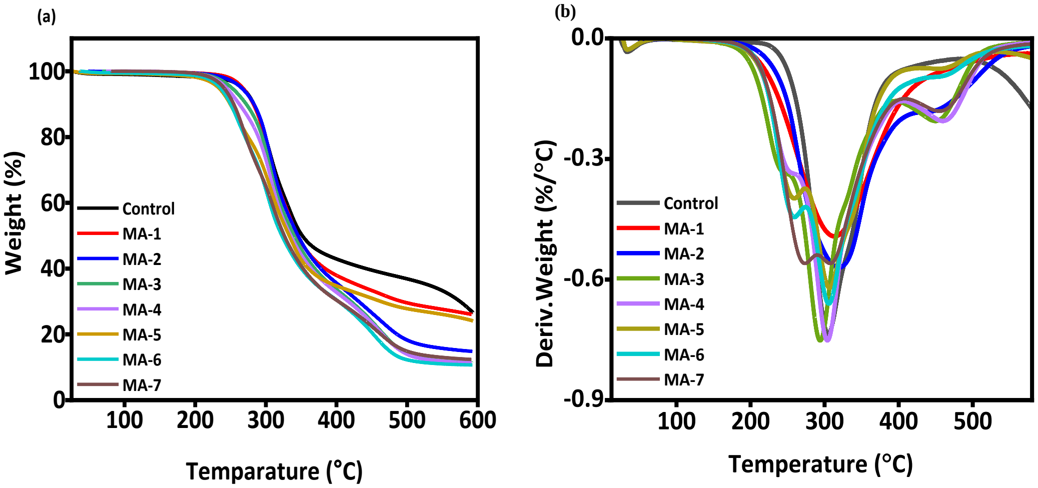


Figure 26. Thermal analysis of RPUFs containing MA.

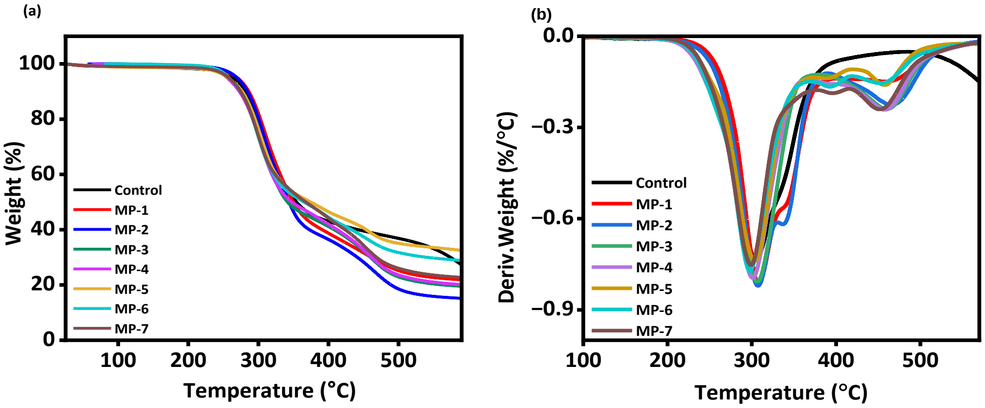


Figure 27. Thermal analysis of RPUFs containing MP.

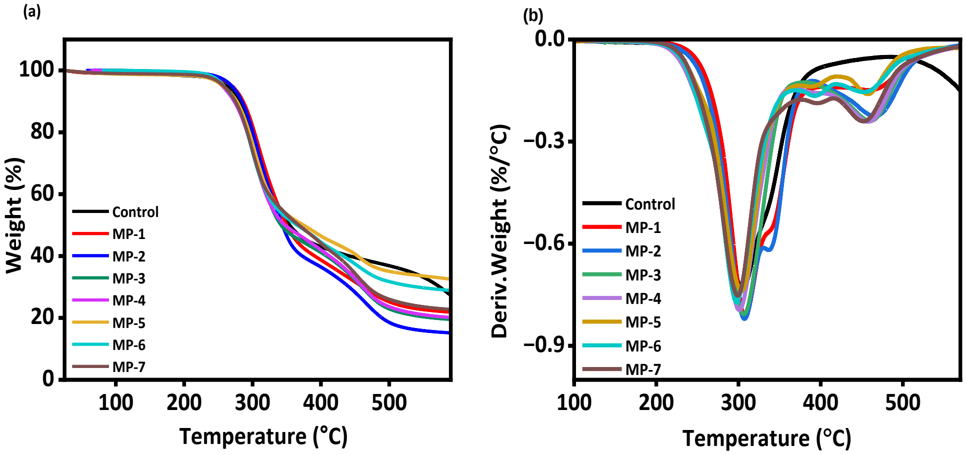


Figure 28. Thermal analysis of RPUFs containing MC.

3.2.5 Scanning electron microscopy

The cell morphology of the foams was observed by using SEM. The microstructure of RPUFs affected the physical and mechanical properties of foams. **Figure 29** illustrates the SEM images of all the foams [75]. The average cell size of neat foam was 130 µm which changed after the addition of FR. In the case of MA foams, the cell size was observed to be decreased, however, no significant change in cell size was with the higher amount of MA. The average cell size of MA-incorporated foams was in the range of 118-162 µm. As a result of the increased number of cells per unit area, the mechanical properties of MA foam increased from 5 MA to 15 MA. However, at 10 MA, the average cell size decreased to 126 µm, and the compressive strength also fell. The opposite trend was seen in the case of MP-based foams. As compared to the control foams, the cell size of the RPUFs having MP was increased. The cell size was also increased (from 165 µm to 257 µm) after the addition of a higher amount of MP. This indicated that the number of cells per unit area declined. The MP-based foams showed bigger cell sizes than the foams with MA and MC. RPUFs with MC had almost similar cell sizes compared to the cell size of the control sample. With the addition of an increasing amount of MC foam from 1 to 15 g, a small variation in cell size from 128 to 144 µm was noted.

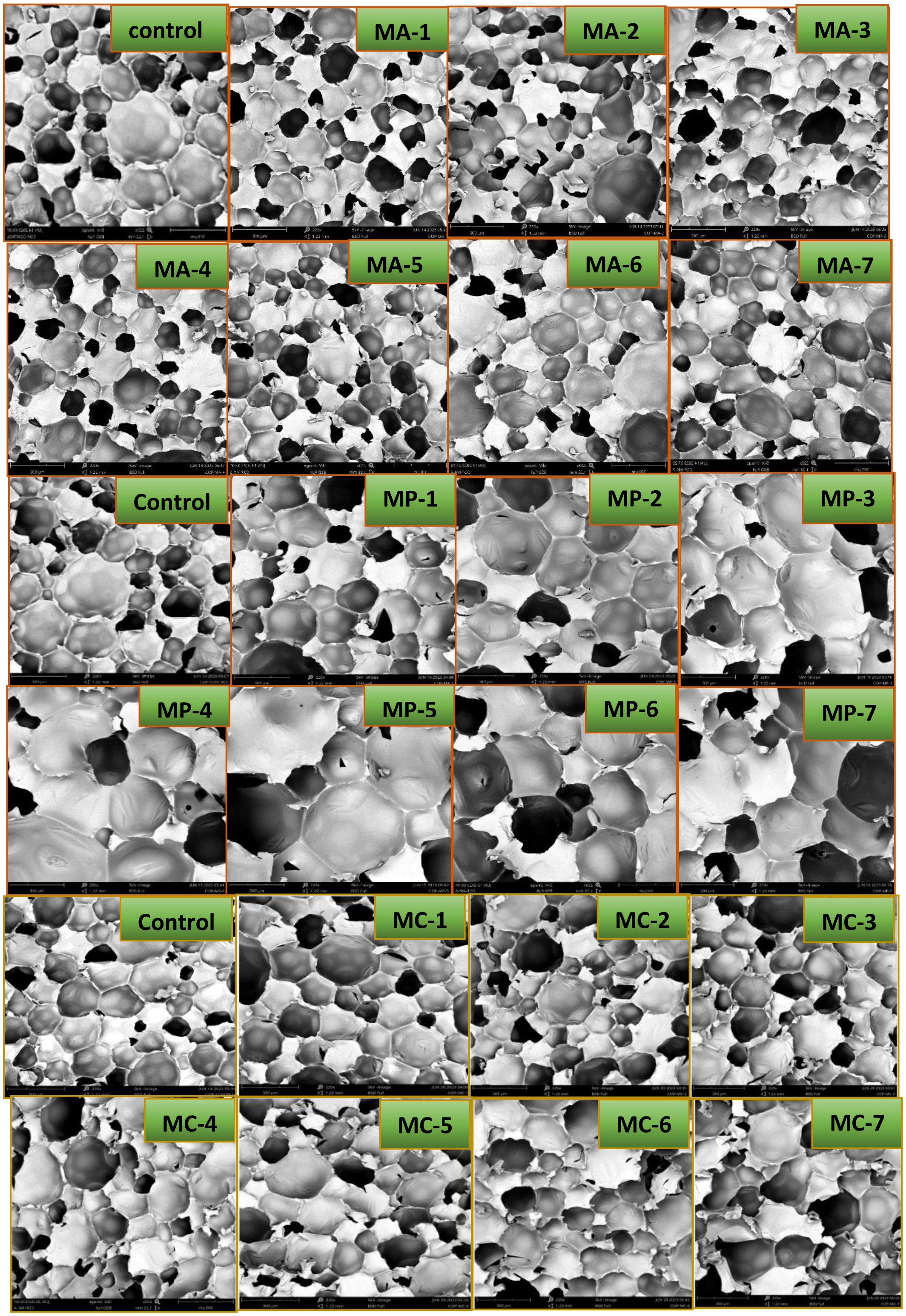


Figure 29. SEM images of RPUF having various amounts of FRs.

3.2.6 Horizontal burning test

The results of horizontal flame tests along with foam pictures before and after the burning test in shown in **Figure 30**. The neat foam burned for 49.0 seconds and 53.28% of weight loss. Following the gradual addition of FR, an effective reduction in burning time and, as a result, weight loss was seen [76]. Foam comprising 28.5 wt.% of MA (15 MA) showed a burning time of 9.5 seconds with a weight loss of 9.68%. The MP-containing foams likewise produced good results for the 15 MP sample, achieving 14.4 seconds of burning time and 7.76% weight loss. For the MC set of foams, the foam containing 11.7 wt.% of MC (7 MC) showed a burning time of 28.8 seconds with a weight loss of 19.29%. The differing results in fire resistance may correspond to the various fire-quenching mechanisms that are used for the process. MA has been seen performing functions in a combination of solid and gas-like phases. As mentioned earlier, the solid-phase action is characterized as the endothermic decomposition of MA, which produces oligomeric and compact counterparts known as melam, melem, and melon. These chemicals created a dense char layer on the PU's surface, reducing the flow of oxygen and other reactive species like H and OH, which could promote the burning of the PU matrix even more. Furthermore, because the deterioration process of MA is endothermic, it absorbs energy, decreasing the temperature and placing it below the ignition point of the PU. MC functions similarly to MA. It offers one additional energy barrier to prevent the PU from bursting into flame: the endothermic inversion of its structure to MA and cyanuric acid. These chemicals can then cross-link with the PU matrix to generate a more compact carbonaceous char layer, preventing the fire and combustion from degrading the foam further. The present study nonetheless did not demonstrate the most productive flame retardancy because flickering maintained the flame over the foam for longer than anticipated. In the case of MP, an equitable synergy effect combines the N supply from ME and the P source from phosphate. Adding a small amount of phosphate enhanced polyphosphoric acid development, resulting in a more effective and compact char layer that protected the fundamental PU from fires. Additionally, research from previously published research in the literature demonstrated that FRs with P in their structure are similarly productive in the gaseous phase. Revolutionary scavenger species like HPO, PO, or PO_2 may arise because of the breakdown of phosphate which can react with H and OH quickly. Consequently, the fire might be put out rapidly through the elimination of these species from the medium. As a result, when MA and phosphate compounds combined, they produced a synergistic action.

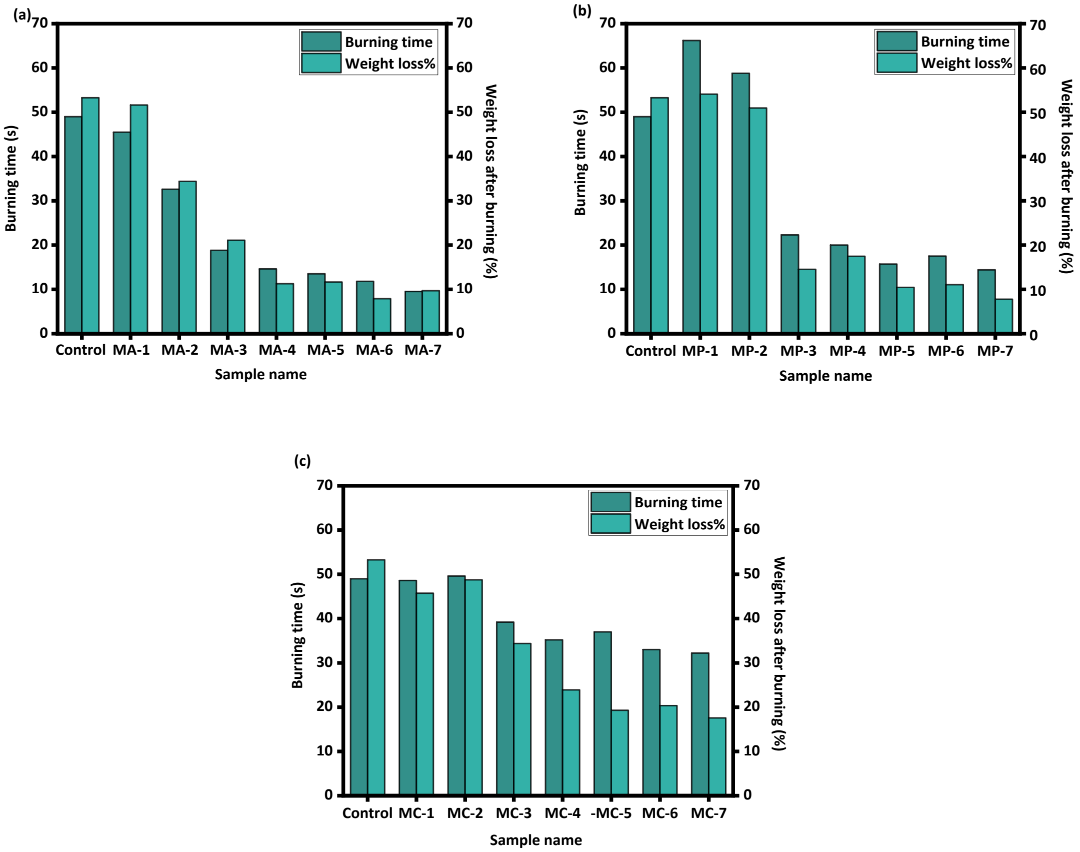
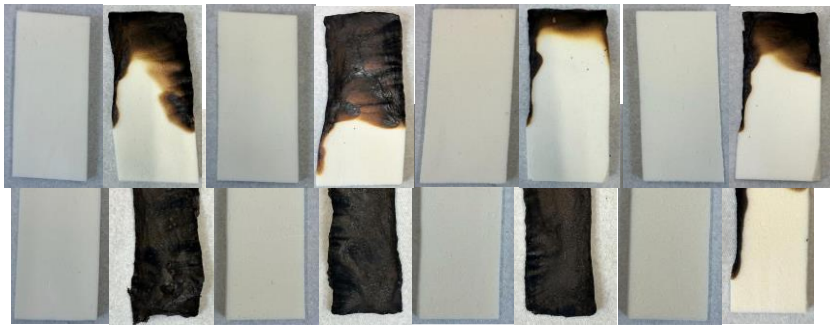
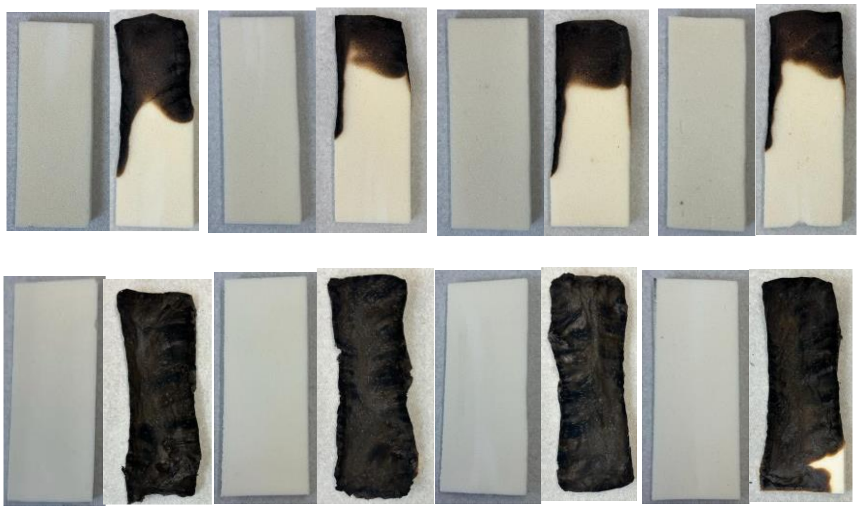


Figure 30. Burning test and weight loss of RPUF containing different FRs.

Melamine



Melamine Phosphate



Melamine Cyanurate

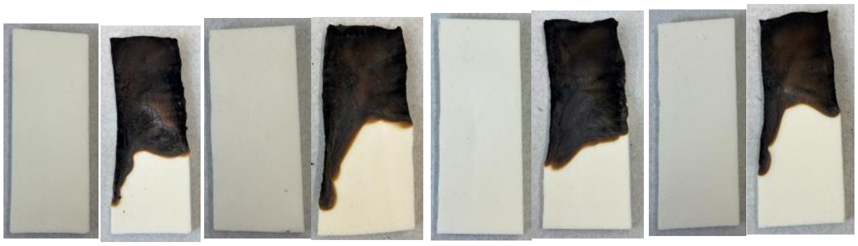


Figure 31. RPUF pictures before and after the burning test with different MA, MC, and MP loadings.

CHAPTER IV

CONCLUSIONS

A practical two-step method of ring-opening and epoxidation processes was used to convert CO into COP. Afterward, RPUFs were made using COP. Three FRs such as MA, MP, and MC were added separately when making the RPUFs. The density of these foams was in the range of 37 to 52 kg/m^3, which is within the range of industrial standards. Closed-cell content increased from 92% to 95%, and all foams showed improved thermal degradation after increasing the amount of FR. The sample with 18.5 wt.% MA (12 MA) showed a maximum compressive strength of 290 kPa. The foam with 28.5 wt.% of MP (15 MA) displayed a burning time of 9.5 seconds and a weight loss of 9.68%. A significant improvement in flame retardancy for MP over MA and MC was caused by the synergistic interaction between nitrogen and phosphorus, which enhanced both the solid phases through the formation of a more compact char layer that served to prevent oxygen from getting into contact with the PU matrix beneath, as well as the gaseous phase due to the release of ammonia to dilute oxygen and radical-scavenging species derived from phosphate.

FUTURE WORKS

- Applications for RPUF are rapidly growing beyond conventional building thermal insulation, including therapeutic cushioning, composite materials, and structural sandwich roofing.
- As a result, an environmentally friendly replacement for the initial components derived from petroleum should be created. It is necessary to carry out more investigations to find new bio-based materials and solutions.
- Based on this, this study provides a practical and adaptable method for producing a more sustainable RPUF made from COP; the addition of other FRs might increase its suitability in a variety of situations.
- Make PUs foams using the non-isocyanate method and assess possible flame-retardant options in these compositions.
- To confirm polyurethanes' potential for commercial use, prepare them on a trial level.
- Examine the life cycle evaluation of flame-retardant-containing RPUF to ensure environmentally friendly production and disposal methods.

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