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SUNFLOWER OIL-BASED POLYOL IN FLAME-RETARDANT RIGID POLYURETHANE FOAMS

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SUNFLOWER OIL-BASED POLYOL IN FLAME-RETARDANT RIGID POLYURETHANE FOAMS

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in Partial Fulfillment of the Requirements
For the Degree of
Master of Science

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Pittsburg, Kansas

December, 2022

SUNFLOWER OIL-BASED POLYOL IN FLAME-RETARDANT RIGID POLYURETHANE FOAMS

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SUNFLOWER OIL-BASED POLYOL IN FLAME-RETARDANT RIGID POLYURETHANE FOAMS

An Abstract of the Thesis by
Magdalene Anima Asare

The current shift from solely depending on petroleum sources to seeking renewable alternatives is due to their fast depletion, spike in prices, and the need to reduce our carbon footprint. For instance, the polyurethane industry currently calls for renewable and less toxic polyols and isocyanates for their synthesis over the traditionally used ones. To tackle an aspect of this matter, this work investigates the generation of polyol from sunflower oil, and further probes their use in rigid foams, one of the widely utilized polyurethanes. Epoxidation and ring-opening reactions were used to convert the sunflower oil into a more reactive form, and tests like iodine value, hydroxyl number, Fourier-transform infrared (FT-IR) spectroscopy, and gel-permeation chromatography (GPC) were performed to validate the synthesis of the intermediates and polyol.

Following this, an easy one-step technique was used to efficiently mix all the foam components in a short time. On the other end of this work, the high flammability of rigid foams is a concern, and strategic efforts to combat it were investigated. Here, non-halogenated flame retardants (FRs) -- aluminum hypophosphite (AHP), dimethyl methylphosphonate (DMMP), and expandable graphite (EG) -- were added into the rigid foam formulation, and their individual flame-retardant and other mechanical effects on the sunflower-based foams were investigated. For an acceptable mechanical, insulating, and reduced flammability of the foams, their density, closed cell content, compression, horizontal burning, and other characteristics were investigated.

On average, all the foams fell in a 30-55 kg/m^3 density range with compressive strengths greater than 160 kN/m^2 and the highest recorded around 290 kN/m^2. With the exception of some high concentrations of the respective flame retardants (FRs) tested, all the foams had closed cells greater than 90%. It was found that the burning time of the foams reduced significantly from 79 seconds in the pure foams, to 5 seconds in AHP-5 (13.61 wt.% of AHP), 2 seconds in DMMP-5 (13.61 wt.5% of DMMP), and 6.5 seconds in EG-5 (13.61 wt.% of EG). The maintained and improved properties of the rigid foams in this work suggested the usefulness of sunflower polyol in the foam synthesis, the effective flame-reducing characteristics of the FRs, and the possibility to explore other renewable sources for polyurethane synthesis.

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CHAPTER I

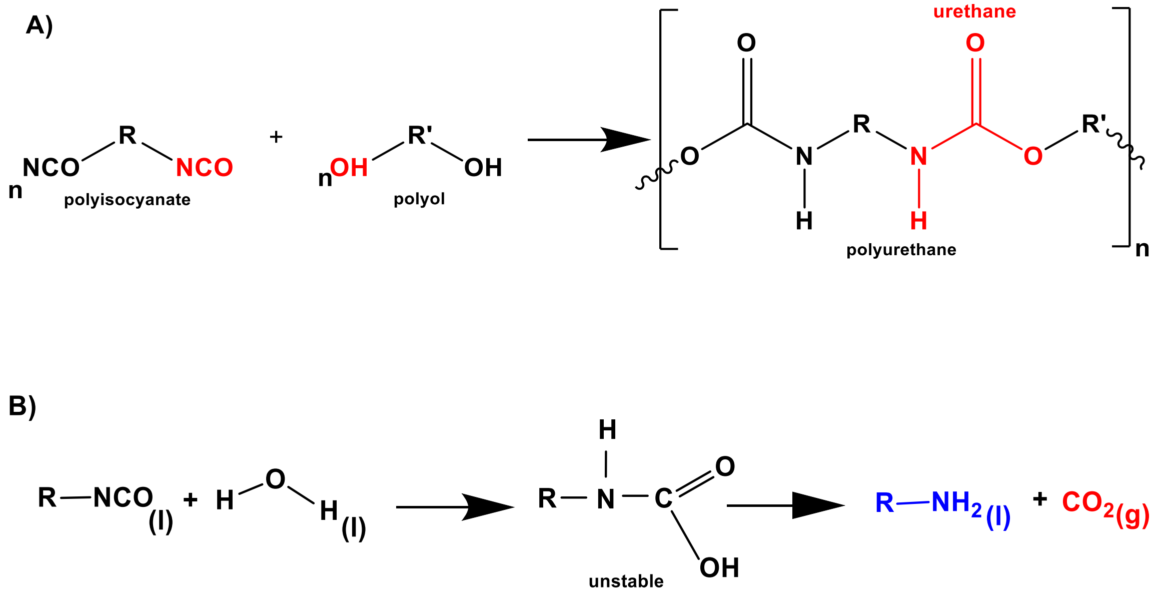
INTRODUCTION

1.1. The chemistry of polyurethanes

Polymers constitute large molecules that are made up of repeating smaller units called monomers. They can be synthetic or natural polymers and serve numerous functions in many sectors [1]. Polyurethanes (PUs) are one of the most versatile polymers in the world that play a vital role in different markets. The first polyurethane was discovered by Professor Otto Bayer and his team in 1937 while synthesizing competitive polymer substitutes for nylon [2,3]. Following this invention, polyurethanes have become an indispensable part of modern life. As shown in **Figure 1**, they can be used in adhesives, coatings, foams, medical devices, construction, aerospace, and sports, just to mention a few [4]. The rapid expansion in their applications ranked them the sixth most-produced polymer in 2018 with a global market value of $65.5 billion which is anticipated to reach $105.2 billion by 2025 [5]. Polyurethane is popularly synthesized from the reaction of polyol and polyisocyanate in the formation of multiple urethane linkages as shown in **Figure 2A**. The reaction here is exothermic and is made possible due to the high reactivity of the isocyanate groups with hydrogen-labile groups and the carbon electron deficiency present [6].

Figure 1. The vast application of polyurethanes. Reproduced with permission [7]. Copyright (2013) John Wiley and Sons.

The high reactivity of the NCO groups in isocyanate is due to their unstable nature as shown in their resonance structures in **Figure 3**. Oxygen has a higher electron density than nitrogen, which is followed by carbon. In its intermediate form, oxygen will have a negative charge, carbon a positive, and nitrogen, an intermediate negative charge. In a chemical reaction, the nucleophilic center of the oxygen from the hydroxyl group (OH) in the polyol will attack the electrophilic center of the carbon in isocyanate, resulting in the addition of hydrogen to the NCO group [8,9]. To have a complete reaction of the monomers of the polyurethane, i.e polyol (OH) and isocyanate (NCO), they must have equal amounts of reactive groups present. However, in practical reactions, the isocyanate is typically added in excess to react with any moisture present, which forms an unstable carbamic acid that decomposes into carbon dioxide and an amine (**Figure 2B**). The carbon dioxide generated is convenient for the expansion and generation of the cellular structure in polyurethane foams [6,8]. The amine can further react with excess isocyanate to form urea as presented in **Figure 2C** [10]. In turn, the main polyurethane structure has not only multiple urethane linkages but can have other moieties like urea, ester, ether, and aromatic groups in their composition [11,12].



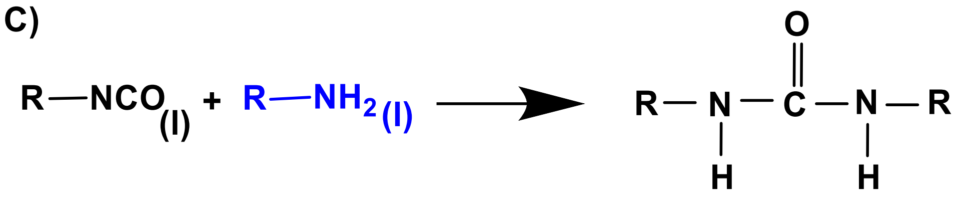


Figure 2. **A**) Basic chemical reaction between isocyanate and polyol, **B**) Reaction of isocyanate with water, **C**) Reaction of amine with isocyanate. Adapted with permission [10]. Copyright (2010) American Chemical Society.

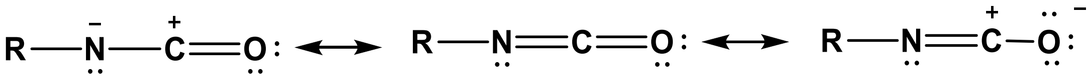


Figure 3. Illustration of resonance structures of isocyanate.

The ubiquity of polyurethanes can be attributed to the flexibility in tuning the different components, such as polyol, isocyanate, catalysts, blowing agents, additives, and surfactants that make them up [13]. Polyols, which constitute more than two hydroxyl groups, are one of the main building blocks of polyurethanes. Polyols had a market value of $26.2 billion in 2019, which is expected to reach $34.4 billion by 2024 due to the rapid growth of the polyurethane market [14]. The most used categories include polyethers, polyesters, and acrylic polyols, which have different methods of synthesis. For instance, polyether polyols are made through the copolymerization of propylene oxide and ethylene oxide with a suitable precursor, while polyester polyols are made similarly to how polyester polymers are made [11,15]. It is worth noting that the functionality, structure, and molecular size of the polyols influence the type of polyurethane formed, so that a low molecular weight polyol with high functionality forms a rigid cross-linked polyurethane, whereas a high molecular weight polyol with low functionality results in an elastic polyurethane [8]. Most conventional polyols used for polyurethane are from petroleum sources; however, with the dire need to reduce the heavy dependence on petroleum-based materials, many state-of-the-art research approaches are in place for bio-based polyols in the polyurethane industries. Classic alternate sources include vegetable oils [16], lignin [17], and other plant-based derivatives [18].

Isocyanates are another major component in the synthesis of different polyurethane products. They are highly reactive towards proton-bearing nucleophiles through a nucleophilic addition across the carbon-nitrogen double bond in their NCO group [12]. In general, aromatic isocyanates such as toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI) are more reactive than aliphatic ones like isophorone diisocyanate (IPDI) and hexamethylene diisocyanate (HMDI). Based on their structures, the delocalization of negative charges on the aromatic rings make aromatic isocyanates more reactive than their aliphatic counterparts [6]. Aromatic isocyanates typically result in applications that have high tensile strength, glass transitioning, and modulus. Aliphatic isocyanates on the other hand are more appropriate for coating, elastomers, or rubbers that require a high elongation break and low tensile strength [9,13]. Regardless of the desirable characteristics of isocyanate, they come with associated health and environmental concerns. Phosgene is a noxious substance required in the popularly followed synthetic route of isocyanate [19]. As a result, scientists have found carcinogenic, respiratory-related, and detrimental effects in humans due to their prolonged exposure to isocyanate [20]. To resolve this, researchers have taken on a replacement task by following different synthesis approaches in the production of non-isocyanate polyurethanes (NIPU) [21–24]. Other components such as catalysts, surfactants, blowing agents, and additives are used to speed up the polyurethane synthesis, improve their appearance and upgrade the properties of polyurethanes respectively.

1.2. Applications of polyurethanes

Due to the vast range of tunability allowed in polyurethane chemistry, polyurethanes have numerous applications that make them challenging to categorize. However, popularly classified groups include flexible foams, rigid foams, thermoplastics, water-borne polyurethanes, coatings, adhesives, sealants, and elastomers (CASE) as shown in **Figure 4**. Flexible polyurethane foams make up the biggest share of the PU foam market [25] with about 37% being produced. As the most popular group, they find specific uses such as cushioning in couches, vehicle seats, mattresses, and for automotive interior design as well as for some medical devices [15,26]. In addition to the other basic components that make up flexible polyurethane foams, longer chain length polyols that have trifunctional alcohol groups differentiate them from rigid foams that can be made with short chain length polyols with trifunctional alcohols [27]. Rigid foams are the second most used PU due to their specific benefits. They can provide insulation and are particularly useful for energy conservation purposes when employed for thermal insulation in buildings [28]. In the coating industry, they can be used for wood, textiles, glass, aerospace, and automotive top coats and finishes. This is owing to their low moisture permeability, high mechanical advantage, corrosion, and chemical resistance [29]. Polyurethanes adhesives are tough, solvent-resistant, have high cohesive strength, and have good abrasion resistance. Thus, they are utilized in soles of footwear, wood flooring, rotor blades, construction, automotive, and for industrial purposes [30]. Other water-borne polyurethanes are desirable for sealant and elastomeric applications [15].

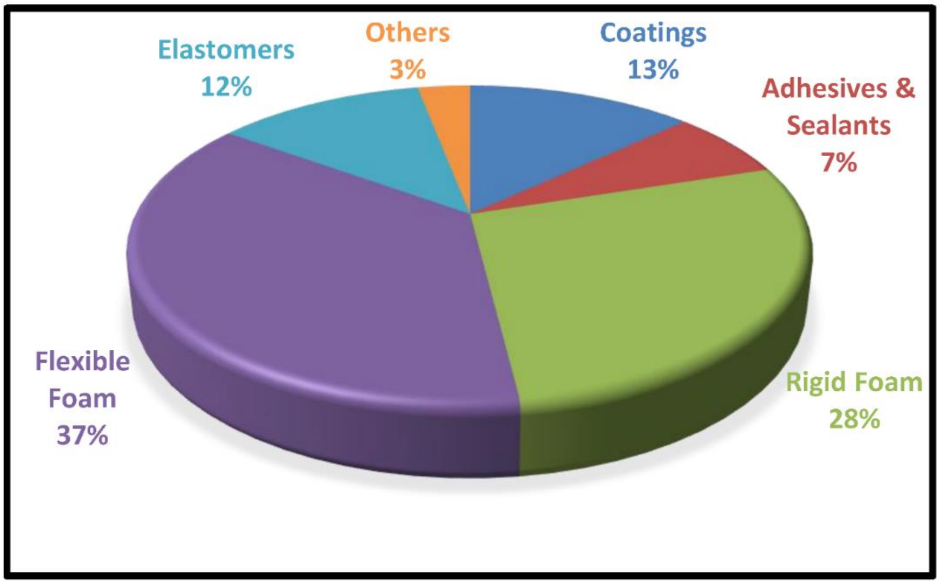


Figure 4. Global consumption of polyurethanes. Reproduced with permission [31]. Copyright (2022) Multidisciplinary Digital Publishing Institute.

1.3. Issues of polyurethane foams

Despite the trendy and enviable advantages of rigid polyurethane foams, when used for soft furnishing and insulation, they are highly flammable due to their low thermal inertia property, porosity, and cellular nature [32–34]. This drawback has resulted in accidents and deaths during fire outbreaks due to rapid combustion and generation of smoke in the early stages of foam combustion. The National Fire Protection Association recorded an annual average of 5,630 fire cases in homes from 2010-2014. Their data shows that these fires are propagated by the fast ignition and burning of upholstered furniture, which is typically filled with polyurethane foams [35]. Additionally, harmful gases such as CO, CO_2, and HCN that are produced from burning polyurethane foams have poisoning and suffocating effects due to oxygen deprivation in victims of fire incidents.

In addition, the dense smoke reduces visibility which impacts the quick evacuation and rescue of trapped individuals. It has been found that the composition and structure of the polyurethane plays a role in the low thermal stability and high smoke generation. Hence, an increased consideration to modify the polyurethane matrix is in place. For instance, the presence of aromatic groups in the backbone has been determined to reduce the amount of smoke generated and to promote the formation of char to reduce flammability. In addition, flame retardants have been heavily researched and used to reduce the high combustion rate of polyurethane foams [36].

The utilization of polyols from petrochemical sources for the synthesis of polyurethanes is another major drawback in the polyurethane industry. Consequently, measures are currently in place to identify renewable, bio-based, and affordable sources of useful polyols [37].

Another issue with the synthesis of polyurethanes is the presence of isocyanate which is produced from a harmful substance, phosgene. Prolonged exposure to isocyanate leads to detrimental respiratory and other health effects [38,39].

1.4. Flame retardants in polyurethane foams

The use of flame retardants (FRs) in polyurethane foams has served an important role in reducing the high flammability and cases of deaths and accidents caused by fire outbreaks in buildings and furniture associated with polyurethane [40]. Effective flame retardants are expected to have three characteristics: 1) increase the limiting oxygen index (LOI), 2) reduce the heat release rate (HRR) and 3) repress smoke generated during combustion [2]. The most common types of chemical flame retardants can be categorized as additives and reactive materials. Additive flame retardants can be added at any point before, during, or after the polymerization reaction. This is because they do not chemically bind to the whole polymer matrix and will not require an additional synthetic reaction, which can be time-saving and economical. However, due to their poor compatibility, they can easily leach and be emitted into the environment, which can eventually reduce the mechanical performance of the PU [41]. Examples include antimony oxide, zinc borate, expandable graphite, triphenylphosphine oxide, and chlorofluorocarbons.

Contrarily, reactive FRs are added during the polymerization reaction since they have reactive functional groups that ultimately bind to form a modified PU matrix. Reactive FRs are more compatible, require a small amount, and have limited detrimental effects on the mechanical properties of the foams; however, they require additional synthetic routes. Typical examples of reactive flame retardants include phosphorous-containing groups such as ethylene glycol bisphosphate and aminomethyl phosphonate [11,42]. Flame retardants can further be classified into inorganic ones that include metal hydroxides and boron salts; organophosphorus, which is composed of phosphate esters; nitrogen-based FRs; and halogenated types typically made of chlorine and bromine [43]. Even though halogenated flame retardants are among the most effective types, they emit corrosive and toxic substances during combustion, which, in the long run, defeats the purpose of protecting lives. Thus, non-halogenated types are more attractive [44,45].

Concerning their fire-combating mechanism, FRs can be grouped into gas-phase, solid-phase, endothermic, or intumescent [2]. Suppressing heat, oxygen, and flammables in the gas-phase with non-flammable gases is characteristic of gas-phase FRs. Solid-phase FRs form an insulating char layer that protects the material from oxygen and heat propagation, resulting in the reduction of the fire (**Figure 5**). In the flaming zone, endothermic radicals that absorb and reduce heat production are typical of endothermic flame retardants.

Intumescent FRs are usually composed of an acid source, blowing agent, and carbonizing agent that lead to the formation of a thick expandable char layer with high flame retarding properties. Intumescent FRs are currently of great interest due to their low toxicity, anti-dripping, and low corrosion attributes [2,46,47].

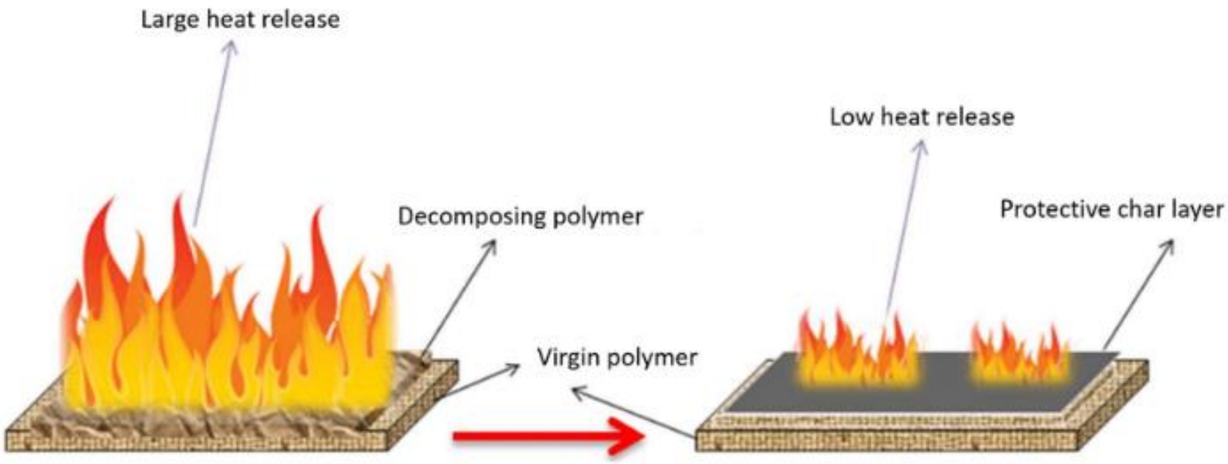


Figure 5. Formation of char layer by flame retardants which reduces fires in polymers. Reproduced with permission [48]. Copyright (2021) Multidisciplinary Digital Publishing Institute.

1.5. Polyurethanes from renewable sources

Attention is currently given to the nature of the starting materials that make up polymers in addition to the assessment of the full life cycle of their final products. This increasing concern is in an effort to reduce their carbon footprint and over-reliance on non-renewable resources, both in response to spikes in the price of crude oil, and to conserve our lands, water bodies, and the ecosystem at large.

In polyurethane chemistry, the main targets for change are polyols and isocyanates. Polyols from sustainable bio-based materials that have been explored in different fields, include biomass from lipids, carbohydrates, polyphenols, and other eco-friendly options as shown in **Figure 6** [6,14]. Researchers like Kwoon and co-workers took advantage of the biodegradability, affordability, and abundance of OH groups present in starch and investigated it as a bio-based polyol for polyurethane foams [49]. Soymeal, which is another inexpensive plant-based material, was investigated as a bio-based alternative polyol for the synthesis of polyurethane foams [18]. Cardanol, a renewable polyol derived from cashew by-products, was successfully utilized in the synthesis of rigid polyurethane foams [50,51].

Vegetable oils such as soybean oil [52], corn oil [53], castor oil [54], and canola oil [55] have been studied for polyurethane applications. In addition to the renewability and relatively low cost of vegetable oils, the presence of unsaturated groups that can be modified into reactive forms makes them desirable for polyols. In addition, oils like castor oil can be directly used as polyols due to the inherent OH groups available [56]. Chemical modifications that have been used include ozonolysis of oils into ozonides, followed by a reduction to an aldehyde, then an alcohol in the generation of polyols [57], hydroformylation of double bonds into aldehydes with catalysts, followed by hydrogenation into triglyceride polyols, and others like transesterification and thiol-ene [58]. In this work, the epoxidation of sunflower oil followed by ring-opening with methanol was investigated as later discussed in **Section 2.2**.

Secondary to this, continuing research for the replacement of isocyanate prepared from phosgene, which results in diverse detrimental health and environmental consequences, has attracted considerable attention. Consequently, the synthesis of non-isocyanate-based polyurethanes (NIPU) is in progress. Isocyanates that have been synthesized with high renewable contents and less toxic pathways include dimer fatty acid-based diisocyanate (DDI), ethyl ester L-lysine diisocyanate (EELDI) made from the lysine, pentamethylene diisocyanate (PDI), and others as shown in **Figure 7** [59].

In addition, non-isocyanates produced by the reaction of cyclocarbonates with amines have been explored and are currently being improved for comparable properties as the isocyanate counterparts [23,60,61]. However, the use of bio-based, or renewable materials, in place of petroleum sources still faces various obstacles. For instance, some of the researched alternatives are not practical for large-scale production, others turn out to be more expensive than fossil derivatives, and some final products from these renewable sources are not sufficiently comparable to the conventional ones; hence, continuous research and augmentations are required in this field to make a more substantial and long-lasting impact [14].

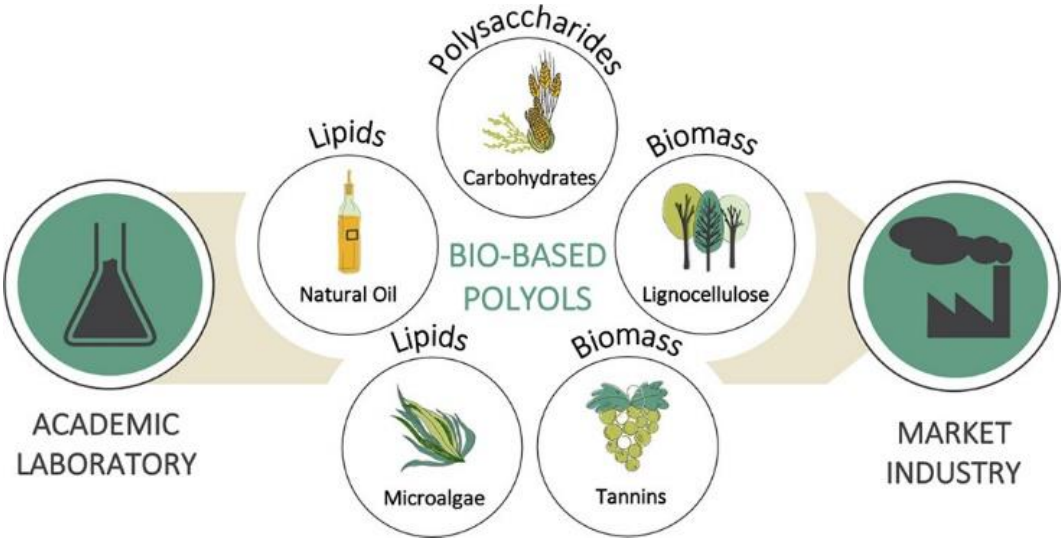


Figure 6. Examples of renewable materials researched for polyols. Reproduced with permission [14]. Copyright (2021) American Chemical Society.

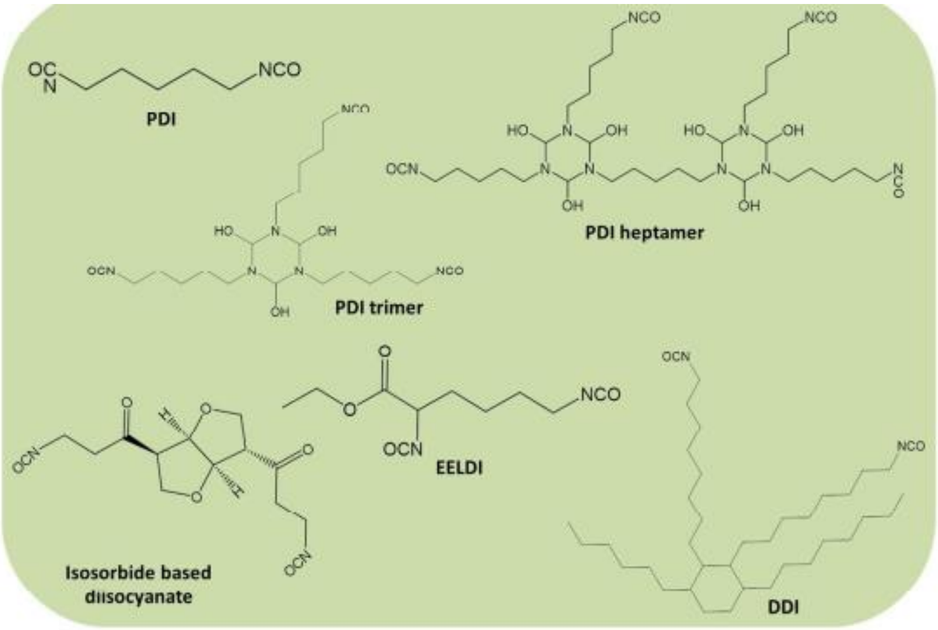


Figure 7. Isocyanates from bio-based sources following less toxic routes. Reproduced with permission [59]. Copyright (2018) Royal Society of Chemistry.

1.6. The objective of this thesis

The objective of this research is to investigate the possibility of converting vegetable oil from sunflower, into another form for the synthesis of rigid polyurethane foams with improved fire resistance properties. Here, epoxidation followed by ring-opening is used to transform the pure sunflower oil into a polyol that is more reactive with isocyanate. Confirmatory tests like FT-IR, hydroxyl value, GPC, and the like were performed to analyze the formation of the bio-based polyol before proceeding to make the foams. Non-halogenated flame retardants such as AHP, DMMP, and EG were separately added in increasing concentrations to study their impact on the flammability and other properties of the foams. The morphology, density, compression, thermal stability, and important characteristic of the sunflower-based foams were investigated.

CHAPTER II

MATERIALS AND METHODS

2.1. Materials

2.1.1. Isocyanate

Isocyanate is the most reactive component in the synthesis of polyurethane and requires caution in handling. To understand the structural properties of polyurethanes formed, it is essential to know the details of the different structures of polyol and isocyanate used. And even though there is a wide variety of polyols on the market that may require a diverse range of isocyanates, very few types of isocyanates are used in reality. The most common are aromatic TDI and MDI due to their high reactivity [8]. MDI is more favorably used since it gives a better homogenous reaction kinetic and is comparatively less hazardous to deal with due to its low vapor pressure [59]. In this experiment, Rubinate M isocyanate, also named MDI, was provided by Huntsman (The Woodlands, TX, USA) and used in the synthesis of bio-based rigid polyurethane foam. The chemical structure of MDI is shown in **Figure 8**. It has a weight equivalence of 135, functionality of 2.7, viscosity of 0.21 Pa.s, and specific gravity of 1.23 at 25 °C, with 31%

reactive NCO groups. Rubinate M isocyanate was used for the synthesis without any further purifications.

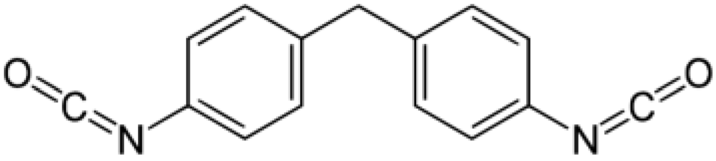


Figure 8. Chemical structure of diphenylmethane diisocyanate.

2.1.2. Sunflower oil

The sunflower, also known as *Helianthus annuus* L., is a short-seasoned plant that is native to North and South America. However, its unique adaptation to diverse soils and climates has permitted its cultivation all over the world, with more than 70 species available. It is called a “sunflower” due to its resemblance to and periodic rotation in the direction of the sun [62,63]. In addition to oil that can be produced from sunflower seeds, other parts of the plant can be used as a delicacy, wine can be made from it, and it can be used for medicinal purposes [64]. After soybean, rapeseed, and safflower, it is ranked the fourth most profitable and economic oilseed in the world [62]. Moreover, it contains a wide variety of fatty acids, including linoleic, oleic, palmitic, and stearic, that encourage their applications in bio-diesel, lubricants, and coatings [65,66]. To probe the potential of creating an additional value for sunflower oil, it was investigated for the synthesis of flame-retardant polyurethane foams.

Sunflower oil is composed of about 15% saturated fat and 85% unsaturated fat with the latter having double bonds, which are suitable for chemical transformations into polyols [67]. The presence of the carbon-carbon double bond in the triglycerides shown in the chemical structure of sunflower (**Figure 9**) was the main target for the generation of more reactive sites in the formation of bio-based polyols in this work [16]. The double bonds were first broken and converted to an epoxide followed by a ring-opening reaction into a polyol with methanol (chemistry explained in more detail in the synthesis section). The sunflower oil used in this experiment was purchased from a local Walmart (Pittsburg, KS, USA) and used without any further purification. The measured viscosity of 0.06 Pa.s was recorded at 25 ℃. In addition, this experiment used Jeffol SG-522, a commercially available polyol, with an OH number of 522 mg KOH/g, which was received from Huntsman.

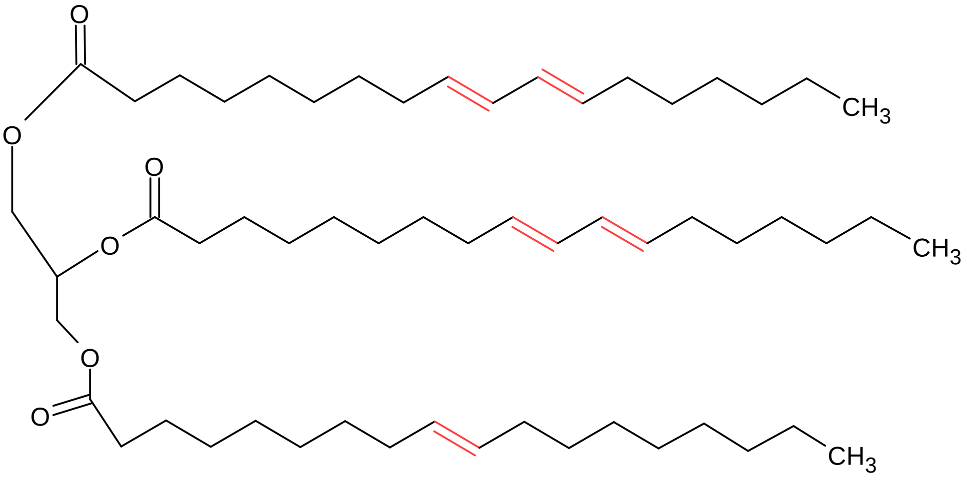


Figure 9. Chemical structure of sunflower oil.

2.1.3. Surfactant

The heterogeneous reagents in the polyurethane formulation must be compatible. Surfactants, which are added to enhance compatibility, are therefore a vital ingredient for the efficient formation of homogenous cell structures. When surfactants are added in the most optimum amounts in foams, they ensure the emulsification of the reagents in the formulation. In addition, surfactants regulate and stabilize the cell sizes of the foams to prevent collapse. In other polyurethane applications, surfactants prevent both pin holes and sink marks while improving the surface appearance of products. Surfactants have a hydrophilic head and hydrophobic tail that drives their mechanism, and depending on the charge on the head, they can be grouped into cationic, anionic, non-ionic, and zwitterionic groups [6,15,68,69]. In this work, Tegostab B-8404, a silicone-based surfactant that is good for rigid foam stabilization was purchased from Evonik USA and used as received.

2.1.4. Blowing agent

As implied by the name, this ingredient is responsible for the blowing of the foams during the polymerization reaction. They can be classified into physical or chemical blowing agents. The former presents a phase change from liquid to gas with the energy generated from the reaction of isocyanate with a polyol. Their efficiency is influenced by factors like molar mass and boiling point, such that a low molar mass physical blowing agent produces a high volume of gas following an inverse relationship.

Chemical blowing agents, on the other hand, react with the matrix during the polymerization reaction to form a gas. The most popularly used chemical blowing agent in rigid polyurethane foam synthesis is water. This is due to its reaction with isocyanate that forms an unstable carbamic acid that decomposes into carbon dioxide, responsible for the full blowing of the foam. Physical blowing agents are less often used than chemical ones because they are typically chlorofluorocarbons that have ozone-damaging effects [6,70]. For this reason, water is utilized in this work as a blowing agent. The distilled water was purchased from a local Walmart (Pittsburg, Kansas).

2.1.5. Catalysts

Catalysts are substances that speed up the rate of a chemical reaction. Since the synthesis of the rigid polyurethane foams in this work was conducted at room temperature, they required catalysts to be form at a faster rate. In the formation of rigid foams, widely used catalysts include amines and organometallics [6]. For this work, 1,4-diazobicyclo[2,2,2]octane (DABCO) and Niax A-1, purchased from Air Products (Allentown, PA, USA) were used.

2.1.6. Non-halogenated flame retardants

To replace the toxic halogenated flame retardants, three non-halogen-based flame retardants, aluminum hypophosphite (AHP), dimethyl methylphosphonate

(DMMP) and expandable graphite (EG) were investigated for their flame retardant properties in the sunflower-based foams.

2.1.6.A Aluminum hypophosphite

Aluminum hypophosphite (AHP) is a cost-effective and environmentally safe inorganic phosphinate flame retardant [71]. It has a chemical formula of $Al(H_2PO_2)_3$ (**Figure 10**) and can be scaled up for production on the industrial level [72]. This flame retardant has been investigated and found to reduce the flammability of some polymers in addition to having less deterioration of their mechanical properties [47,73].

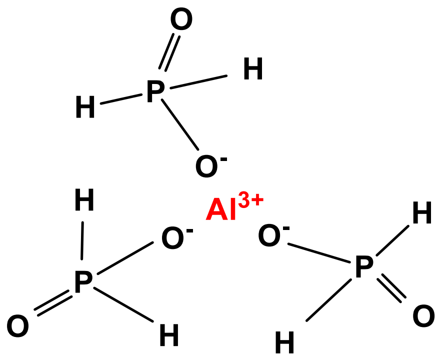


Figure 10. Chemical structure of AHP. Adapted with permission [74]. Copyright (2019) Sage Publications.

2.1.6.B Dimethyl methylphosphonate

Dimethyl methylphosphonate (DMMP) can be considered one of the most effective phosphorous-based flame retardants (**Figure 11**). Due to its low molecular weight and viscosity, it has been investigated in different polymeric materials. Additionally, it is non-corrosive, has good stability, and has a high content of phosphorous, which makes it suitable for fire-retardant situations. It is also less inclined to participate in undesired reactions with other components, such as the blowing agents, or amine catalysts [75,76]. For this work, DMMP was purchased from Sigma Aldrich, USA.

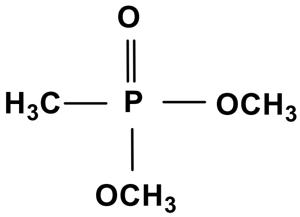


Figure 11. Chemical structure of DMMP.

2.1.6.C Expandable graphite

Expandable graphite has a flake-like graphite composition with stacked layers of hexagonal sp^2 hybridized carbons, as shown in **Figure 12**. Upon heating, expandable graphite works in the condensed phase with an expansion in its structure to form a voluminous protective layer, hence reducing the amount of smoke generated and reducing the flammability of foams. The synthesis of EG entails treatment with sulfuric acid, nitric acid, or acetic acid into its intercalated crystal structure [11,77]. EG is an attractive additive flame retardant due to its low toxicity and efficient flame retardancy [78]. For this research, EG was purchased from Sigma Aldrich and used without modification.

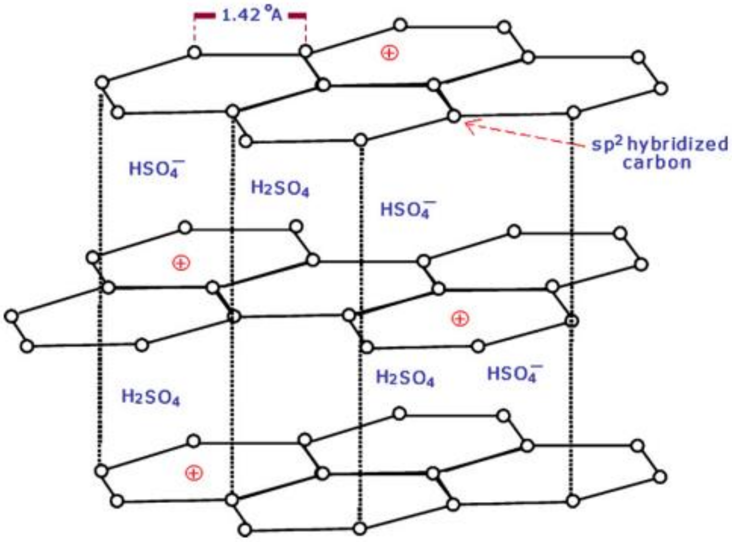


Figure 12. The intercalated structure of expandable graphite. Adapted with permission [77]. Copyright (2003) John Wiley and Sons.

2.2. Synthesis of polyol from sunflower oil

Epoxidation and ring-opening with methanol was used for the synthesis of the bio-based polyol from sunflower oil.

2.2.1. Epoxidation of sunflower oil

The synthesis of epoxies from alkenes (carbon-carbon double bonds) can take four different routes, which include epoxidation with a) percarboxylic acid, b) organic and inorganic peroxides, c) halohydrins and d) molecular oxygen. However, the reaction of an alkene with peracetic acid or the epoxidation with percarboxylic acid, is one of the widely used routes. Epoxidation reactions are typically done with the in-situ formation of peracids due to the high conversion and feasibility on an industrial scale.

Here, acetic acid functions as an oxygen carrier, and hydrogen peroxide as an oxygen donor. When the two react, peracetic acid is formed [79], which further breaks the double bonds present in the oil into an epoxide ring (**Figure 13**). The temperature, catalysts, and environmental conditions are vital components for an effective epoxidation reaction [9,80–82].

In this reaction, 300 g of sunflower oil, 75 g of amberlite resin, and 150 ml of toluene based on a 1:0.5:1.5 molar ratio were mechanically stirred in a 3-necked flask in a water bath with a controlled heating set-up. The mixture was continually stirred while reducing the reaction temperature to about 5-10 ℃. From there, 43.9 ml of acetic acid and 180 ml hydrogen peroxide (30%), were added one after the other in a dropwise fashion as a precaution to prevent overheating that could happen from the exothermic nature of epoxidation reactions [81]. After the complete addition of all reagents, the mixture was stirred for about 7 hours at 70 ℃. The reaction mixture was then cooled to room temperature, and the resin was filtered out.

To purify the mixture, it was placed in a separatory funnel and washed with 10% brine. Brine was periodically added, and after shaking, the mixture was allowed to stand so that the aqueous layer could be removed from the oil. Anhydrous sodium sulfate was added and stirred in the mixture as a drying agent.

Finally, the sodium sulfate was filtered out and excess solvents in the mixture were removed with rotary evaporation at both low and high vacuum pressures. The successful synthesis of the epoxide sunflower oil (ESFO) was then analyzed with confirmatory tests including FT-IR, epoxy number, and GPC.

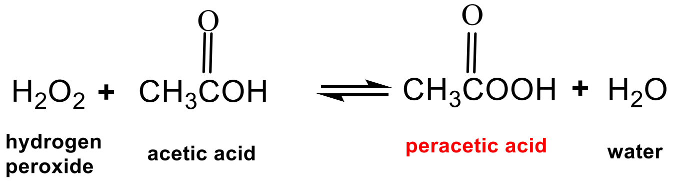


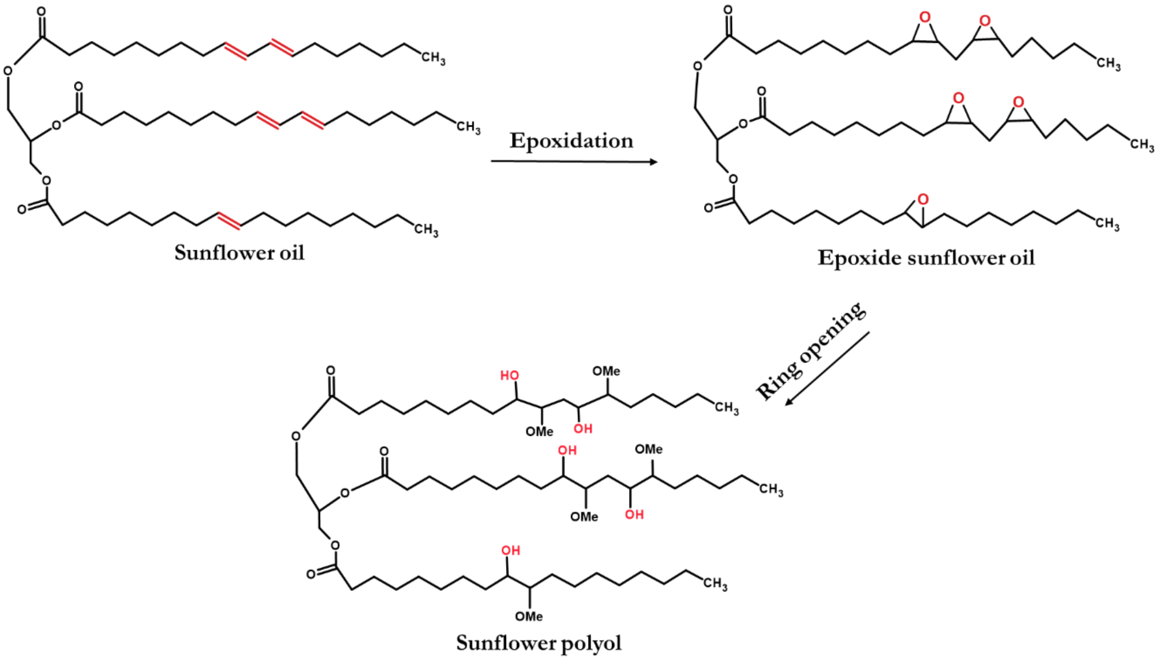
Figure 13. Formation of peracetic acid.

2.2.2. Ring-opening of epoxide sunflower oil into polyol

Epoxides are useful intermediates for the synthesis of high-value alcohols, glycols, and carbonyls. They can also directly be used as plasticizers and detergents [83]. The basic structure of an epoxy ring consists of an oxygen bonded to two adjacent carbons. In the ring-opening reaction, the presence of an electrophilic strained epoxy ring allows a nucleophilic attack by a beta-substituted hydroxyl group [82]. The most explored nucleophiles for ring-opening include mono-alcohols, diols, and carboxylic acids, however, weaker nucleophiles like amines, water, and thiols have been tested and found to have low reaction rates [6,84–86]. In this reaction, methanol was the nucleophile and tetrafluoroboric acid was used as a catalyst.

In this experiment, a mole ratio of 7:1 of methanol and epoxidized sunflower oil was used. The amount of tetrafluoroboric acid (HBF_4) measured, was equal to 50% weight of water, plus 0.05% of methanol and epoxidized oil. The reaction mixture of methanol and tetrafluoroboric acid was prepared at around 70 °C in a three-necked flask attached to a condenser and dropping funnel. After several minutes of mechanical stirring, the previously synthesized ESFO was added in a dropwise manner, and the reaction was refluxed for an hour. To avoid hydrolysis, the mixture was cooled before the addition of Lewatit MP 64 ion exchange resin. The resin was mechanically stirred in the mixture to neutralize the acid.

After confirming the neutral pH, the mixture was filtered to remove the resin, followed by rotary evaporation. The synthesized polyol was further characterized to confirm the formation of the hydroxyl group. The schematic of the epoxidation and ring-opening of sunflower oil is presented in **Scheme 1**.



Scheme 1. Reaction pathway and conversion of sunflower oil into epoxide and polyol.

2.3. Characterization of sunflower-based polyol

2.3.1. Iodine value

Determination of the iodine value of sunflower oil was one of the most important and preliminary experiments of this work. This is because the iodine value gives an indication of the number of double bonds present in an unsaturated compound, based on the amount of iodine that will react with 100 g of the sample. A high iodine value indicates the presence of the high unsaturation in fatty acids [87].

In this experiment, the Hanus method was used to measure the approximate amount of double bonds present in the sunflower oil used in the polyol synthesis. In a 250 ml Erlenmeyer flask, about 0.2-0.3 g of sunflower oil was dissolved in 10 ml chloroform ($CHCl_3$) solvent. 20 ml of Hanus reagent (BrI) was pipetted into the solution, and after a gentle shake, it was placed in the dark for an hour. Then, 20 ml of 10% potassium iodine solution and 50 ml of HPLC grade water were added to the flask and stirred into a uniform solution. 6 drops of starch indicator were added, and the blue solution was titrated with sodium thiosulphate ($Na_2S_2O_3$) until a colorless solution formed.

The volume was recorded and used to calculate the iodine value of the sunflower oil purchased from the local Walmart. This analysis was done in triplicate, and the average value was used to calculate the amount of reagent required for the epoxidation reaction.

2.3.2. Epoxide number

The epoxy oxygen content (EOC%) was determined using glacial acetic acid and tetraethylammonium bromide. This test was used to investigate and confirm the formation of the epoxide groups from the double bonds. 0.3-0.5 g of epoxide sunflower oil was dissolved in 50 ml of tetraethylammonium bromide (TEAB) solution. A drop of crystal violet indicator was added and the solution was titrated with 0.1 N perchloric acid ($HClO_4$). A color change from blue to green indicated the end point of the titration and the recorded volume was used to calculate the epoxy content in the epoxidized sunflower oil. This test was done three times and the average value was used for further calculation for the ring-opening experiment.

2.3.3. Hydroxyl value

The OH number of a polyol is an important indication of its functionality and the amount of isocyanate required for an efficient chemical reaction to occur. To determine this value for the sunflower polyol, the phthalic anhydride pyridine (PAP) method was used following ASTM-D 4274. Here, 0.5 g of the synthesized sunflower polyol was dissolved in 10 ml of a hydroxyl solution in a glass bottle. The bottles were loosely capped and placed in a preheated oven at 100 °C for 70 minutes. During this time, the mixture was shaken every 15 minutes. After that, the solution was cooled to room temperature, and 10 ml of HPLC-grade water and 20 ml isopropanol was added and stirred for about 10 minutes. It was then titrated with 1 N sodium (NaOH) until a pink color was seen. The volume was recorded and used in the calculation of the hydroxyl number. This test was done in triplicate and the average value was used for further analysis.

2.3.4. Acid value

To ensure the optimum pH values required for the synthesis of the polyurethane foams, the acid value for the various stages in the synthesis of the polyols was measured. This identification was made following the IUPAC 2.201 standard procedure. Approximately 1 g of material was dissolved in 30 ml of solvent mixture (isopropanol, toluene, and phenolphthalein indicator). It was then titrated with 0.1 N potassium hydroxide until a pink color change was observed. The volume was then recorded and used to calculate the acid values.

2.3.5. Fourier-transform infrared spectroscopy

Fourier-transform infrared spectrocopy (FT-IR) is used as a rapid identification technique for the presence of different functional groups in a compound. It usually does not require any purification step as compared to other tests and demands no solvents. In this experiment, the PerkinElmer Spectrum Two Spectrophotometer (**Figure 14**) was used to generate the spectral results of our synthesized materials at room temperature. The unique spectral fingerprints of our respective materials were generated based on their peaks observed in the wavelength spectrum.

Figure 14. Instrument for FT-IR analysis.

2.3.6. Viscosity

Viscosity is an important measure of the resistance of a substance to flow. A high viscosity can signify a high molecular weight and a low viscosity, a low molecular weight. In addition, a low viscosity correlates with an increased ease of processibility. In this experiment, the viscosity of the sunflower polyol will have an impact on the ease of polyurethane synthesis. In addition, this parameter will confirm the actual synthesis of the polyol from the epoxide and sunflower. An AR 2000 dynamic stress rheometer (TA Instruments, USA) as shown in **Figure 15** was used for this analysis. The viscosity was measured at 25 °C with shear stress increasing from 1 to 2000 Pa linearly. The dynamic rheometer was equipped with a cone plate having an angle of 2° and a cone diameter of 25 mm.

Figure 15. AR 2000 dynamic stress rheometer for measuring viscosity.

2.3.7. Gel permeation chromatography

This is a size exclusion technique that separates compounds based on their excluded volume, which correlates with molecular weight. This characterization method was adopted to study and confirm the synthesis of the sunflower epoxide and polyol from the oil after the epoxidation and ring-opening reaction. This work used the Waters GPC instrument from Milford, MA, USA (**Figure 16**). The GPC instrument was composed of four 300 × 7.8 mm phenogel 5μ columns with different pore sizes of 50, 102, 103, and 104 Å. The range of pore sizes facilitates the separation of molecules with different molecular weights. The eluent solvent was tetrahydrofuran (THF), and the eluent rate was 1 ml/ min at 30 °C.

Figure 16. GPC instrumental set-up.

2.4. Preparation of rigid flame-retardant foams from sunflower polyol

After confirming the synthesis of sunflower polyol from the pure sunflower oil, the polyol was incorporated into the formulation of the rigid polyurethane foams. As discussed earlier, non-halogenated flame retardants like AHP, DMMP, and EG were separately added in varying concentrations shown in **Tables 1**, **2**, and **3**. The impact of the FRs on the properties of the resulting rigid foams was studied. A one-shot technique, which is an easy, fast and efficient way of mixing different components, was employed to make the rigid foams [8]. In the foaming process, the synthesized sunflower polyol (SF P), commercial polyol (SG-522), A-1, T-12, B8404, surfactant, water, and increasing concentrations of AHP, DMMP, and EG in the respective formulations were mixed with a mechanical stirrer at high speed to form a uniform mixture. Then, the highly reactive isocyanate was cautiously added and thoroughly mixed. The foams were allowed to rise and kept at room temperature for about a week to fully cure before their desired chemical and physical properties were tested.

Table 1. Composition of rigid foams with varying amounts of AHP* (*All weights are in grams).

Ingredients	AHP-0	AHP-1	AHP -2	AHP -3	AHP -4	AHP -5	AHP -6	AHP -7	AHP -8
SFP	10	10	10	10	10	10	10	10	10
SG-522	10	10	10	10	10	10	10	10	10
A-1	0.18	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	0.8
T-12	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
B8404	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Isocyanate	29.4	29.4	29.4	29.4	29.4	29.4	29.4	29.4	29.4
AHP	0	0.5	1.5	3	5	8	10	12	14
Wt.% of AHP	0	0.97	2.87	5.57	8.96	13.61	16.44	19.10	21.60

Table 2. Composition of rigid foams with varying amounts of DMMP* (*All weights are in grams).

Ingredients	DMMP -0	DMMP -1	DMMP -2	DMMP -3	DMMP -4	DMMP -5	DMMP -6	DMMP -7	DMMP -8
SFP	10	10	10	10	10	10	10	10	10
SG-522	10	10	10	10	10	10	10	10	10
A-1	0.18	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	0.8
T-12	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
B8404	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Isocyanate	29.4	29.4	29.4	29.4	29.4	29.4	29.4	29.4	29.4
DMMP	0	0.5	1.5	3	5	8	10	12	14
Wt.% of DMMP	0	0.97	2.87	5.57	8.96	13.61	16.44	19.10	21.60

Table 3. Composition of rigid foams with varying amounts of EG* (*All weights are in grams).

Ingredients	EG-0	EG -1	EG -2	EG -3	EG -4	EG -5	EG -6	EG -7	EG -8
SFP	10	10	10	10	10	10	10	10	10
SG-522	10	10	10	10	10	10	10	10	10
A-1	0.18	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	0.8
T-12	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
B8404	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Isocyanate	29.4	29.4	29.4	29.4	29.4	29.4	29.4	29.4	29.4
EG	0	0.5	1.5	3	5	8	10	12	14
Wt.% of EG	0	0.97	2.87	5.57	8.96	13.61	16.44	19.10	21.60

2.5. Characterization of the bio-based foams

After one week, the foams were cut into the standard sizes and shapes, and the average of three samples was used to test the apparent density, burning time, and weight loss. Other tests included the closed cell content, compressive strength, thermal stability, and cell morphology as described in detail below.

2.5.1. Apparent density

Density measures the mass-to-volume ratio of a material. In polyurethane foam applications, the apparent density plays a huge role and gives information on the foam's physicochemical properties. In this work, cylindrical foam sizes of 45 mm (diameter) x 30 mm (height) were used to calculate the apparent densities of all the foams following ASTM D1622 standard protocol.

2.5.2. Closed cell content

To determine the amount of closed or open cells in the sunflower-based flame-retardant foams, their closed cell content (CCC) was measured. The ultrapyncnometer (Ultrafoam 1000) (**Figure 17**) was used to facilitate this investigation using ASTM 2856 method. The ultrapyncnometer has a cylindrical chamber that is linked to a pressure-temperature sensor that uses argon gas. To ensure accuracy in determining the number of closed cells present, the empty chamber is first measured before subsequent tests with the actual foams.

Figure 17. Ultrapyncnometer for closed cell content measuring.

2.5.3. Scanning electron microscope imaging

The cell morphology of the foams was characterized based on images generated by the scanning electron microscope. SEM generates images based on the interactions of the electrons from the SEM instrument with the atoms of samples. From this, information regarding the surface structure of the foams was captured and analyzed using the

Phenom instrument as seen in **Figure 18** (**left**). Sunflower foam cubes of 0.5 cm^3 were used for imaging. Due to the non-conducting nature of the foams, they were first coated with a thin layer of gold, using a gold sputtering instrument, to enhance the images. The magnetron sputtering instrument attached with a monitor from Kurt J. Lesker Company (Jefferson Hills, PA, USA) as seen in **Figure 18** (**right**) was used.

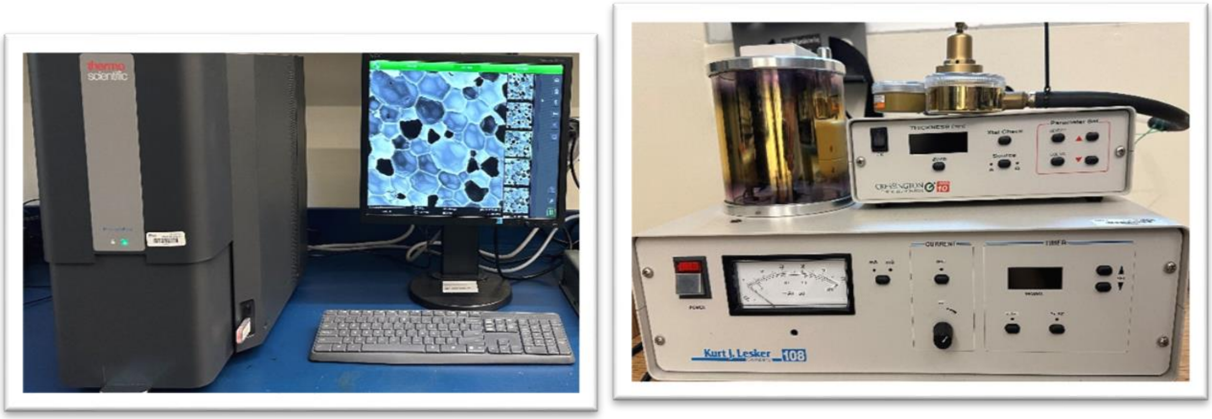


Figure 18. Left) SEM for morphology study, **Right**) Magnetron for gold deposition thin film.

2.5.4. Compressive strength test

The compressive strength of the foams was tested with a Q-Test 2-tensile machine (MTS, USA), as seen in **Figure 19**. With respect to ASTM 1621, the foams were cut into blocks of 50 mm (length) × 50 mm (breadth) × 25 (height) mm. The yield break and strain at 10% were measured with Blue Hill software, and the compressive strength applied was at a strain rate of 3 cm/min from the top, or parallel to the sunflower-based foams.

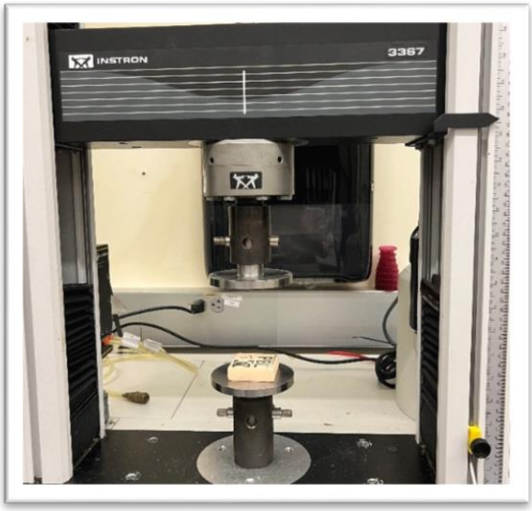


Figure 19. Instrument for measuring compressive strength.

2.5.5. Horizontal burning test

Sunflower-based polyurethane foams were cut into strips of 150 mm (length), 50 mm (width), and 12.5 mm (thickness) to test the impact of the selected flame retardants on their flame-retardant abilities. Following the ASTM D 4986-18 standard, the foams were laid horizontally in a chamber equipped with a fume hood as seen in **Figure 20**. This fume hood was a safety feature put in place to improve ventilation and prevent contact with any unknown volatiles associated with the burning of the foams. The flame was applied perpendicularly to the foam for 10 seconds, and the total time taken for the sample to quench after the removal of the fire source was recorded. Before burning, the weight of the foam was recorded and the value after burning was also measured to calculate the weight loss percentage.

Figure 20. Chamber for horizontal burning test equipped with a fume hood.

2.5.6. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed to explore the stability of the bio-based polyurethane foams under increasing temperatures up to 700 ℃. Here, the change in the initial weight of the foams with respect to temperature changes was monitored. This experiment was done on a TA instrument (TGA Q500) as seen in **Figure 21**. The samples were tested from room temperature with a heating ramp of 10 ℃/min in an inert nitrogen atmosphere.

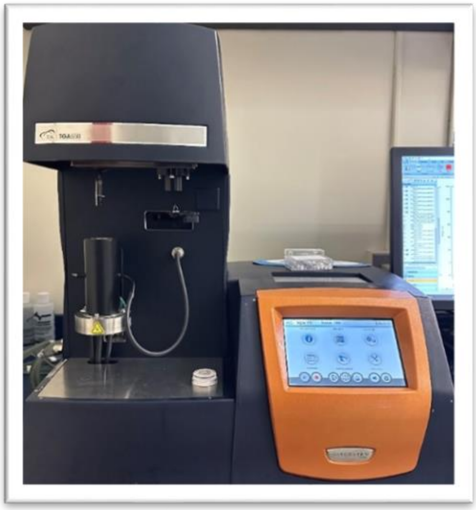


Figure 21. TGA instrument for thermal analysis.

CHAPTER III

RESULTS AND DISCUSSION

3.1. Synthesis of sunflower-based epoxide and polyol

3.1.1. Iodine value

Following the Hanus method, the iodine value was measured to determine the level of unsaturation or the number of double bonds present in the sunflower oil and its derivatives. The iodine value of sunflower was 100 g I_2/ 100 g oil which means, 0.39 moles of double bonds were present in 100 g of the purchased sunflower oil. In reference to this value, stoichiometric calculations were made to determine the quantity of reagents required for the epoxidation reaction of the sunflower oil. After the epoxidation and ring-opening reactions, the measured iodine value for the epoxide was 0.02 g I_2/ 100 g and 0.01 g I_2/ 100 g for the polyol, indicating the conversion of the double bonds in sunflower oil into a more reactive and useful form for rigid polyurethane foams.

3.1.2. Epoxide number

The percent oxirane number measures the amount of epoxide groups present in a compound. In this work, the epoxide number measured after the epoxidation reaction of the sunflower oil with hydrogen peroxide and acetic acid in the presence of the catalyst was 5.7%. About 0.1% was measured for the epoxy content in the sunflower polyol after the ring-opening reaction, indicating the conversion of the epoxide ring into hydroxyl groups.

3.1.3. Hydroxyl value

One of the most important parameters of polyols is the hydroxyl number since it determines the reactivity and amount of isocyanate needed for the synthesis of polyurethanes. In this experiment, the OH number measured for the sunflower polyol was 180 mg KOH/g. Based on this amount, the quantity of MDI was determined for the synthesis of the rigid polyurethane foams.

3.1.4. Acid value

The catalyst used in the formation of the sunflower-based polyurethane foams was amine-based. Hence, having a very high acid value for the sunflower polyol will inhibit foaming due to an unwanted reaction of the amine-based catalysts with the acidic polyol. After the synthesis of the sunflower polyol, the acid value determined was 0.37 mg

KOH/g. This low value had a negligible effect on the catalysis of the polyurethane foam synthesis.

3.1.5. Fourier-transform infrared spectroscopy

Fourier spectroscopy identifies the presence of different chemical bonds in a molecule. This technique was used as one of the convenient ways of confirming the synthesis of the epoxide and polyol from the sunflower oil. In FT-IR spectra results of some fats and vegetable oils, one of the common identifiers of unsaturation is seen around 2989-3029 cm^{-1} [88]. Based on the infrared absorbance spectrum in **Figure 22**, a peak around the wavelength at 3008 cm^{-1} is observed. This specific peak is indicative of the presence of the carbon-carbon double bond in the sunflower oil based on the stretching vibration from the =C-H bonded to it [89,90]. However, after the epoxidation reaction, this peak disappears and a new one forms around 834 cm^{-1}. This current peak is associated with the bending from the epoxy group in the C-O-C ring [81].

Similar wavelengths of the epoxide peak in the work were observed by other researchers for epoxides from vegetable oils such as soybean oil [91]. For confirmation of the sunflower polyol, a wide peak around 3477 cm^{-1} appears. This broad peak is characteristic of stretching vibration from the hydroxyl groups present in a molecule [92–94]. In addition to other tests, this validates the synthesis of sunflower-based polyol and its suitability for use in the synthesis of rigid polyurethane foams.

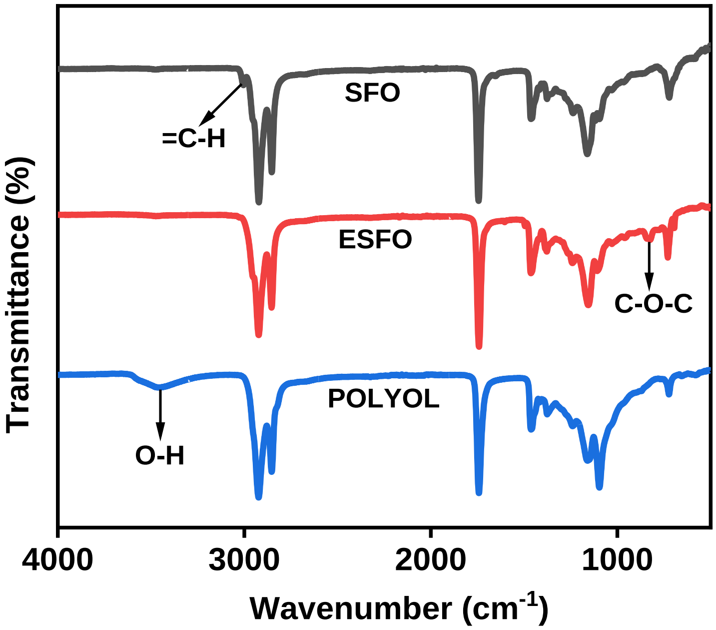


Figure 22. FT-IR results of sunflower oil-SFO (**black**), epoxide sunflower oil-ESFO (**red**), and sunflower polyol (**blue**).

3.1.6. Viscosity measurement

Viscosity is an analysis of the resistance of a material to flow and this can play a significant role in the processability of samples. The measured viscosity of the sunflower oil was 0.06 Pa.s, 0.1 Pa.s was recorded for epoxide sunflower oil, and 1.6 Pa.s was determined for the sunflower polyol. A gradual increase in the viscosity from sunflower oil to the polyol indicates an increase in molecular weights during the transformation reactions. Compared to other polyols, the low viscosity for the sunflower polyol was advantageous of an easy processability of the foams.

3.1.7. Gel permeation chromatography

This is an analytical method that can be used to monitor the progress of a reaction. Based on the range of weights for a specific GPC column, analytes can be separated. Due to the porous beads in the column, smaller molecules can easily enter the pores, spend more time in the column and have a longer retention time. Larger molecules on the other hand will have fewer pores to enter, spend a shorter time in the column, and will be easily eluted. As shown in **Figure 23**, the sunflower polyol comes out first at 23.1 minutes. The retention time for the epoxide and sunflower oil is 23.4 and 23.6 minutes respectively.

The shorter retention time of the sunflower polyol compared to the starting and intermediate products indicate an increase in the molecular weight and polymerization of the polyol. A smaller peak is observed around 21.6 minutes as part of the sunflower polyol. This peak could be a result of the formation of dimers and trimers due to the variation in the fatty acids present and the oligomerization of a small portion of the polyol during the conversion [95].

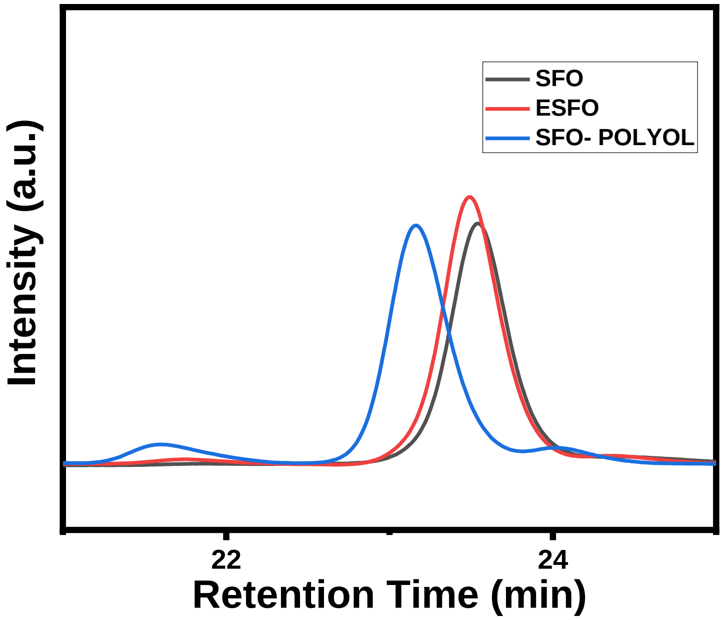


Figure 23. GPC of SFO (**black**), ESFO (**red**), and polyol (**blue**).

3.2. Properties of the sunflower-based rigid foams

After confirming the suitable properties of the sunflower polyol, rigid polyurethane foams with varying amounts of flame retardants were made. The sunflower-based foams had comparable physical features to commercially available ones. The foams were cut into appropriate sizes and investigated for various properties under standardized methods. Examples include cell morphology, apparent density, closed cell content, thermal stability, flame retardancy, and mechanical properties.

3.2.1. Apparent density

The apparent density of rigid polyurethane foams is an influential parameter for their mechanical properties, thermal conductivity, and overall performance [32]. Rigid foams are commercialized and suitable for construction applications, soundproofing, and especially for insulation due to their low density, low thermal conductivity, and high compression [96]. However, their flammability is an issue. The apparent density of foams can be affected by blowing agents, additives, and other components [32,97]. To better analyze the effect of AHP, DMMP, and EG, they were added in varying amounts and all other components were kept constant. The density of the rigid foams with increasing amounts of AHP (**Figure 24**) are in the 31- 45 kg/m^3 range that falls under the acceptable commercial bracket for specific applications [98].

However, it is observed that increasing the amount of AHP gradually increases the density of the rigid sunflower-based foams. In an already published work on the effect of AHP on the fire retardancy and thermal degradation of rigid polyurethane foams, it was found that high loadings of AHP led to a slight increase in the density [32] of the foams as similarly observed in this work.

In other studies, DMMP was shown to have a slight effect on the density of foams when added in high loadings; however, depending on the polyol and other additives, there could be a different turn out [53,99]. In **Figure 25** however, the density of the sunflower foams gradually increases from 32 kg/m^3 to 55 kg/m^3 as the amount of DMMP added rises. Irrespective of this, all the foam densities fell under the acceptable category and had a modest effect on the mechanical properties of the foams.

Foams containing expandable graphite did not have a significant difference in their densities when compared to the pure foams without flame retardants. This trend is somewhat contrary to the significant difference observed in other reported works with the increase in EG [76,100]. The densities of sunflower-based foams with EG (**Figure 26**), fall in a 30-40 kg/m^3 range with slight changes which are still suitable for commercial purposes. This indicates that there could be better compatibility of the sunflower polyol with EG.

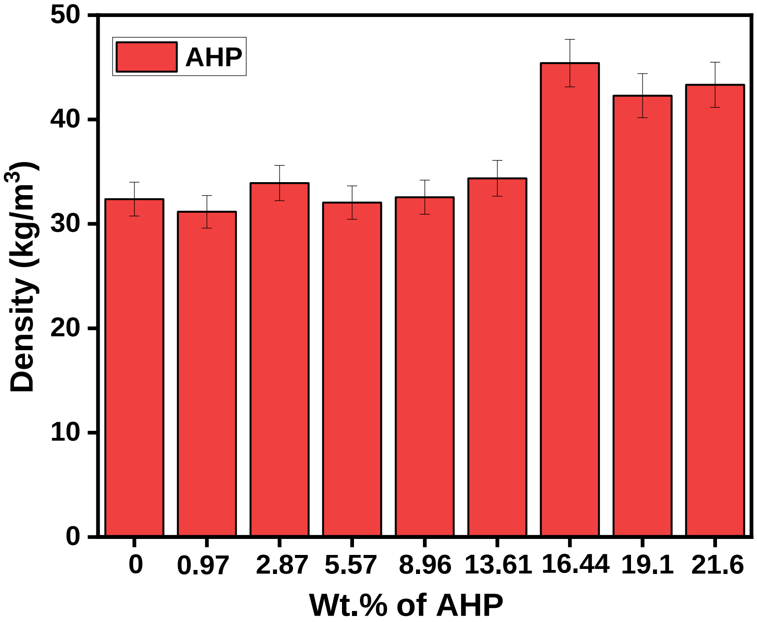


Figure 24. Density for sunflower-based foams with varying amounts of AHP.

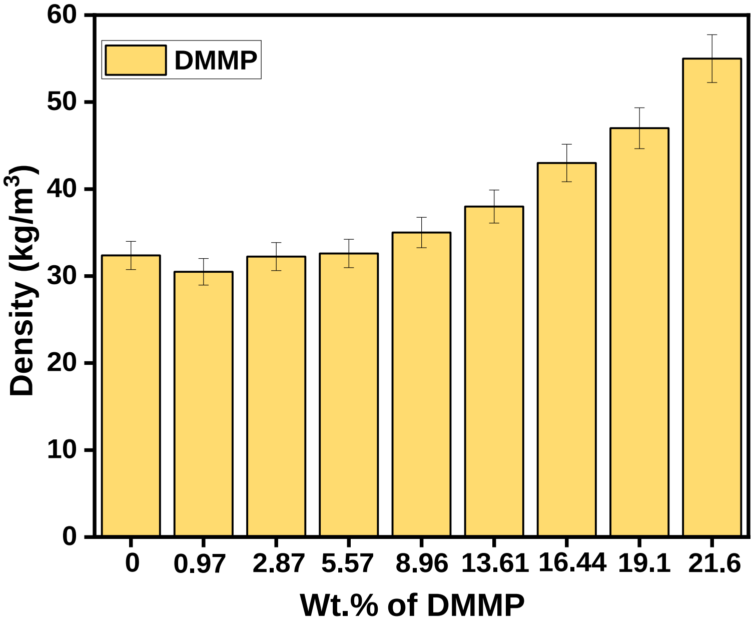


Figure 25. Density for sunflower-based foams with varying amounts of DMMP.

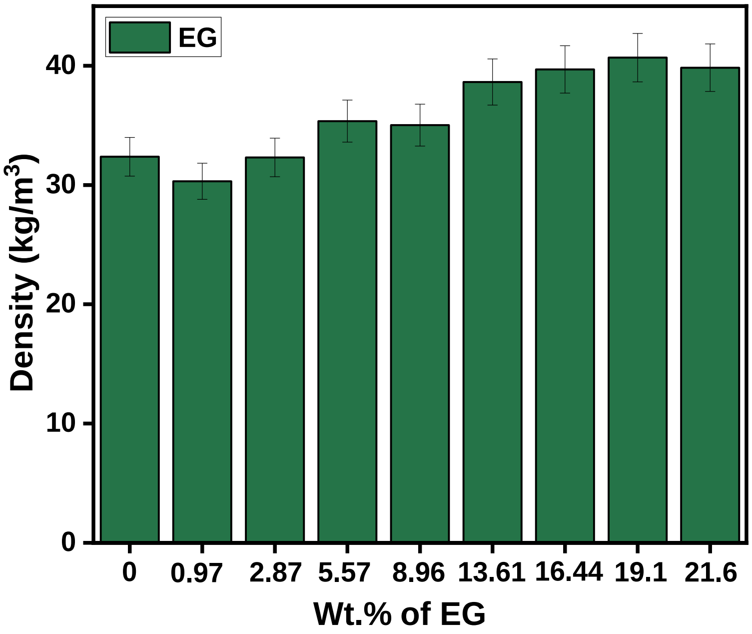


Figure 26. Density for sunflower-based foams with varying amounts of EG.

3.2.2. Closed cell content

The number of closed or open cells present in polymeric foams is indicative of their durability through aging and thermal insulating properties [101,102]. One of the qualifications for improved thermal insulation is a high closed cell content in rigid polyurethane foams. Here, the air trapped between the cells limits their transmission in the empty spaces, prevents the rapid spread of heat and oxygen, and increases the thermal barrier [103]. **Figure 27** shows that foams with AHP have a closed cell content (CCC) greater than 90%, however, this amount fluctuates a little bit around AHP-3 (5.57 wt.% of AHP), and with high loadings above AHP-6 (16.44 wt.% of AHP), the CCC declines.

Similarly, foams containing varying amounts of DMMP (**Figure 28**) have a CCC higher than 90% up until DMMP-4 (8.96 wt.% of DMMP). However, the reduction of the CCC in higher loadings of DMMP does not cause a significant difference in the overall performance of the foams.

In **Figure 29**, rigid sunflower foams with varying amounts of EG have similar CCC with the foams without EG. This is another indication of the limiting deteriorating impact the EG has on the foams, irrespective of their loading amounts. Overall, all the foams showed good closed cell content suitable for insulating purposes with little compromise of their properties while increasing the concentration of the non-halogenated flame retardant.

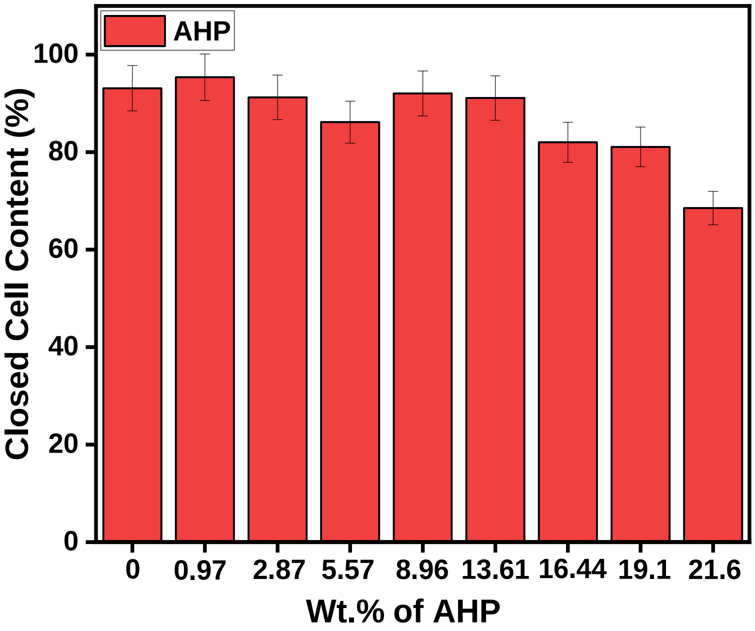


Figure 27. CCC for sunflower-based foams with varying amounts of AHP.

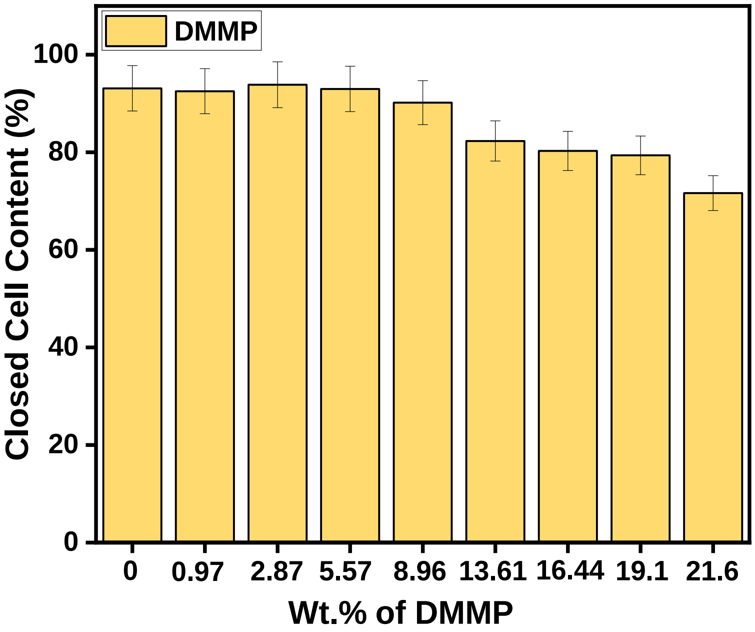


Figure 28. CCC for sunflower-based foams with varying amounts of DMMP.

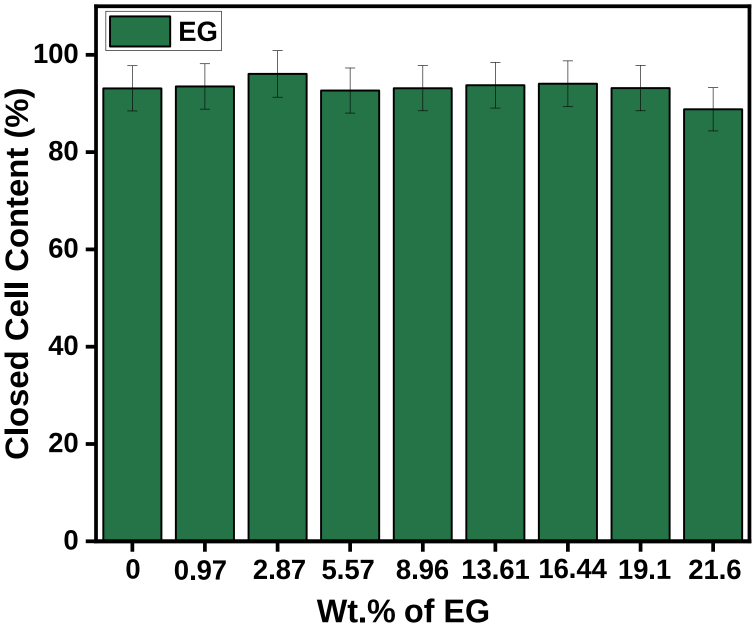


Figure 29. CCC for sunflower-based foams with varying amounts of EG.

3.2.3. Compressive strength test

The compression strength of the rigid sunflower foams was tested under different concentrations of flame retardants. In this analysis, the yield strength (which is the compressive strength above which the foams do not recover back to their original shapes) was measured and compared to study the effects of the respective flame retardants. On average, this value was observed after a 10% strain or compression. In rigid polyurethane foams, their compressive strength is valuable for assessing their mechanical properties.

Based on **Figure 30**, foams with AHP have very few inconsistencies in the compressive strengths; however, the overall trend suggests that the addition of high loadings of AHP has a reducing effect on the compressive strength of the foams. The pure foam has the highest compression of 280 kN/m^2, and this value is seen to be the lowest in AHP-6 (16.44 wt.% of AHP) at 160 kN/m^2. For rigid foams that contain DMMP, a clearer pattern is observed except for DMMP-7 (19.10 wt.% of DMMP).

Figure 31 illustrates that increasing the amount of DMMP results in a reduction in the amount of compressive force required to reach the yield point in these flame-retardant foams. For instance, DMMP-0 has a compressive force of 280 kN/m^2 and this is seen to gradually drop to 260, 200, 180, and 170 kN/m^2 in DMMP-2, 4, 6, and 8 respectively. This trend can be observed because, based on the SEM described below, amounts of DMMP above DMMP-4 (8.96 wt.% of DMMP) resulted in an increase in cell sizes and a reduction in the number of cells; hence, less force will be required to have a massive compressive effect.

Expandable graphite did not cause a significant difference in the compressive strength of the sunflower foam **Figure 32**. The compressive strength was 260 kN/m^2 in EG-2 (2.87 wt.% of EG) and 250 kN/m^2 in EG-5 (13.61 wt.% of EG). The maintained yield strength in EG irrespective of the high loading suggests minimal effect on the mechanical properties of the rigid foams as a result of the speculated analysis that the sunflower polyol has better compatibility with EG.

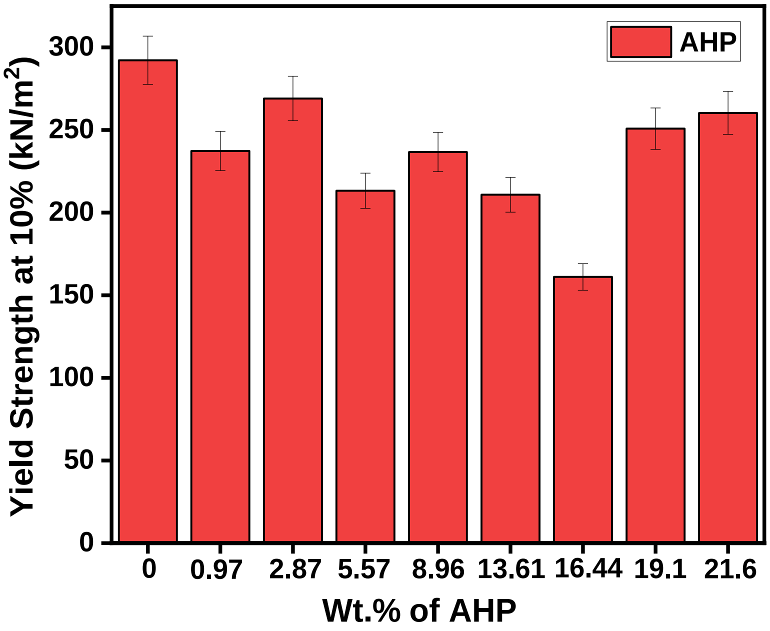


Figure 30. Compressive strength for rigid foams with varying amounts of AHP.

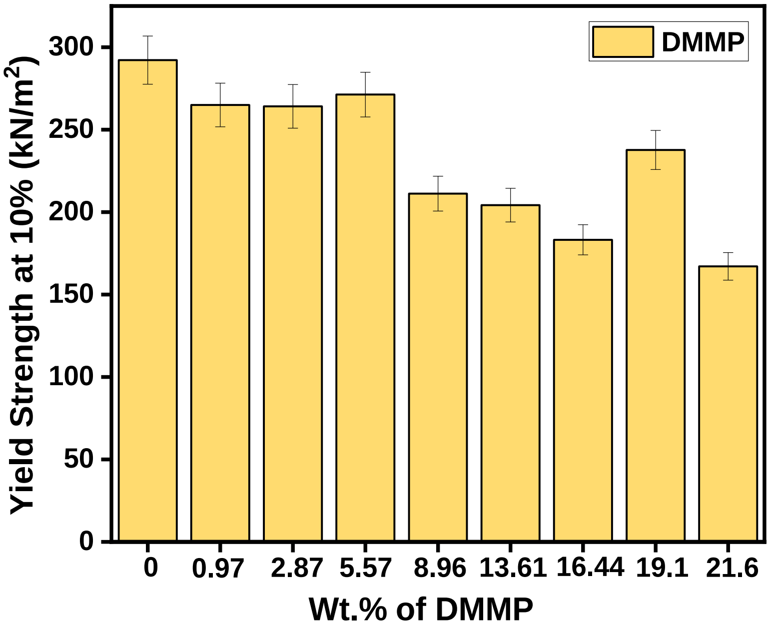


Figure 31. Compressive strength for rigid foams with varying amounts of DMMP.

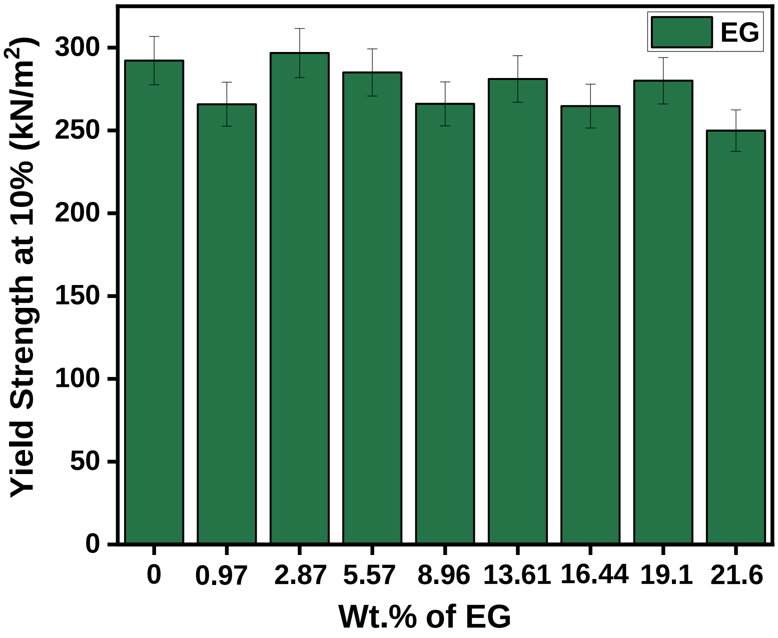


Figure 32. Compressive strength for rigid foams with varying amounts of EG.

3.2.4. Scanning electron microscope imaging

Based on SEM images generated to study the microstructure and morphology as shown in **Figures 33**, **34**, and **35**, it is observed that the cell structures of the sunflower foams are comparatively similar to the honeycomb or polyhedral structure and are uniformly distributed. The pure foams without flame retardants have a consistent cell size distribution with an approximate range of 180-250 µm. The addition of different amounts of AHP resulted in an increase in the cell sizes of the foams (**Figure 33**), which affects the compressive strength of the foams. However, this does not have a detrimental effect on the thermal and other mechanical properties of the foams with AHP.

With the addition of DMMP (**Figure 34**), there is a gradual increase in the cell sizes resulting in a reduction in the number of cells present. For example, it increased from 180-250 µm in the pure foams to 280- 370 µm with concentrations above DMMP-5 (13.61 wt.% of DMMP) in addition to some distortions in DMMP-7 (19.10 wt.% of DMMP) and DMMP-8 (21.60 wt.% of DMMP) due to the plasticizing effect of the DMMP [99]. The increase in the cell sizes and reduction in the number of cells correlates to the reduction in the compression strength of the foams with increasing amounts of DMMP as seen in the compressive test above. This trend has been observed by some scientists who have researched other bio-based materials in rigid polyurethane foams under the influence of DMMP for flame retardant purposes [99][104].

As **Figure 35** shows, the addition of expandable graphite results in a slight reduction in the number of cells and an increase in the cell sizes, compared to the pure rigid foams. Despite that, consistent and uniform cell size, shapes, and distribution are maintained. Increasing the concentration of EG had very little impact on the overall morphology of the polyurethane foams which could be attributed to the great interaction and compatibility of the EG and the sunflower-based polyol.

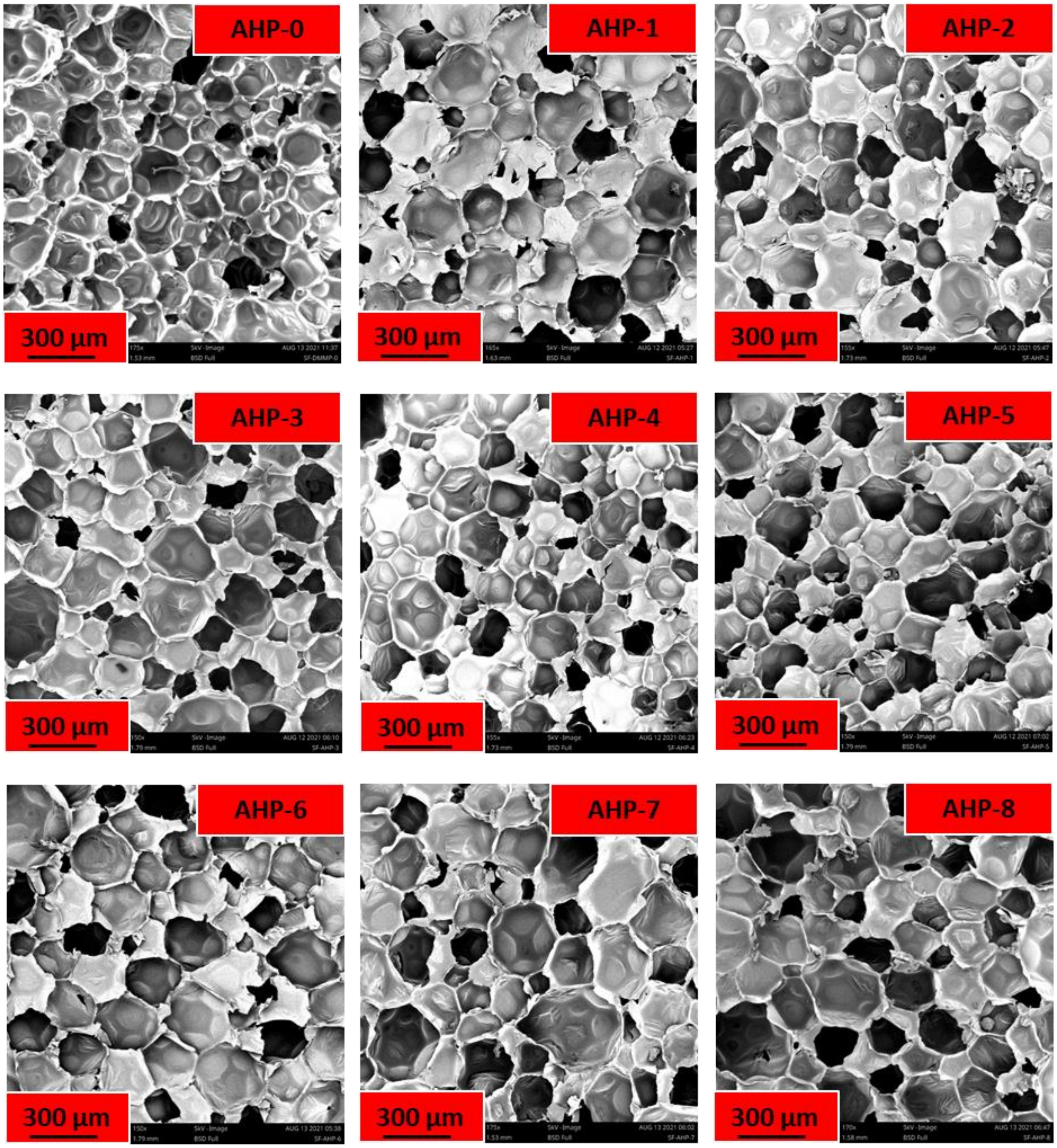


Figure 33. SEM images for sunflower-based foams with varying amounts of AHP.

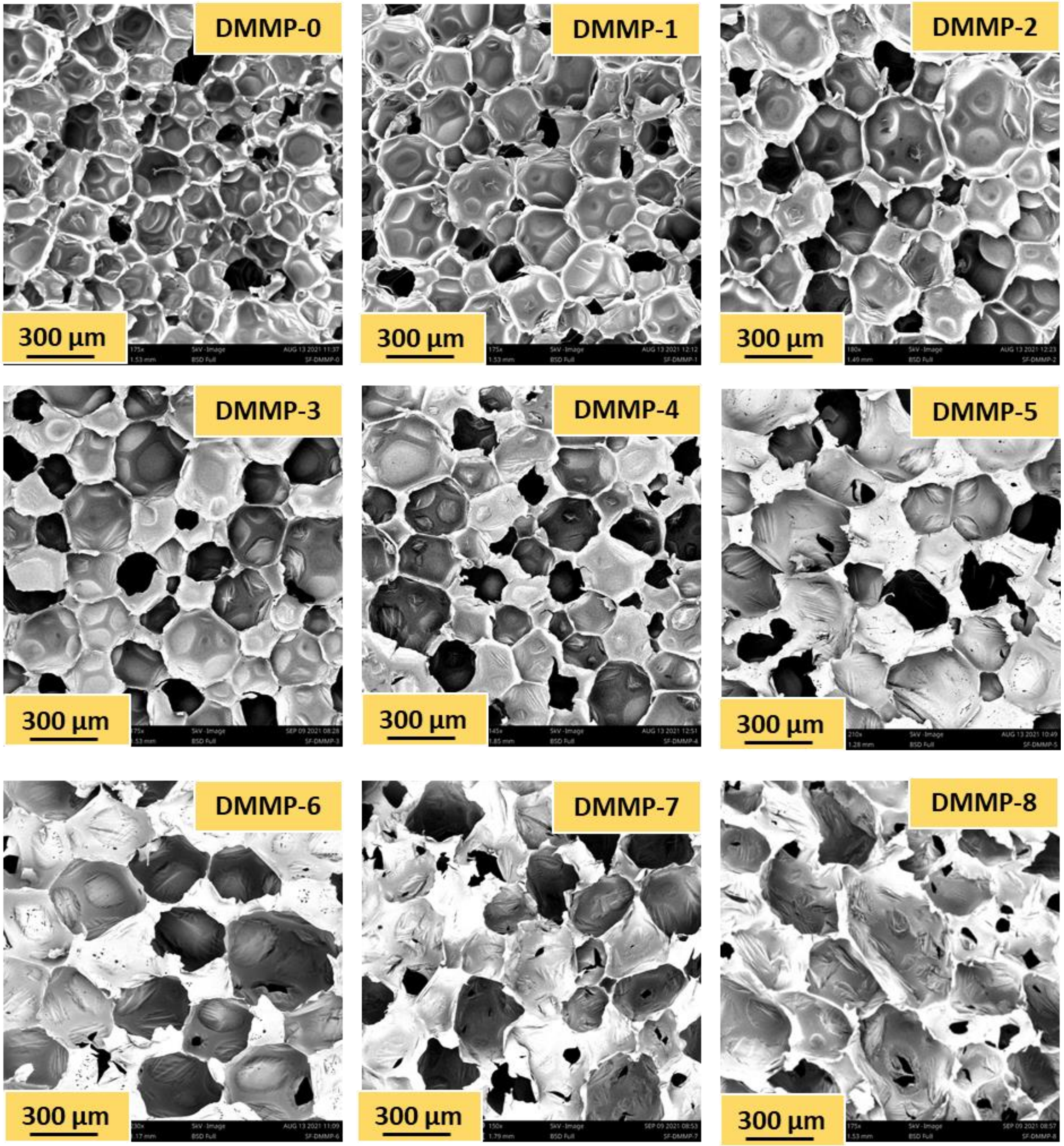


Figure 34. SEM images for sunflower-based foams with varying amounts of DMMP.

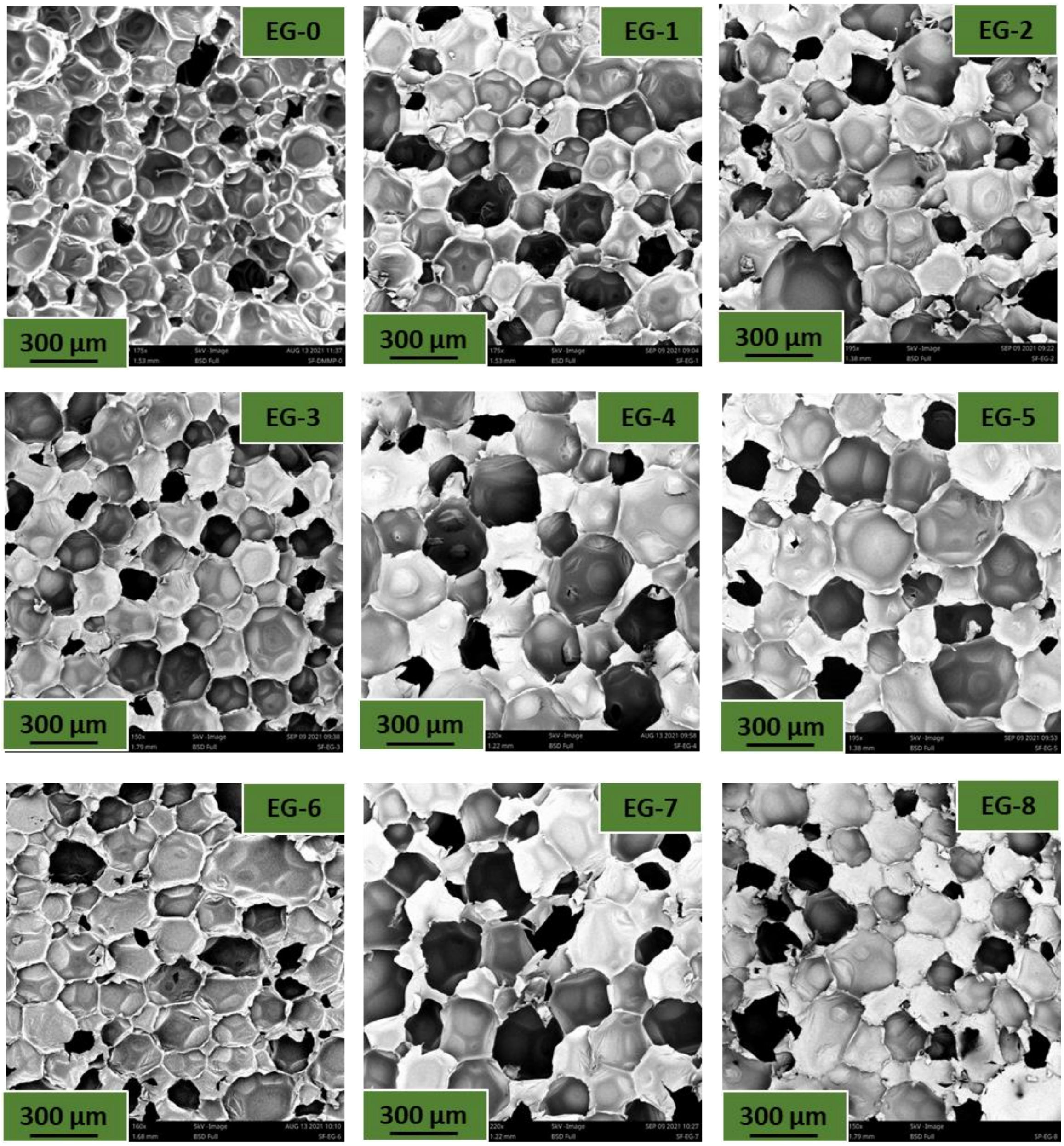


Figure 35. SEM images for sunflower-based foams with varying amounts of EG.

3.2.5. Horizontal burning test

This gave a visual perspective of the effect of the three selected non-halogenated flame retardants on their respective fire-defense mechanisms on the sunflower-based foams. The weights of the foams before and after exposure to the 10 seconds flame were recorded, in addition to the time it took to self-quench after removing the fire source. **Figure 36 A**, **B**, and **37**, show the burning time, weight loss, and images of the foams before and after the flammability test in the presence of AHP. The total time taken for fire to extinguish in the pure rigid foam was 79 seconds; however, this time drastically reduces to about 9 seconds in AHP-4 (8.96 wt.% of AHP) and to even lower times in higher concentrations. As expected, the weight loss reduced from 50% in the pure foams to 3% in AHP-4.

Under the influence of AHP, images of the foams before and after burning can directly be correlated with the burning time and weight loss. Only a very small fraction of the foams is burned as shown in **Figure 37**. This is indicative of the flame retardant properties of AHP.

Hypothesized mechanisms for AHP explain that in a fire incident, AHP can break into PH_3 and $Al_2(HPO_4)_3$, which will then decompose into $Al_4(P_2O_7)_3$ and water as shown in **Figure 38**. The PH_3 generated can oxidize into phosphoric acid and its derivatives, which can form stable structures when combined with aluminum phosphate to generate a protective char layer. This compact layer will form a barrier that will impede the easy spread and penetration of volatiles, heat, and flammables to other parts of the foams, hence decreasing propagation of the fire. In addition, the water vapor produced can inhibit any oxygen and flammable gases from propagating the spread of the fire [72,105]. This gas and solid-phase mechanism portrayed by AHP proves its merit as an additive flame retardant in the sunflower-based foams without compromising the other properties of the foam.

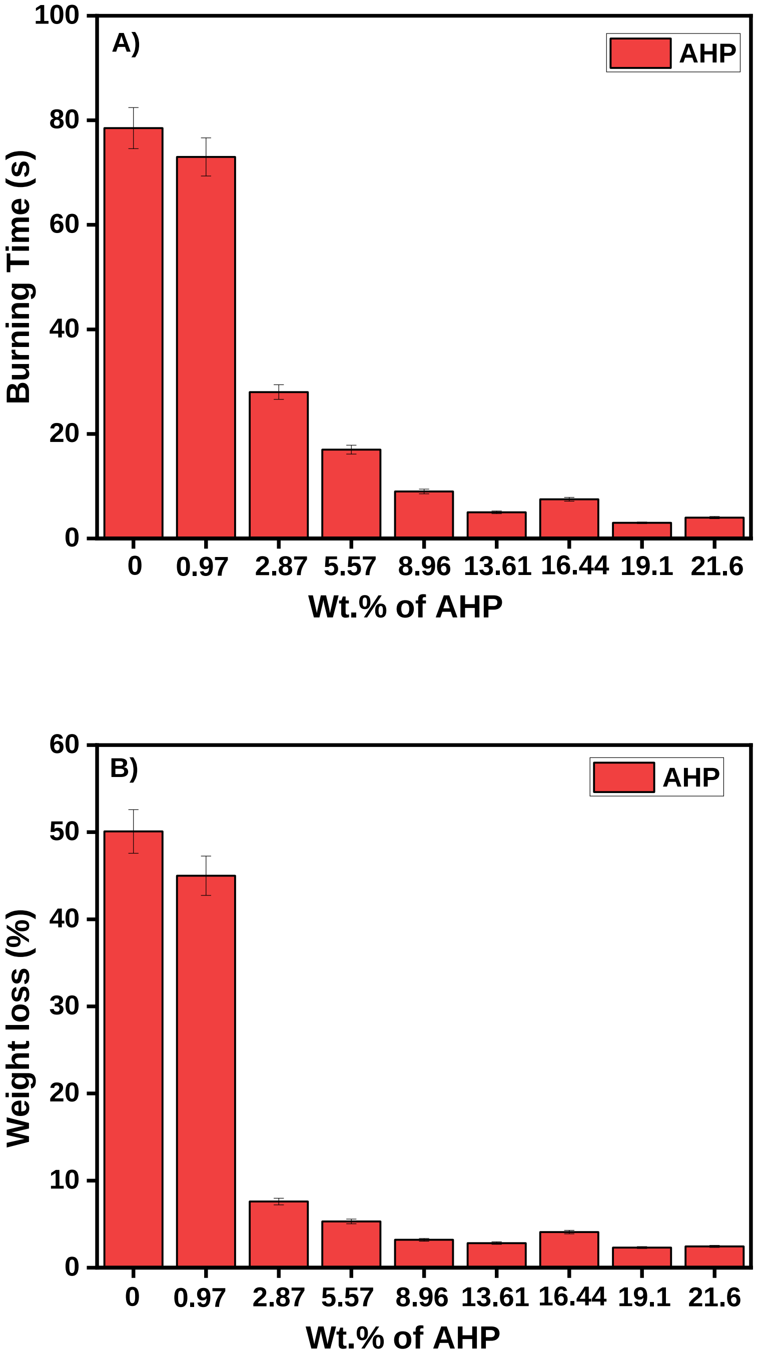


Figure 36. A) Burning time, **B**) weight loss of foams with varying amounts of AHP.

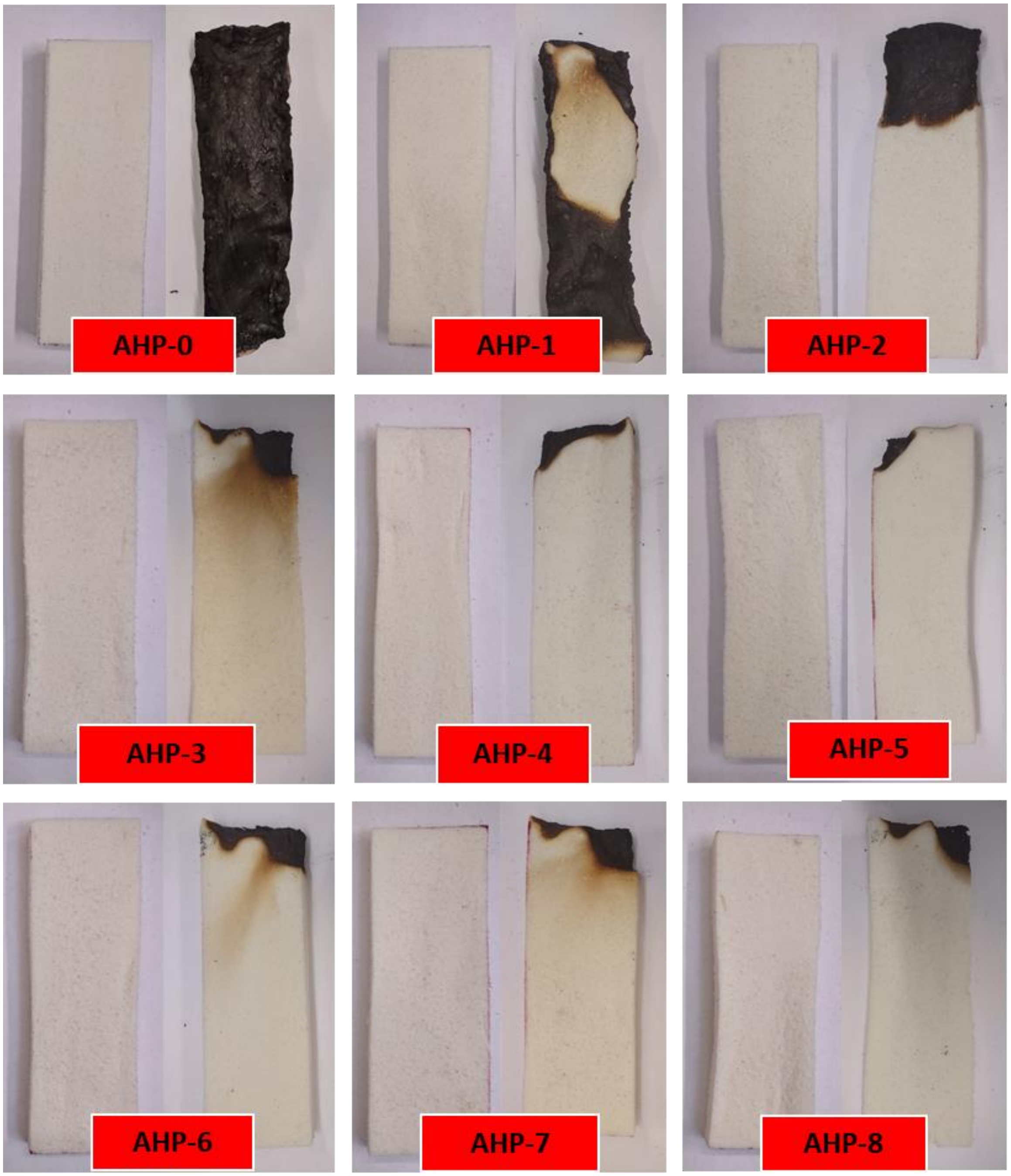


Figure 37. Pictures of foams with varying amounts of AHP before and after the horizontal burning test.

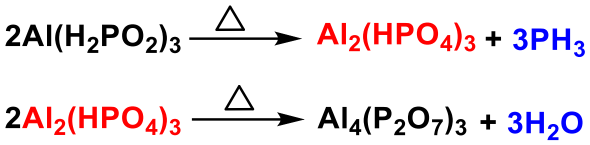


Figure 38. Chemical breakdown of AHP during combustion. Image reproduced with permission [72]. Copyright (2011) John Wiley and Sons.

In DMMP, the burning time of 79 seconds and weight loss of 50% in the foams is seen to reduce to 5.5 seconds and 1.9% respectively in the presence of DMMP-4 (8.96 wt.% of DMMP) (**Figure 39 A & B**). These numbers significantly reduce to about 1 second of burning time and 1.8% weight loss in the highest concentration DMMP-8 (21.60 wt.% of DMMP). It is interesting to note that after about DMMP-3 (5.57 wt.% of DMMP) amounts in the foams, the burning time and weight loss levels off with little to no change even with the increasing concentrations of DMMP. Even though DMMP is an additive flame retardant, this observation is an advantage that rules out the need to add high loadings of DMMP to have satisfactory flame-retardant results.

Images from the burning test (**Figure 40**) also show that the presence of DMMP reduces the flammability of the foams. Researchers like Feng and partners found that in the gas phase, DMMP generates free radicals like PO_2 and PO that can suppress other free radicals with flammable attributes. This further inhibits the instigators of the flame, which reduces the intensity of the spread of fire in the foams. These phosphorous-containing radicals can also form phosphoric acid and other components suitable for both reducing the heat in the polymer matrix in addition to forming a char layer that protects the rest of the polyurethane foam from combusting [102].

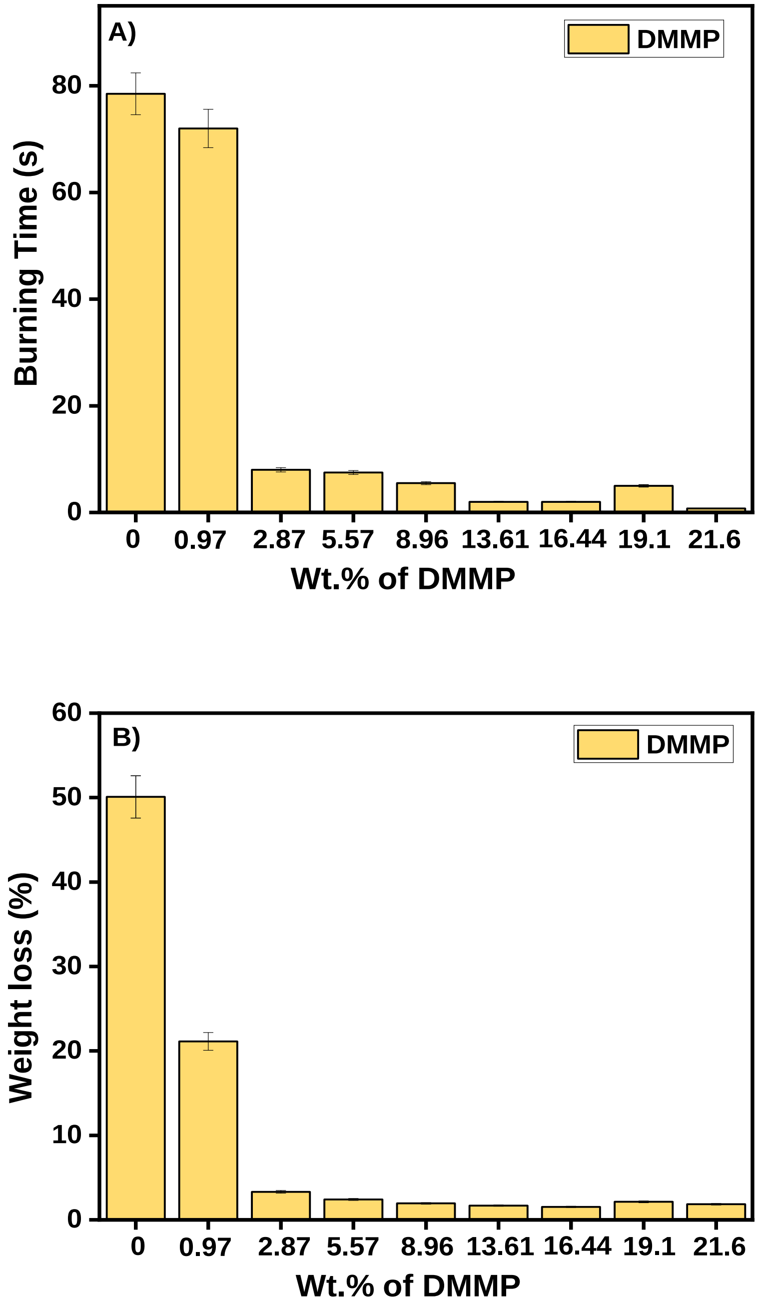


Figure 39. A) Burning time, **B**) weight loss of foams with varying amounts of DMMP.

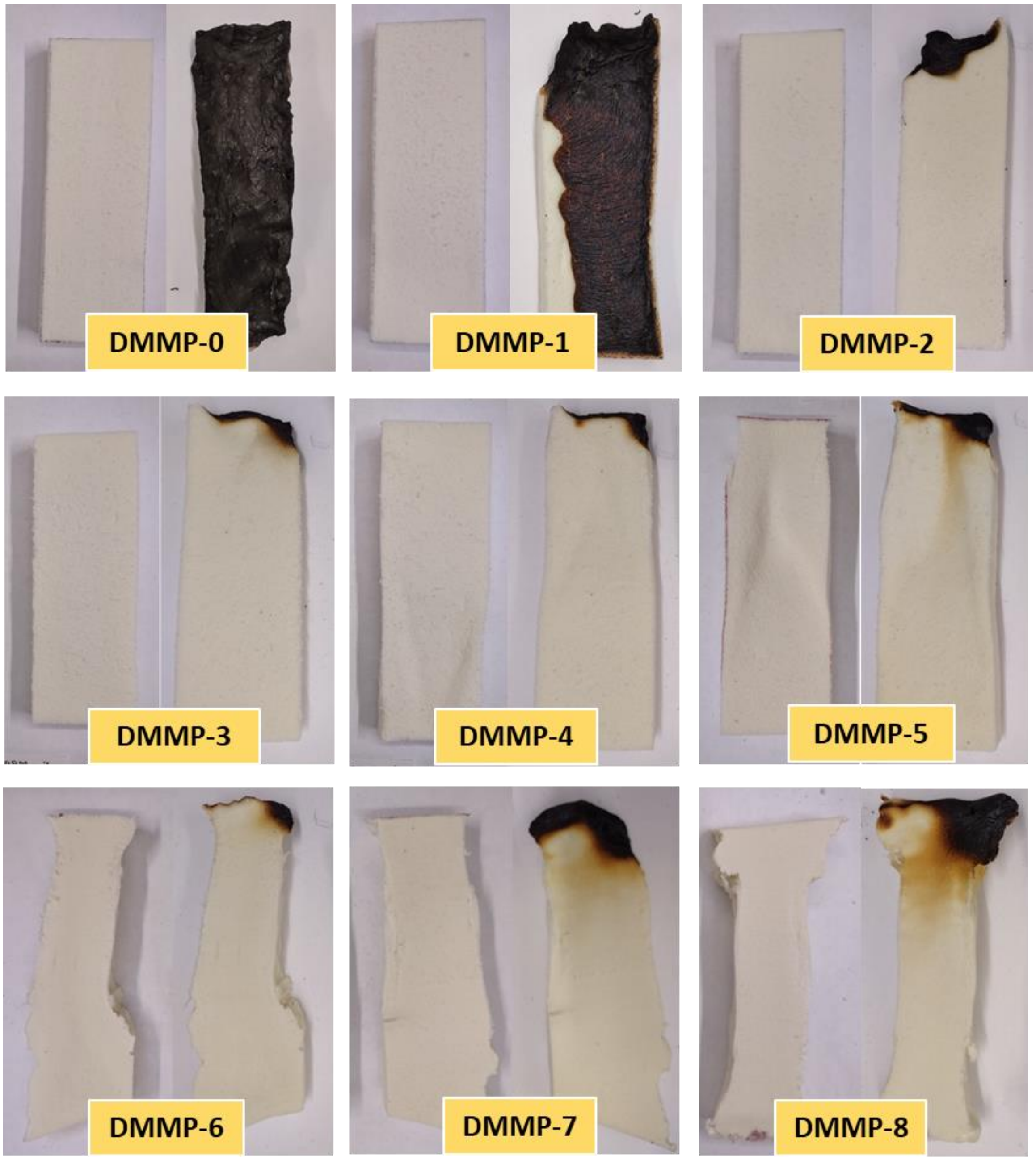


Figure 40. Pictures of foams with varying amounts of DMMP before and after the horizontal burning test.

A similar trend is observed where the presence of EG reduces the burning time and weight loss. **Figures 41 A** shows that the burning time of the pure foams is 79 seconds, and this reduces to 5 seconds in EG-5 (13.61 wt.% of EG). Similarly, the weight loss reduces from 50% to about 4% in the case of EG-5 (**Figure 41 B**).

A distinct appearance of loose hair-like structures can be seen from the burning photos of foams with EG (**Figure 42**). In a fire incident, the intercalated compounds like sulfuric acid (H_2SO_4) in the structure of EG decompose around 220 ℃. This process generates high pressure and force that pushes against the graphitic layers. As deduced by experts, this force is greater than the binding force between the graphite layers, which results in a push against the walls and an expansion that forms a protective layer. Additionally, the redox reaction between expandable graphite and the sulfuric acid produces CO_2, SO_2, and H_2O that facilitate the formation of the tight wormlike structures. These hair-like particles interspersed on the foams reduce the spread of heat and combustibles and protect the rest of the foam from further decomposition [106,107].

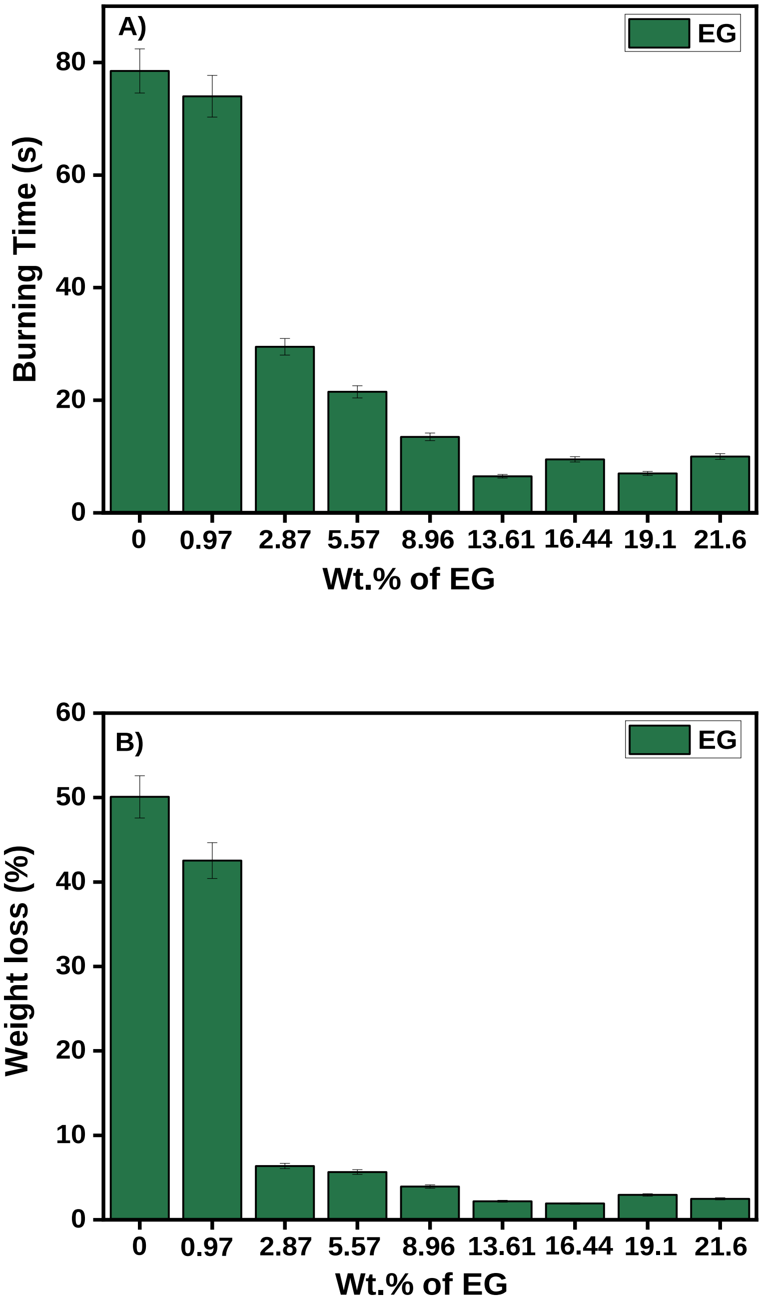


Figure 41. A) Burning time, **B**) weight loss of foams with varying amounts of EG.

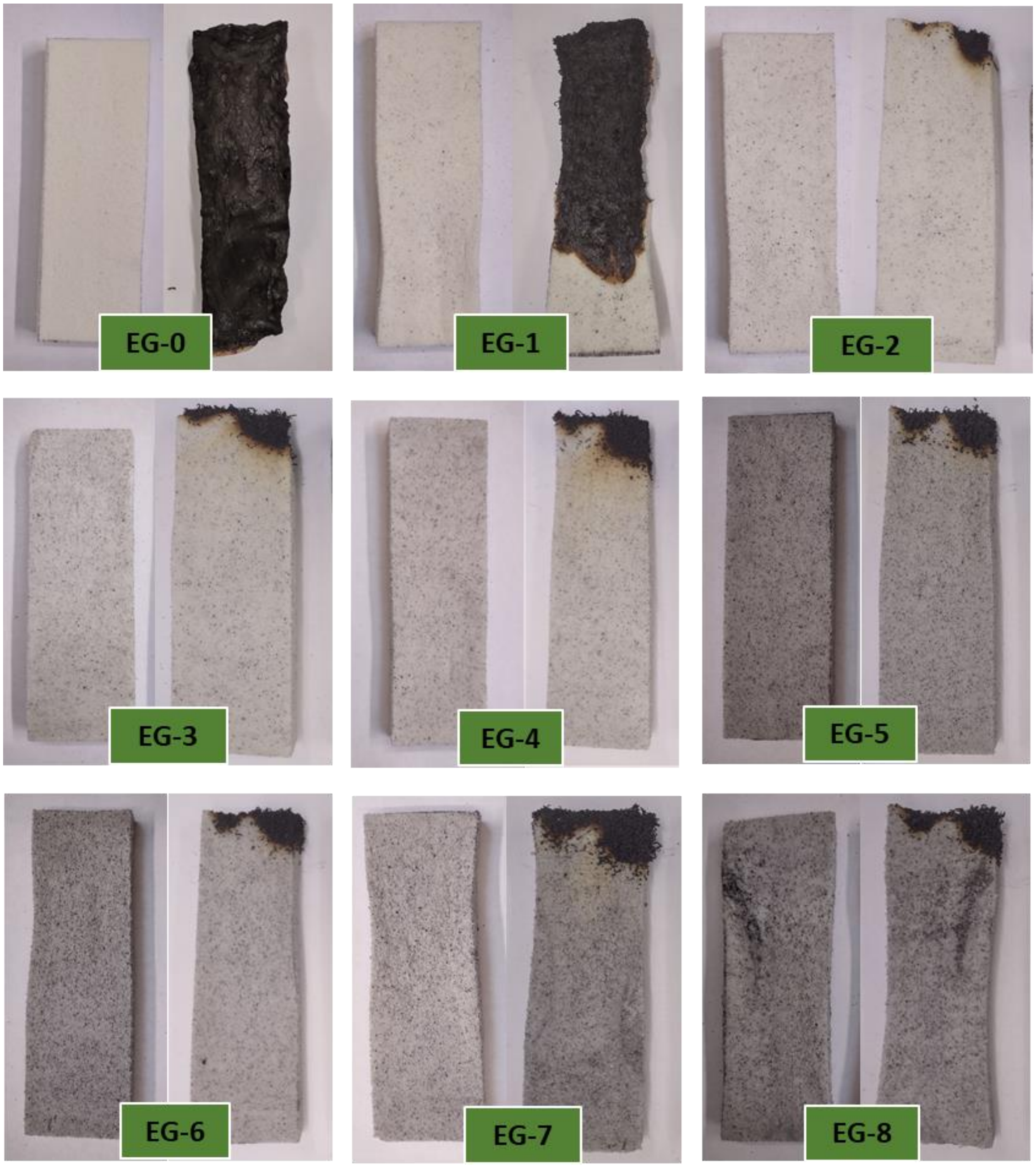


Figure 42. Pictures of foams with varying amounts of DMMP before and after the horizontal burning test.

3.2.6. TGA and derivative TGA (DTGA)

The thermal stability of the rigid foams with respect to their weight loss under the influence of varying flame retardant concentrations was investigated using TGA analysis. In addition, the first derivative of the graphs was plotted to extrapolate the point at which the weight loss of the foams was obvious. All samples were tested under a nitrogenous atmosphere. It was observed that the foams without flame retardants had two main degradation steps associated with the decomposition of the polyurethane matrix, as illustrated in **Figures 43**, **44**, **and 45**. The first, which is seen around 180-240 ℃, is characteristic of the breakage of the urethane linkages. The second phase around 450-600 ℃ is the period with the most weight loss due to the depolymerization of the polyol and polyisocyanate that constitute the rigid foams [102]. Except for AHP-1 (0.97 wt.% of AHP) (**Figure 43**) as an anomaly, the weight loss of the foams in the presence of AHP is seen to be significantly less as compared to the pure foam. For instance, the ash content at 700 ℃ of the pure foams was about 2.46%; however, the addition of AHP-4 (8.96 wt.% of AHP) and AHP-8 (21.60 wt.% of AHP) increases this value to 19.04% and 31.79% respectively due to the formation of the protective char layer, which serves to reduce the combustion of the foams in its defense mechanism. This, again, is consistent with the earlier experienced burning time and weight loss values recorded from the horizontal burning test. Due to the fire-fighting performance of AHP through the gas and solid phase with the formation of the protective char layer, the foams exhibited improved thermal stability and flame resistance [32,108].

A similar but different route is seen in the case of DMMP. From about 100-150 ℃ shown in TGA (**Figure 44 A**) and DTGA (**Figure 44 B**), an additional transitioning is observed which is associated with the boiling point of DMMP. Here, the volatilization of DMMP produces fire-combating segments that repress any ignitable segments and eventually reduce the fire spread [75,99]. Foams with increased DMMP loadings have a lower weight loss at the end of the thermal analysis due to the formation of the protective char layer. At 700 ℃, the ash content in DMMP-8 was 11.01% as compared to 2.46% recorded in the foam with any flame retardant.

The virgin foams required a temperature of around 337.84 ℃ for a 50% weight loss analysis ($T_{d50\%}$), but in the case of EG (**Figure 45**), this temperature increased to 348.57 ℃, 363.51 ℃, 393.3 ℃ in EG-5, EG-6 and EG-7 respectively. This indicates an increased thermal stability in the foams with EG as well as the other non-halogenated flame retardants as detailed in **Table 4**.

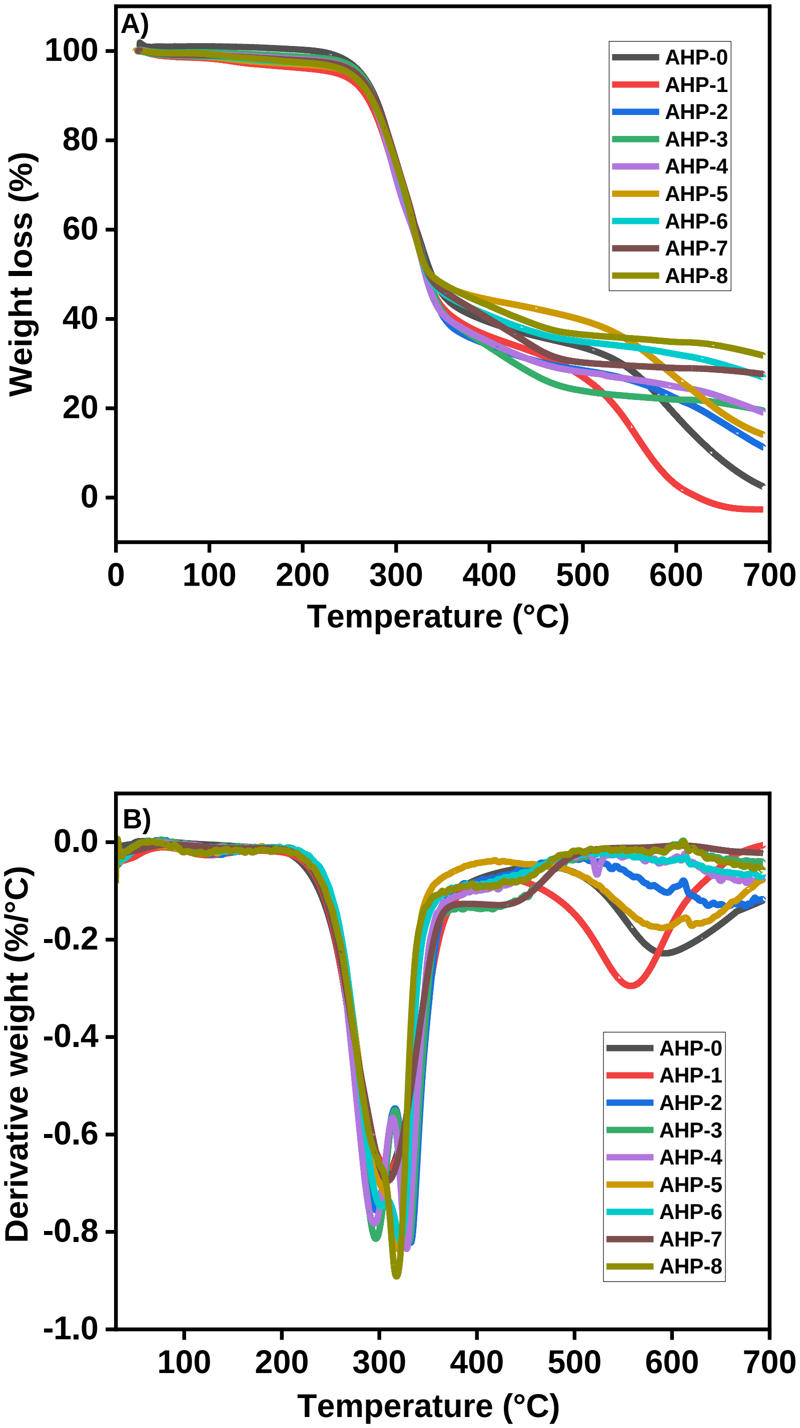


Figure 43. Thermal analysis for foams with varying amounts of AHP **A**) TGA, **B**) DTGA.

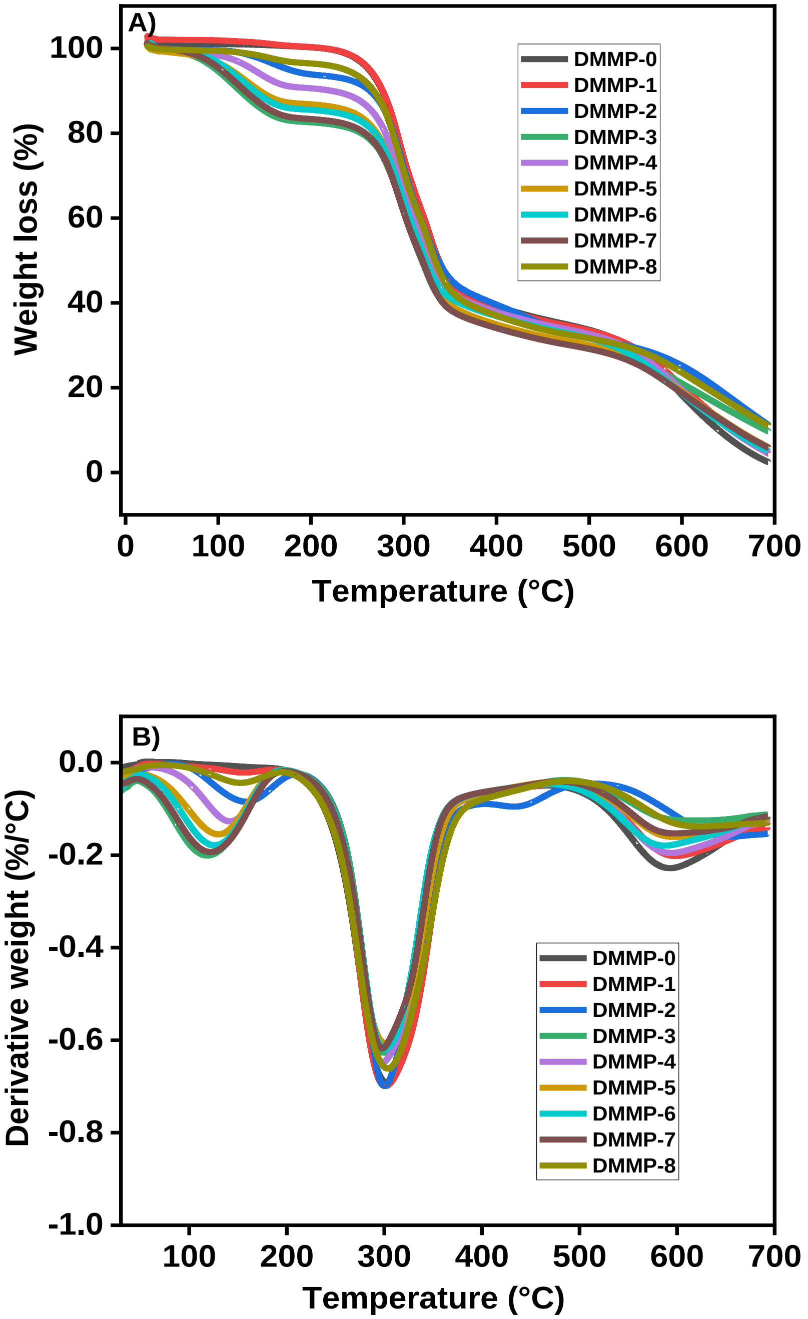


Figure 44. Thermal analysis for foams with varying amounts of DMMP **A**) TGA, **B**) DTGA.

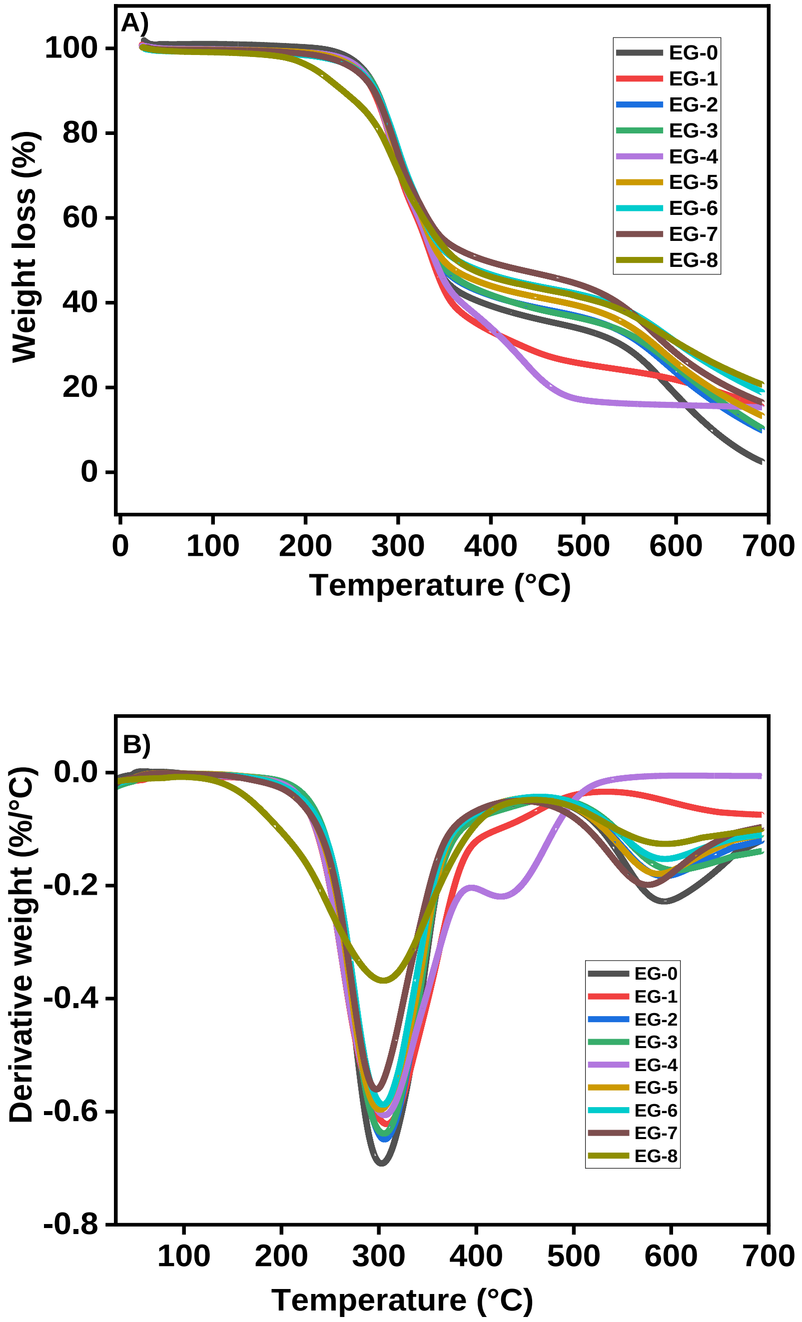


Figure 45. Thermal analysis for foams with varying amounts of EG **A**) TGA, **B**) DTGA.

Table 4. Analysis of the thermal stability of the rigid PU foams based on sunflower polyol.

	AHP		DMMP		EG	
FOAMS	$T_{d50\%}$ (°C)	Ash Content (%)	$T_{d50\%}$ (°C)	Ash Content (%)	$T_{d50\%}$ (°C)	Ash Content (%)
0	337.84	2.46	337.84	2.46	337.84	2.46
1	332.66	0	337.55	4.51	337.04	15.45
2	333.66	11.24	336.86	11.23	342.34	9.90
3	333.55	19.47	319.54	9.73	343.76	10.32
4	331.28	19.04	328.96	4.58	339.68	15.31
5	335.61	14.09	324.11	5.96	348.57	13.29
6	335.67	26.95	323.69	5.08	363.51	18.87
7	334.86	27.65	320.13	5.87	393.3	16.47
8	336.75	31.79	333.79	11.01	363.38	20.65

CHAPTER IV

CONCLUSION

Finding renewable and cost-effective starting materials for polymers is of vital interest. In this work, the utility of sunflower as starting raw material was investigated in the synthesis of a more reactive polyol, for rigid foam production. The presence of unsaturated bonds in the sunflower oil structure was advantageous for an epoxidation and ring-opening reaction with methanol for the generation of a bio-based polyol. After confirmatory tests like hydroxyl number (180 mg KOH/g), the sunflower polyol was deemed suitable for the foam reaction. To reduce the flammability associated with rigid polyurethane foams, varying amounts of non-halogenated flame retardants like AHP, DMMP, and EG were incorporated into this work.

The apparent density of the synthesized foams fell in a 30-55 kg/m^3 range which is suitable for insulation and other commercial applications. From the SEM imaging, it was observed that increasing the concentration of AHP and DMMP increased the cell sizes and slightly reduced the mechanical properties of the sunflower-based foams. However, very few changes were observed when high loadings of EG were tested due to its good compatibility with the sunflower polyol. Irrespective of some variations in the analysis of the work, most of the foams maintained their mechanical properties, with closed cell contents greater than 90%, compressive strength greater than 160 kN/m^{2,} and uniform cell sizes. In addition, the burning time of the foams reduced significantly from 79 seconds in the virgin foams, to as low as 5 seconds in AHP-5 (13.61 wt.% of AHP), 2 seconds in DMMP-5 (13.61 wt.% of DMMP), and 6.5 seconds in EG-5 (13.61 wt.% of EG). In summary, sunflower oil was a suitable raw material in the synthesis of high flame-retardant rigid polyurethane foams.

FUTURE SUGGESTIONS

1. Investigate other conversion routes such as thiol-ene reaction and compare their yield and polyol characteristics with that generated from epoxidation and ring - opening.
2. Explore the mechanism of the synergistic relationship between the selected flame retardants (AHP, DMMP, and EG).
3. Evaluate the volatiles generated from the horizontal burning and TGA analysis of the sunflower-based foams.
4. Probe the scalability of sunflower-based foams and study their product life cycle including recycling.
5. Compare the properties of sunflower-based rigid foams to other bio-based polyurethane foams.

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