Spring 4-19-2021

MELAMINE DERIVATIVES AS HIGHLY FLAME RETARDANT ADDITIVES FOR BIO-BASED RIGID POLYURETHANE FOAMS

Niloofar Arastehnejad
Pittsburg State University, narastehnejad@gus.pittstate.edu

Recommended Citation

Arastehnejad, Niloofar, "MELAMINE DERIVATIVES AS HIGHLY FLAME RETARDANT ADDITIVES FOR BIO-BASED RIGID POLYURETHANE FOAMS" (2021). *Electronic Theses & Dissertations*. 362.
https://digitalcommons.pittstate.edu/etd/362

MELAMINE DERIVATIVES AS HIGHLY FLAME RETARDANT ADDITIVES FOR BIO-BASED RIGID POLYURETHANE FOAMS

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

Niloofar Arastehnejad

Pittsburg State University

Pittsburg, Kansas

May, 2021

MELAMINE DERIVATIVES AS HIGHLY FLAME RETARDANT ADDITIVES FOR BIO-BASED RIGID POLYURETHANE FOAMS

Niloofar Arastehnejad

APPROVED:

Thesis Advisor	Dr. Ram K. Gupta, Department of Chemistry
Committee Member	Dr. Khamis Siam, Department of Chemistry
Committee Member	Dr. Charles Neef, Department of Chemistry
Committee Member	Dr. John Franklin, Department of English and Modern Languages

ACKNOWLEDGEMENTS

I would like to express my deepest appreciation to my advisor Dr. Ram K. Gupta for his invaluable supervision and unparalleled support and tutelage during my Master of Science degree. I’m extremely grateful to him for all his assistance and unfailing encouragement in every step of the process. Dr. Gupta is an endless source of ideas, and his exceptional passion for science will encourage me to learn until the lap of the grave.

I would like to extend my sincere thanks to Dr. Siam, Dr. Neef, and Dr. Franklin for reviewing my thesis and giving me helpful suggestions and critical reviews of my thesis. It was a great honor for me that they were willing to serve as Committee members for my thesis. I would also like to extend my deepest gratitude to Dr. Bobby Winters, Department Chair, for providing me a Graduate Research Assistantship position. I am sincerely grateful for the work of Dr. Zepernick, the director of the Pittsburg State University Writing Center, for her insightful comments and valuable guidance during the editing of my master's thesis. Her patience during corrections of grammatical errors, her unyielding professionalism, and her attention to detail deserve the utmost praise and was immensely appreciated. Many thanks, also to the Kansas Polymer Research Center and also to Pittsburg State University for supporting me while I completed this work.

Thanks are extended to my group members, who particularly helped me with practical suggestions and useful advice during this project. They also made my lab life very enjoyable with their enthusiasm and energy. I wish them all successful careers.

Special thanks to my best friends Riley Zerr and Shane Mann for their emotional support and for being positive every day of my life. Their support made me stronger as I conquered many difficulties.

I must not forget to express my deepest love to my family in Iran. The love, affection, and support provided by my whole family constantly motivated me to reach this stage. My deep thanks to my mother and my brother, for without their enduring support and advice I would not have been able to do this. They are my greatest reason to live well and to work hard, and I would like to dedicate this thesis to my family.

MELAMINE DERIVATIVES AS HIGHLY FLAME RETARDANT ADDITIVES FOR BIO-BASED RIGID POLYURETHANE FOAMS

An Abstract of the Thesis by
Niloofar Arastehnejad

Rigid foams, which are mainly used in construction, refrigerators, automotive industries are one of the important types of polyurethanes with great potential in insulation and energy efficiency. Unfortunately, rigid polyurethane foams are highly flammable and catch fire in a short amount of time as well as spread the flame quickly. Hence, rigid foams are considered hazardous materials due to life-threatening situations and environmental issues.

To counter that, nitrogen-based compounds as non-halogenated flame retardants are an effective, low-cost, and eco-friendly option. It has been shown that melamine derivates as nitrogen-based flame retardants are the proper choice to be incorporated with rigid polyurethane foams. Melamine and its derivates improve the thermal stability of the rigid foam, as well as providing effective performance in avoiding fire propagation.

The objective of this thesis is to implement greener materials into the synthesis of bio-polyol used for the preparation of rigid polyurethane foams. Myrcene is a natural alkene found in bay leaves and hops, that is functionalized with hydroxyl groups through thiol-ene reaction to obtain a bio-polyol. The physicomechanical and thermal properties of bio-based rigid polyurethane foam containing different amounts of melamine (ME), melamine cyanurate (MC), and melamine phosphate (MP) were studied. In the burning test, the neat foam was burnt for 75 seconds with 40% weight loss. In comparison to neat foam, time of self-extinguishment and weight loss decreased by increasing flame retardants. Also, MC and MP-based foams showed better thermal stability than ME-based foams. The addition of MC and MP showed burning times decreased to 21 and 11 seconds, respectively, while the values of weight loss also reduced to 4% and 3%, respectively. The presence of melamine-based flame retardants showed a short burning time as well as a low amount of smoke. This research indicates that a bio-based polyurethane foam could be synthesized successfully with satisfactory melamine-based flame retardant properties. As a result, using eco-friendly materials such as myrcene and nitrogen-based flame retardants offered an effective option to enhance the physicomechanical and thermal stability of rigid polyurethane foams.

TABLE OF CONTENTS

CHAPTER PAGE

LIST OF TABLES

TABLE PAGE

LIST OF FIGURES

Chapter I

INTRODUCTION

1.1 Overview of polyurethane

Polyurethanes belong to a specific group of polymers with unique characteristics such as light weight, superior resilience, and absorption resistance. They are used extensively in many applications such as foams, elastomers, coating, paint, etc. The creation of isocyanates by Wurtz brought about the invention of polyurethane in 1937 by Otto Bayer *(1)*. The different types of polyurethanes in use today have all have been developed from the discovery of Bayer and his team. Polyurethanes were first used as a replacement for rubber throughout WWII *(2)*.

Typically, polyurethane is synthesized via a reaction between a polyol and an isocyanate which the urethane group contains as the main repeating unit of its structure. The properties of polyurethanes are dependent on the types of polyol, isocyanate, and other additives. Also, the characteristics of the molecular structure affect the qualities of the product. Today, polyurethanes are considered as one of the most versatile class of polymers in the world. Polyurethanes can combine the toughness and durability of metals along with the flexibility and resistance of rubber to produce an appropriate replacement for metals, rubber, or plastic in different engineered productions *(3)*. Due to their excellent properties, polyurethanes have been broadly used in construction, insulations, automotive manufacturing, biomedical applications, and other industries *(4)*.

The production of polyurethane is a significant portion of the total annual plastic production. Global polyurethane's production was valued at 20.5 Mt in 2015 and exhibited a moderate growth rate till 2020. It is predicted world production of polyurethane will reach ~24.2 Mt in the next five years. Because they are very demanded in construction, packaging, and automotive industries *(5)*, the polyurethane's industry is steadily growing due to the rapid rate of development in thermal insulation, and civil engineering.

1.2 Chemistry of polyurethanes

In general, polyurethane is synthesized via a reaction between a polyol and an isocyanate molecule as shown in **Figure 1**. This reaction is a step growth polymerization. The term "polyurethane" is associated with the forming of urethane linkages in the reaction. Isocyanate can react with active hydrogens in alcohol, amine, water, and carboxylic acid compounds. In **Figure 2**, the reaction between isocyanate and water results in the expansion and generation of carbamic acid with the liberation of carbon dioxide. The unstable carbamic acid forms primary amine, which reacts with isocyanate iteratively to make disubstituted urea. Similar to the reaction between alcohol and isocyanate, this reaction is exothermic *(6)*.

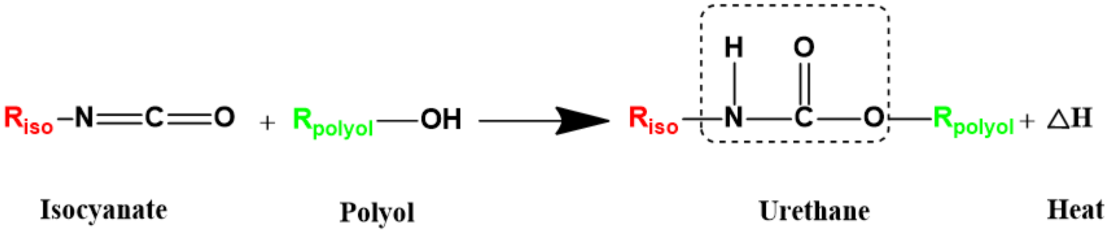


Figure 1. Urethane production via isocyanate and alcohol. Reproduced with permission from reference 6. Copyright 2018, MDPI. The article was printed under a CC-BY license.

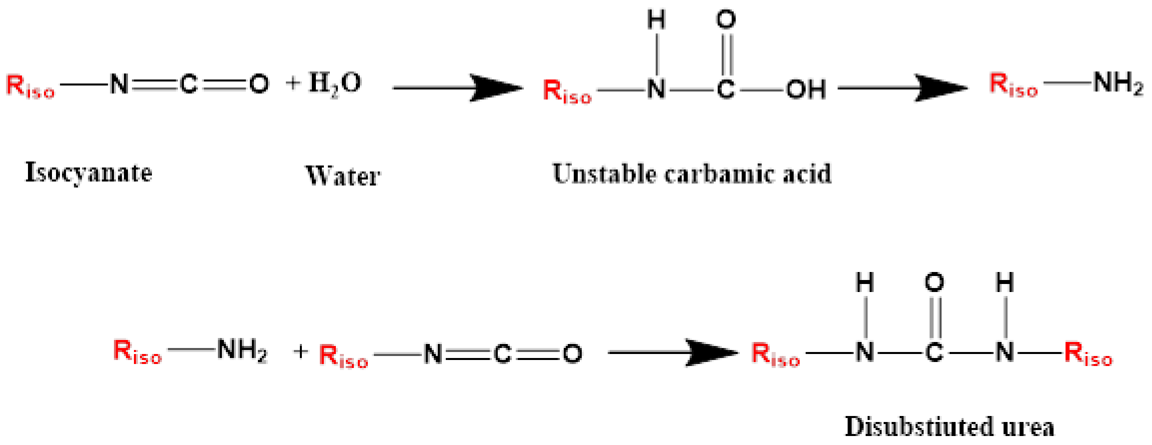


Figure 2. Urea production via isocyanate and water. Reproduced with permission from reference 6. Copyright 2018, MDPI. The article was printed under a CC-BY license.

Polyurethane has a segmented structure where a soft segment is related to polyol and a hard segment is formed from isocyanates. The molecular weight and length of the molecules affect the class of polyurethane. Polyols are often used as mixtures of diol molecules that have the same nature but different molecular weights and number of functionalities. Hence, it is important to find the average number of polyol functionalities. For example, rigid polyurethane requires low molecular weights with short length segments that have a higher amount of cross-linking, while flexible foam requires long segments with high molecular weights of polyols *(4)*.

1.3 Classification of polyurethanes

Due to the wide versatility of polyurethanes, it is not easy to categorize them based on name *(7)*. Instead, the best way to describe and classify all the formats is based on the tree diagram as shown in **Figure 3**.

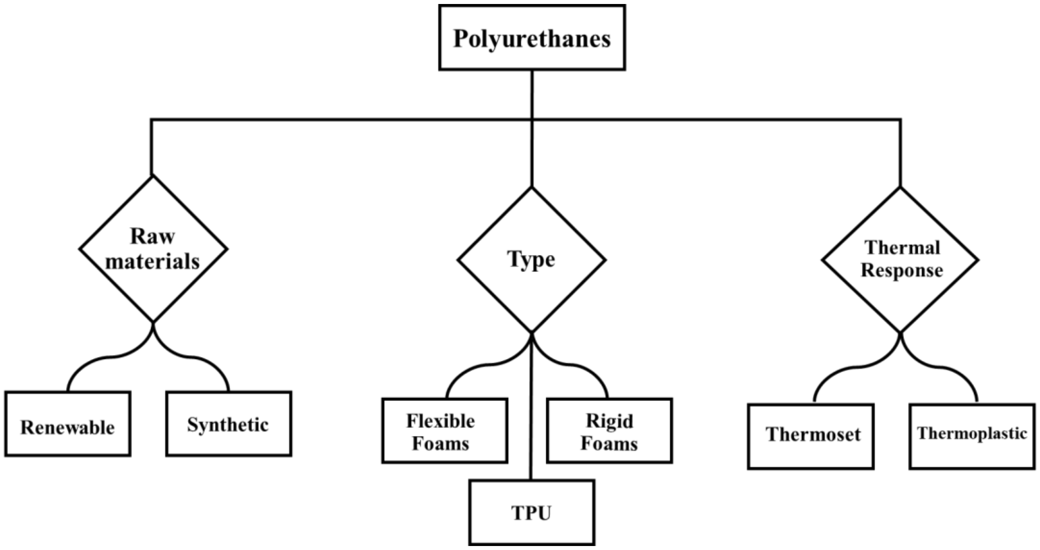


Figure 3. Classification of polyurethane.

1.3.1 Raw materials

The polyurethane industry is dependent on petroleum-based feedstocks. Much recent work has been done to develop alternative, renewable sources instead of synthetic materials. Although isocyanate has not yet been produced from bio-based resources, attempts to formulate bio-mass polyols have been successful. During recent decades, the demand for non-petroleum-based materials has increased due to government policies, substantial concerns about environmental issues, and low cost. Different renewable feedstocks have been explored for biobased polyol productions, such as fatty acids, vegetable oils, and protein-based resources *(8)*.

1.3.2 Types of polyurethanes

A large variety of polyurethane applications is related to the composition and the type of its components in the polymerization procedure. As shown in **Table 1**, the spectrum of polyurethanes includes rigid foams, flexible foams, elastomers, coatings, and adhesives. Approximately 68% of total polyurethane consumption is in the form of foams *(9)*.

Table 1. Polyurethane applications. Reproduced with permission from reference 9. Copyright 2020, Elsevier.

Categories	Application	Production
Flexible foams	Vehicle, seating, matresses	36%
Rigid foams	Household applications, insulation board, packaging	32%
Elastomers	Medical applications, glues	8%
Adhesives & sealant	Casting, sealant	6%
Coating	Vehicle (bumpers, side panels)	14%
Binder	Assembling of wood broads, rubber, or elastomer flooring surfaces	4%

1.3.2.1 Rigid polyurethane foams

About 32% of the total polyurethane production is used for rigid polyurethane foams due to its efficient performance in thermal insulation, high mechanical properties, and low density *(9)*. The superior insulating and stable characteristics of rigid foams are advantageous in the construction industry. Rigid foams have shown remarkable performance in decreasing energy costs in residential and commercial applications. Therefore, rigid polyurethane foam insulation can be used in the construction industry and in refrigeration, and tank insulation *(10)*. According to a report by the U.S. Department of Energy about 48% of all energy consumed in U.S. homes is related to the cooling and heating of homes *(4)*.

1.3.2.2 Thermoplastic polyurethane (TPU)

Thermoplastic polyurethane (TPU) is an extremely versatile elastomer that reveals a broad combination of physical properties and processing flexibility. TPU materials provide enormous physical properties such as high impact resistance, high absorption, high shear strength, etc. TPU materials can be processed from the molten condition by extrusion, injection, blow and compression molding equipment. TPU materials are a bridge between plastics and rubbers that offer both flexibility and elasticity properties. They have strong interchain forces such as hydrogen bonding, van der Waals forces, and chain entanglements. Due to all these properties, TPU materials are useful in many demanding applications such as automotive, construction, and footwear *(11)*.

1.3.2.3 Flexible polyurethane foams

As yet, there is no material to compete with flexible polyurethane foam that can match its wide range of properties such as light weight, good surface elasticity, durability, etc *(12)*. Flexible polyurethane foams have become widely used in the last decade due to the wide range of applications in commercial and consumer products, such as furniture, mattresses, automotive interiors, cushions, packaging, etc. Some physical properties may be selected in flexible foams in terms of durability, toughness, density, tearing resistance, and surface elasticity. In addition, new approaches in formulation and processing techniques will probably lead to further development of materials with improved properties. As a class, flexible foams have the following properties: 1) large diversity of foam categories, 2) suitability for long-term use, 3) open-cell and breathability, and 4) methodical manufacturing process for molded and slab foams *(13)*. However, they are highly flammable and release a large volume of smoke and toxic gases, including CO and HCN, during combustion due to the open cell structure and its low density. Therefore, it is required to use flame retardants for their use in a variety of applications *(4) (12)*.

1.3.3 Thermal response

Polyurethanes can be categorized as thermoset or thermoplastic materials based on their response to thermal energy. Thermoset materials are chemically crosslinked and generated network structures. Thermoset elastomers, which are molded using casting techniques, are set when heated, so it is impossible to reshape them after initial formation. Also, they have a higher melting point and can sustain higher temperatures without loss of structural integrity *(14)*. Unlike thermosets, thermoplastic materials can be remolded without any chemical changes. They can be softened and melted by the application of heat. Thermoplastic polyurethanes can process and transform into thermoset form when crosslink bonds occur. Notably, the market demand for thermoset production is three times higher than the demand for thermoplastic materials *(15)*.

1.4 Flammability of polyurethane

The porous structure of polyurethane foams is the reason for their rapid ignition. When polyurethane foam is exposed to a source of heat, ignition occurs and various bonds are broken at different temperature ranges; after combustion, residue may remain. **Table 2** shows the temperature ranges at which different polyurethane bonds break *(16)*.

At the same time, an adequate volume of oxygen promotes the flame to combust the foam. During combustion, polyurethane foams generate flammable and inflammable gases, particulate solid, and carbonic char. Decomposition of polyurethane is an exothermic reaction, which produces a large amount of hazardous and toxic gases, including N_2, CO, HCN, CO_2, H_2O, and NO_x. Therefore, the flammability of polyurethane foams is a major issue, which can be decreased by the addition of flame retardants. If a polyurethane foam contains flame retardants, it may decrease the ability to ignite or stop the spread of fire *(17)*.

Table 2. Dissociation of polyurethane foam linkages at different temperatures. Reproduced with permission from reference 16. Copyright 2008, John Wiley and Sons.

Linkage	Dissociation Temp (°C)
Allophanate	100-120
Biuret	115-125
Urea	160-200
Urethane	180-200
Disubstituted urea	235-250
Carbodiimide	250-280
Isocyanate	270-300

Typically, there are three mechanisms for reducing combustibility. First, additive flame retardants are merged into the foam ingredients without binds chemically. Additive flame retardants act as following: (a) emit gases that displace oxygen for a flame to burn, (b) form a char layer to protect the surface of foam, or (c) act in a combination of the foregoing. Second, reactive flame retardants are bonded chemically into polyurethane backbone structure. Third, the foams can be coated with fire-resistant materials *(16)*.

1.5 What are flame retardants ?

Flame retardants are chemicals that can be incorporated into other materials in order to reduce or delay flame propagation. Flame retardant agents cannot fully protect polymers from fire, but polymers that include flame retardants can be much more challenging and difficult to burn. Sometimes, flame retardants may be self-extinguishing when exposed to an external source of flame, but the polymer may smolder and flare up to start ignition.

Therefore, flame retardants materials help to slow down and retard the burning rate or to self-extinguish the flame *(18)*.

1.6 General mechanism of flame retardants

Thermal degradation and burning of polymers occur in different stages. When a polymer is exposed to an ignition source, it is pyrolyzed and produces combustible products. Generally, the combustion process consists of two stages. In the first stage, combustible material is heated in the presence of oxygen until combustion occurs. In the second stage, heat is released into the environment, which can promote further combustion in the presence of available fuel. The flammability of a polymer can be correlated to the energy necessary to heat the polymer to the point where thermal degradation occurs. Therefore, the addition of flame retardants results in a reduction of heat release *(19)*.

The mechanism of flame retardants can be divided into chemical and physical action. The chemical reactions are categorized as gas-phase and condensed phase *(19)*. The mechanism of the gas-phase shows that the amount of thermal emission and flame propagation is reduced by increasing the mass of flame retardants. The principal mechanism of flame retardation at the gas-phase is diluting by means of a shield gas and quenching free-radicals. In the dilution process, a huge volume of nonflammable gases is vaporized in order to dilute combustible gases and oxygen. This is an endothermic process and non-flammable gases like water (steam) and carbon dioxide are generated. Secondly, flame retardants break down and trap free radicals to quench atoms like H•, OH•. The termination of fire-spreading radicals is an exothermic reaction around combustion periods. Notably, the mode of action for the reduction of flame in the gas-phase relies on the form and quality of fire resistance *(20)*.

On the other hand, the mechanism of condensed phase combustion suggests that molecules in a solid or liquid state are more densely packed and more organized than molecules in a gas-state. Hence, it displays chemical interlinkages between fire resistance substances and matrix polymer *(21)*. The responsibility of condensed-phase is the creation of this fundamental interaction below the temperature of pyrolysis disintegration. There are two main modes for cooperation: as oxidative hydrogenation; and, as crosslink structures. Dehydration helps decrease the activity and concentration of oxygen in the polymer. Then, the formation of char causes interruption burning between the flame and polymer. Similarly, the presence of cross-linked structures reduces flammability by increasing the number of covalent bonds between the chains; the presence of these bonds increases the amount of energy required in order for combustion to occur. In contrast, weak and long-distance chains can decrease the level of crosslinking which decreases stability to heat *(19)*.

However, physical activity is involved in cooling, coating, and dilution *(19)*. Firstly, cooling is an endothermic reaction; additives and released water help to decrease the temperature of the base lower than necessary for supporting the ignition process. Secondly, the coating mechanism is based on the formation of a shield layer, which prevents combustion by interaction of the material with oxygen and heat. Lastly, the dilution effect can diminish the fire in both gas and solid-phase via inert material and inflammable gases *(22)*.

1.7 The benefit of non-halogenated flame retardants

There are two main groups of flame retardants: halogenated and non-halogenated. Halogenated flame retardants are created by the incorporation of bromine, fluorine, chlorine, or iodine into materials. Halogen-containing flame retardants have good characteristics for minimizing the risk of fires. The action of halogenated flame-retardant materials was highly robust; however, they were banned due to the high toxicity and environmental issues. Based on the new environmental regulations, manufacturers must use new materials with similar characteristics instead of traditional halogenated flame-retardants. Therefore, non-halogenated flame retardants have been identified as a superior additive in engineering plastics during the last decade. Halogen-free flame retardants can reduce the risk of hazard and fire when used in low concentrations in polyurethane foams. The advantages of non-halogenated flame retardants are low toxicity with effective performance in preventing fire propagation. Moreover, polymers treated with non-halogenated flame retardants can meet end-user requirements while being environmentally friendly, non-toxic, and relatively inexpensive *(23)*.

1.8 Nitrogen-based flame retardants

Due to environmental regulations, nitrogen-based materials have begun to be used as flame retardants. The main difference between nitrogen-containing and halogen-based flame retardants is that the nitrogen-based materials do not generate free-radicals or diminish the effectiveness of hindered amine light stabilizers (HLAS). Other advantages of nitrogen-based flame retardants are that they are eco-friendly, as they emit a low amount of toxic gases and smoke when burned. Therefore, nitrogenous compounds like melamine and its derivates are becoming increasingly popular. Nitrogen-containing flame retardants may proceed by liberation of inert gases within combustion, nitrogenous agents into the solid-phase condensation reaction, or gas-phase. The mechanism of nitrogen-based flame retardants is based on charring. Consequently, they are a good choice to be incorporated with thermoplastic materials because of their ability to be re-extruded multiple times without losing mechanical properties or fire resistance. Nitrogen-based materials can be used in both additive and reactive flame retardants in polyurethane foams. The use of melamine salt in the development of nitrogen-containing flame retardants like melamine phosphate, or melamine cyanurate can foster the insulating char forming. Since the presence of acid contributes to the effect of a flame retardant, the choice of a proper acid is very important for its efficiency. Hence, the thermal stability of the melamine derivates is correlated to the acid source *(24)*.

1.8.1 Melamine and its derivatives

Melamine and its derivatives are the main organic nitrogen chemicals used as additive flame retardants. Melamine (2, 4, 6-triamino-1, 3, 5 triazine) is a stable white crystalline product that contains 67% nitrogen. Melamine absorbs heat (an endothermic process) and eliminates ammonia, which acts as a flame dilution and forms condensed products such as melam, melem, and melon. These products have higher thermal stability than pure melamine due to the formation of the char layer. Melam, melem, and melon can endure heat to 350 °C, 450 °C, and 600 °C, respectively. The structures of melamine and its condensation salts are shown in **Figure 4** *(25) (26)*.

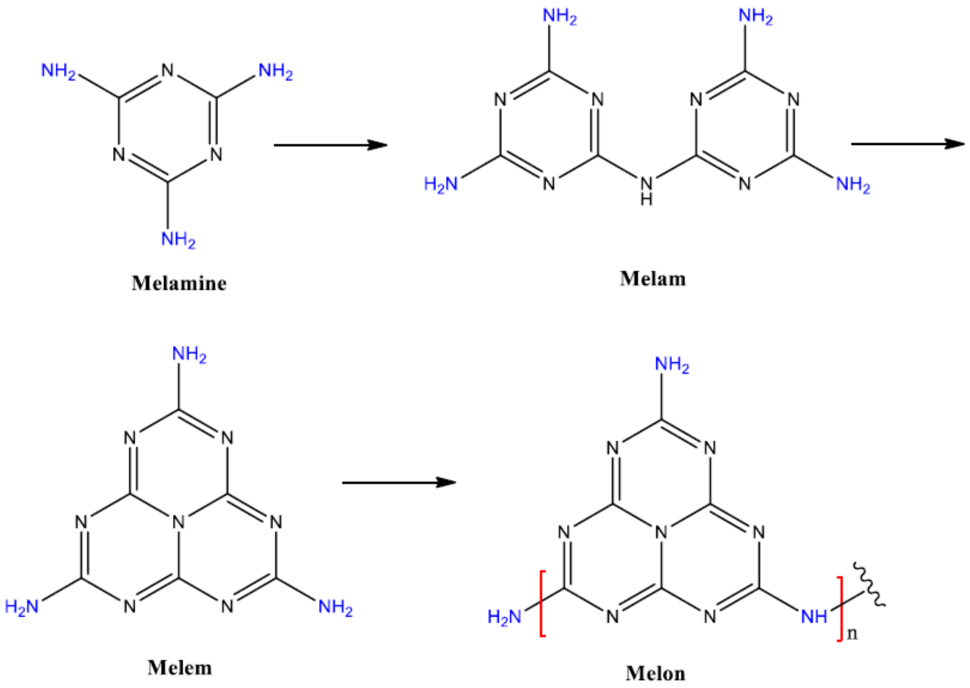


Figure 4. Structure of melamine and condensed products. Reproduced with permission from reference 26. Copyright 2014, John Wiley and Sons.

Melamine is broadly used in polyurethanes especially for foam applications. Melamine has proven to have excellent thermostability in high-density polyurethane but König et al. investigated the efficiency of heat-resistant melamine in low-density polyurethane foam *(27)*. They found that even though melamine was presented in the foam matrix, the decomposition of polyurethane and its burning temperature was not influenced in the first step. However, the temperature was raised in the next decomposition step. Therefore, when melamine concentration increases, the thermostability increases linearly. This is likely due to the heat-generation from the temporary oxidative char formation by the production of melamine condensation that causes an increase residue on the surface area. It is known that liberated carbon dioxide continually spreads with the addition of melamine, and this theory may support better effectiveness of oxidation. Moreover, the authors found that increasing melamine concentration reduces smoke density, which makes melamine a useful additive for smoke suppression. In addition, as an additive to flexible polyurethane foam, melamine’s heat absorbing qualities are ascribed to the ability of its products of sublimation or degradation to dilute oxygen and combustible gases *(28)*.

The option of derivatives is controlled under processing temperature and sensibility to hydrolysis of the matrix polymer. The incorporation of strong acids with melamine causes the creation of thermostable melamine salts. The right choice of acids impacts the efficiency of flame retardants. Notably, melamine salt contains higher thermal stability than pure melamine.

1.8.2 Melamine cyanurate

Melamine cyanurate (MCA) proved to have better fire-resistant properties due to its different modes of action and its special structure. As shown in **Figure 5**, it has a particular 2D network structure of hydrogen bonds which are connected between melamine and cyanuric acid, that enhance the thermal stability and decrease the overall volatility of MCA, further forming a proper fire resistance for flammable polymers and other substrates. It possesses a higher processing temperature of around 300 °C and experiences endothermic decomposition. It eliminates melamine and cyanuric acid and then decomposes to NH_3, CO_2, and H_2O at an elevated-temperature *(29)*. There are two different particle dimensions for MCA: micro and nano size. Therefore, decomposition temperature and thermal stability increase when the size of the MCA particle is smaller because it ensures better interaction and formation of strong hydrogen bonds between MCA and matrix polymers. MCA acts in both the condensed phase thorugh the formation of the barrier char layer to protect polymers against the flame as well as in the gas phase by releasing inert gases as shown in **Figure 6** *(30)*.

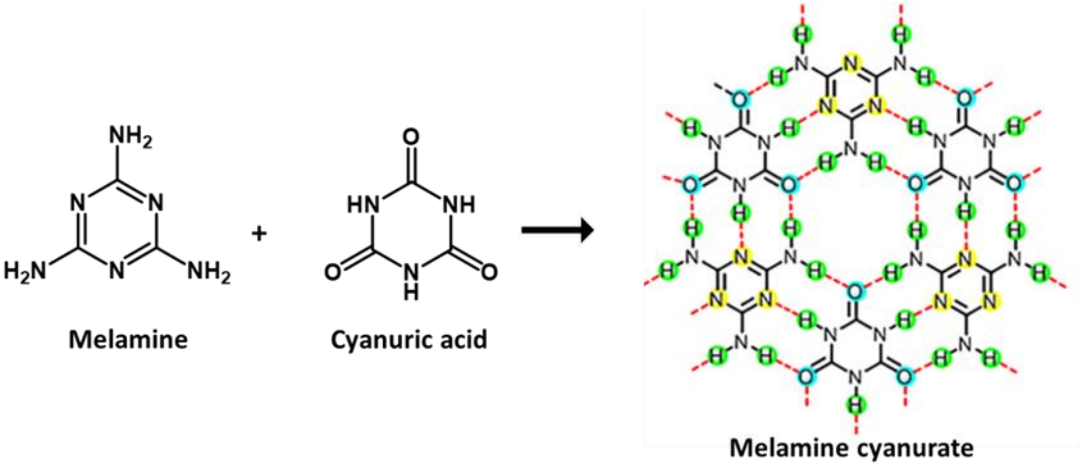


Figure 5. Structure of melamine cyanurate. Reproduced with permission from reference 29. Copyright 2018, Elsevier.

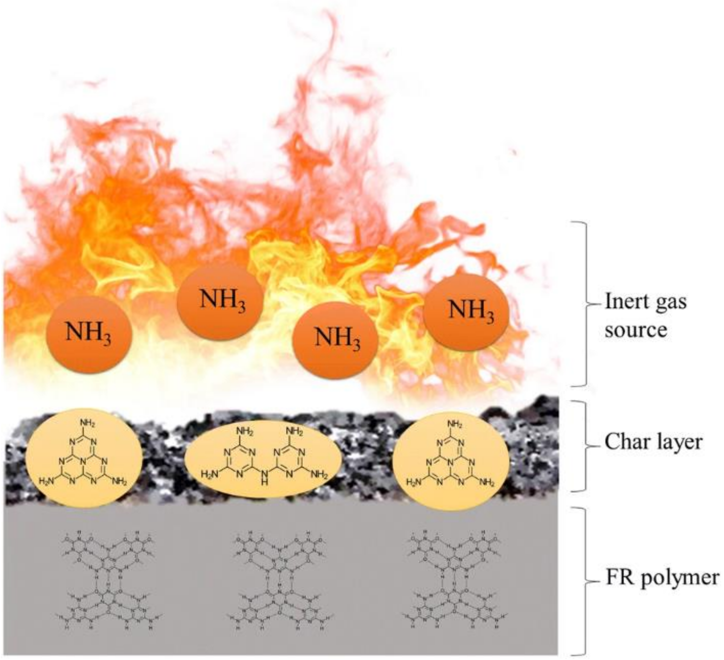


Figure 6. Mode of action of melamine cyanurate. Reproduced with permission from reference 30. Copyright 2019, Springer Nature.

MCA has been applied in many polymers, especially polyurethane, due to its excellent thermal properties. Thirumal et al. *(31)* investigated the thermal stability of flexible polyurethane foam in the presence of melamine cyanurate. They showed that when melamine cyanurate was added to polyurethane foam, the peak heat release rate (HRR) decreased due to its endothermal behavior and char formation ability. They also found that polyurethane foam with melamine cyanurate released less smoke than untreated foam and limited oxygen index (LOI) increased as expected. However, the rate of weight loss for MC and neat foams was similar which suggests that the mechanism of MC foams is mostly in a gas-phase. Modesti and his teams reported the successful thermostability of melamine cyanurate and ammonium polyphosphate (APP) in a foam *(32)*. They showed better fire-resistant behavior and better mechanical properties with a lesser volume of smoke when phosphorus was incorporated with nitrogen-based flame retardants compared to only APP foam *(32)*.

1.8.3 Melamine phosphate

Melamine phosphate is synthesized from a reaction between melamine and phosphoric acid. This salt shows better thermostability than pure melamine. Melamine phosphate can act in both condensed and gas phases during burning. Therefore, when heat is applied to melamine phosphate, phosphorus acid is released to create a dense and stabilized carbonaceous layer in the condensation phase, which results in reducing the combustibility of materials. Nitrogen bonds, which are connected to the triazine ring, may proceed to the gas-phase to protect a polymer against flame. The breakdown species of melamine phosphate is shown in **Figure 7**. When melamine phosphate is heated to 250-300 °C melamine pyrophosphate is formed and melamine is liberated. At a higher temperature around 300-330 °C, melamine polyphosphate is formed along with the liberation of phosphoric acid and melamine. Melam and ammonium polyphosphate (APP) are the outcome products from the disintegration of melamine polyphosphate between 330-410 °C. Melam as the condensation product of melamine endures higher temperatures than melamine. At temperatures over 300 °C, ammonium polyphosphate is formed via melamine polyphosphate and free ammonia, ultraphosphate, and water. The degradation process of ultraphosphate encounters limitation at over 410 °C and a stable residue is formed at approximately 650 °C *(33)*.

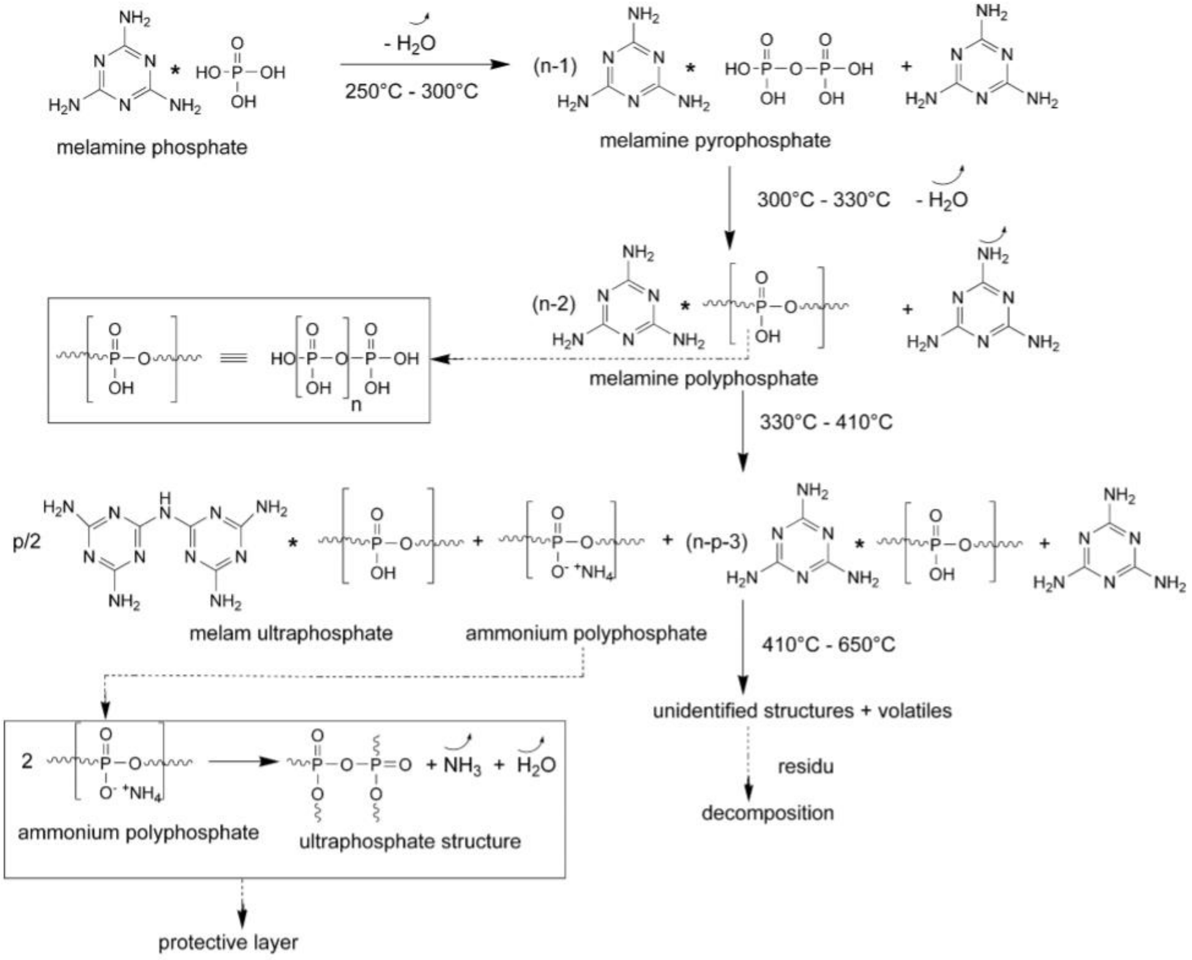


Figure 7. Thermal degradation of melamine phosphate. Reproduced with permission from reference 33. Copyright 2009, Elsevier.

Thirumal et al. *(31)* used melamine polyphosphate (MPP) as a flame retardant in rigid polyurethane foams. According to their report, MPP showed a substantial decrease in heat release due to the endothermic dissociation of melamine. Similar to melamine and melamine cyanurate, MPP also made a dense and stabilized char layer. Char protected the polymer's surface from contact with air to prevent decomposition. MPP showed better fire resistance, a low rate of smoke density, and released nonflammable gases. Although the production of smoke relies on the amount and availability of oxygen, source of fire, and properties of flammable polymers, the authors showed that adding MPP to the foam matrix resulted in a declining trend of smoke generation. Therefore, a higher concentration of MPP encourages the formation of intumescent char in the condensed-phase and can act as a shield or protective layer for polyurethane foam to hinder the progress of toxic gases and smoke *(31)*.

1.9 Bio-based polyol

Historically, polyurethanes have been produced from non-renewable petroleum-based starting materials. Today almost 95% of polyurethane foam is made from petroleum sources of polyols and isocyanates. Consumption of petroleum-based resources raises many concerns, including environmental issues, the fluctuating price of crude oil, depletion of global fossil reserves, and the product's low thermal resistance. Consequently, polyurethane industries have shown growing interest in utilizing renewable materials *(34)*.

Plant oils are found in nature and formed via a large amount of triglyceride-based in their main chain as well as saturated and/or unsaturated fatty acids, which contain more than 90% fatty acid components. Researchers have been continuously investigating to modify unsaturated fatty acids to get hydroxyl functionality in the backbone and synthesize bio-based polyol. Vegetable oils are the most advantageous of the potential renewable resources in the production of polyurethane foams. They are highly sustainable, readily available, low-priced, and eco-friendly. Hence, the consumption of natural oils in the production of bio-based polyols is increasing. Many science activities have been undertaken to develop bio-based polyols using plant oils such as cardanol, sunflower oil, castor oil, rapeseed oil, and soybean oil. The properties of polyurethane foams are strongly dependent on different kinds of polyols *(35)*. In this research, β-myrcene was used for the synthesis of the bio-based polyol.

1.9.1 β-myrcene oil

β-myrcene is a significant source of alkene natural hydrocarbon and has been used as a starting material in a variety of areas such as fragrances, cosmetics, flavors, and pharmaceuticals due to its highly reactive diene structure. Properly sourced myrcene is a water-insoluble yellowish oily liquid with a pleasant odor. Commercially available technical grade β-myrcene oil is rated at approximately 75% purity; however, myrcene can be purchased at a 90% purity grade from manufacturers that utilize more rigorous purification methods *(36)*.

β-myrcene naturally occurs in the flowers, leaves, and fruits of a number of plants, including hops, bay, lemongrass, citrus fruits, cherry, guava, carrots, celery, anise seed, ginger, cardamom, parsley, dill, and caraway *(36)*. **Table 3** offers a brief summary of some natural materials that contains β-myrcene in essential oils *(37)*.

Table 3. Percentage of myrcene in several plants. Reproduced with permission from reference 37. Copyright 1969, John Wiley and Sons.

Origin	Percentage	Origin	Percentage
Field wormwood	11.2	Jambu flower	11.8
Bay leaf, type "anise"	12.8	Juniper berry	11.0
Bay leaf, type "clove"	6.4	Juniper needle	5.5
Ylang-ylang fruit	24.7	Lemongrass	10.3
Carrot leaf	7.5	Leaf oil from Zanthoxylum ovalifolium	19.8
Wild thyme	39.1		

1.9.2 Production and utilization of β-myrcene

Although myrcene compounds occur naturally in more than 200 different plant sources, its extraction may not be economical. Therefore, industrial β-myrcene is produced via pyrolysis and dehydration of β-pinene, which is a main component of turpentine. β-myrcene is a member of the terpene family which contains a diverse group of hydrocarbons and various structures. Terpenes are commonly used in the production of fragrances, but they are also excellent solvents and dilatants in paints and varnishes, and terpenes may provide an excellent renewable source for pharmaceutical syntheses for insecticides and vitamins. Monoterpene is a versatile bio-alternative to the unsaturated hydrocarbons derived from petrochemicals. As a renewable starting material for green chemistry, myrcene is an acyclic monoterpene with a particularly reactive polyconjugated structure. Myrcene is utilized in many industrial applications including the synthesis of polyols, biodegradable surfactants, and perfumes because of its chemical durability, synthetic utility, and low sourcing costs *(37)*.

1.10 Purpose of the thesis

The purpose of this study is to improve the fire-resistant properties of rigid polyurethane foams through the use of melamine and its derivates as non-halogenated flame retardants. The impact of additive flame retardants such as melamine, melamine cyanurate, and melamine phosphate on the thermal stability, physicomechanical, cell morphology, and flame retardancy properties of rigid polyurethane foams were investigated. Additionally, a novel myrcene oil-based polyol was synthesized in a single step at room temperature using a facile thiol-ene reaction. The obtained polyol was characterized via hydroxyl value, viscosity, FT-IR, and GPC to confirm the synthesis successfully occurred. The prepared polyol was used to synthesize bio-based rigid polyurethane foam.

Chapter II

MATERIALS AND EXPERIMENTS

2.1 Materials

β-myrcene oil and 2-mercaptoethanol (2-ME) (99%) were purchased from Sigma-Aldrich and Acros Organic (Pittsburgh, PA, USA), respectively. Jeffol-522 and Rubinate M isocyanate (methylene diphenyl diisocyanate) were donated from Huntsman (The Woodlands, TX, USA). The catalysts NIAX A-1, DABCO T-12 (> 95%) were obtained from Air Products (Allentown, PA, USA), and Tegostab B-8404 as a silicon surfactant was purchased from Evonik, USA, and 2-hydroxy-2-methyl propiophenone was obtained from Sigma-Aldrich, (St. Louis, MO, USA). Melamine and melamine cyanurate as flame retardants were ordered from Sigma-Aldrich, (St. Louis, MO, USA) and (JLS Chemical Inc., Pomona, California, USA), respectively, while o-phosphoric acid, 85% was purchased from Fisher Chemical (Hampton, NH, USA).

2.2 Synthesis of myrcene oil-based polyol

Trifunctional polyol was synthesized via a UV catalyzed “click” reaction between myrcene and 2-mercaptoethanol at a mole ratio of 1:3 respectively. As a photoinitiator, 2.0 wt./wt. % of 2-hydroxy-2-methyl propiophenone was added. The reaction vessel was irradiated with UV light at a wavelength of approximately 365 nm using a UVP Blak-Ray™ UV Benchtop Lamp. The reaction was carried out at room temperature for 8 hours under stirring using a magnetic stir bar as illustrated in **Figure 8**. Purification of the desired polyol was achieved via the use of a high vacuum rotary evaporator in order to remove unreacted 2-ME. **Figure 9** details the complete thiol-ene reaction between myrcene and 2-mercaptoethanol.

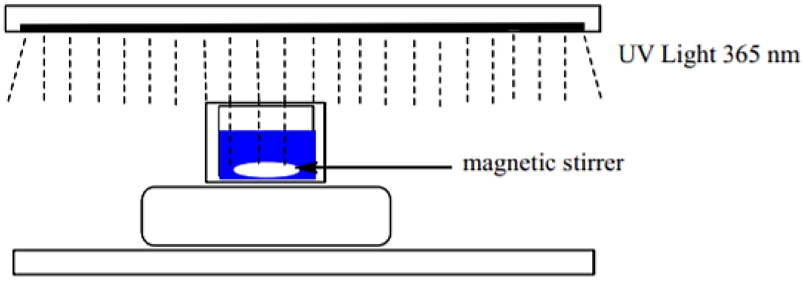


Figure 8. Synthesis of myrcene based bio-polyol by thiol-ene reaction. Reproduced with permission from reference 38. Copyright 2015, Elsevier.

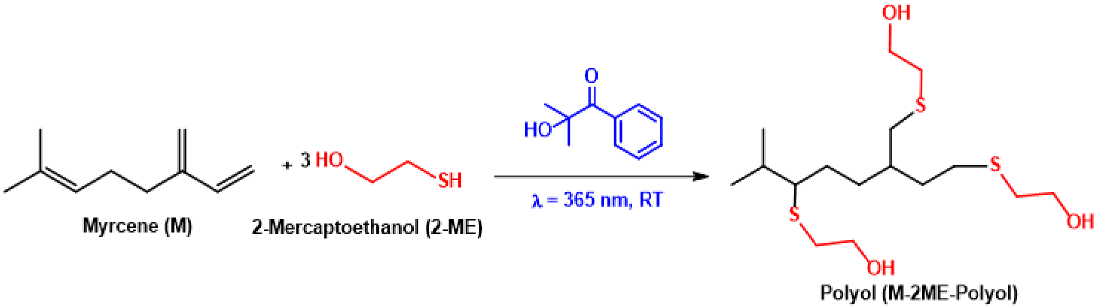
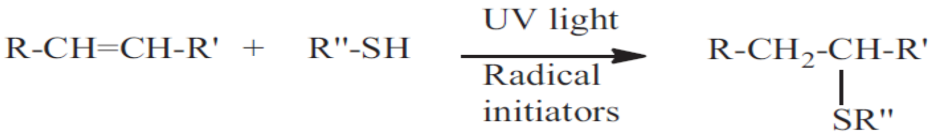


Figure 9. Chemical reactions of the synthesized myrcene-2ME-Polyol

2.3 Mechanism of thiol-ene reaction

Thiol-ene reaction occurs between an equimolar ratio of thiol functional groups (S-H) and carbon-carbon double bond to form thioether (C-S). This reaction is characterized by high reaction rates, high yielding, and without side products. Thiol-ene reaction occurs under UV irradiation in the presence of photoinitiators. The reaction initiates with a suitable photoinitiator, which is able to generate free radicals by radiation of UV light with a wavelength between 200-400 nm to start the photochemical reactions *(38)*. Thiols functional groups can be added to double bonds, like those found in myrcene, in the presence of UV light and a photoinitiator via the generalized free radical thiol-ene addition reaction scheme shown in **Figure 10** and **Figure 11**.

The thiol-ene reaction is often used for chain-growth polymerization, although not in this case, and contains four principal steps: 1) The thiol functional group in 2-ME undergoes a proton dissociation when exposed to UV light and a photoinitiator; 2) This reaction generates a highly reactive alkylthiyl radical (RS*) active center; 3) Propagation occurs as the alkylthiyl radicals add to unsaturated carbon-carbon double bonds sites, subsequently forming a new carbon-centered free-radical intermediate; and 4) New forward reactions continue until the radical terminates with either a secondary thiol functional groups by proton abstraction, making yet another thiyl radical, or an adjacent radical center by radical recombination *(38)*.



$$\text{R-CH=CH-R'} + \text{R''-SH} \xrightarrow[\text{Radical initiators}]{\text{UV light}} \text{R-CH}_2\text{-}\underset{\text{SR''}}{\underset{|}{\text{CH}}}\text{-R'}$$

Figure 10. One-step thiol-ene reaction in the presence of UV irradiation. Reproduced with permission from reference 38. Copyright 2015, Elsevier.

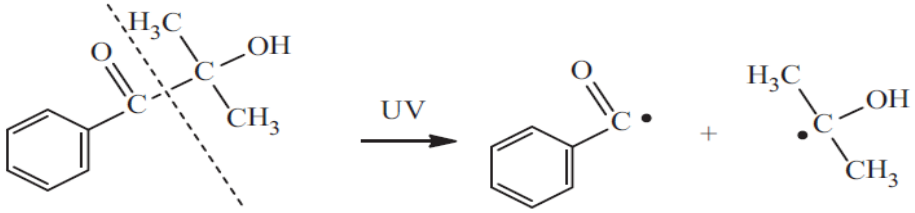


Figure 11. Structure and photochemical splitting to radicals of photoinitiator. Reproduced with permission from reference 38. Copyright 2015, Elsevier.

2.4 Synthesis of melamine phosphate

Melamine phosphate was synthesized in a one-step reaction using one mole of melamine and one mole of o-phosphoric acid. Reagents were mixed into a 500 mL vessel and stirred in an ultrasonic bath for approximately 30 minutes. The final product was filtered and then placed in the oven at 110 °C overnight for drying in **Figure 12**. Then, the synthesized melamine phosphate was ground using a mortar and pestle. Melamine phosphate contains 37.5% nitrogen and 13.8% phosphorus and displays flame retardant characteristics of both nitrogen and phosphorus-based flame retardants. The chemical reaction used to prepare melamine phosphate is shown in **Figure 13**.

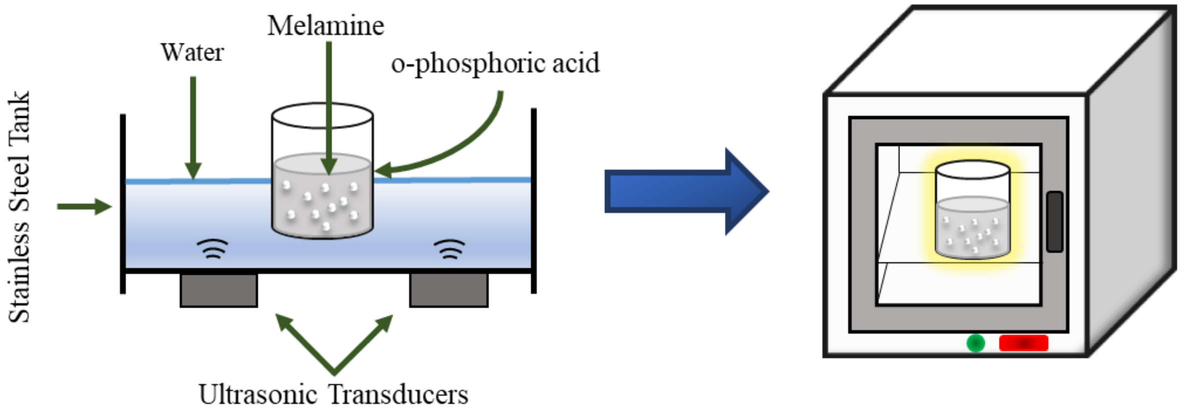


Figure 12. Schematic of mixing melamine and o-phosphoric acid in the ultrasonic bath.

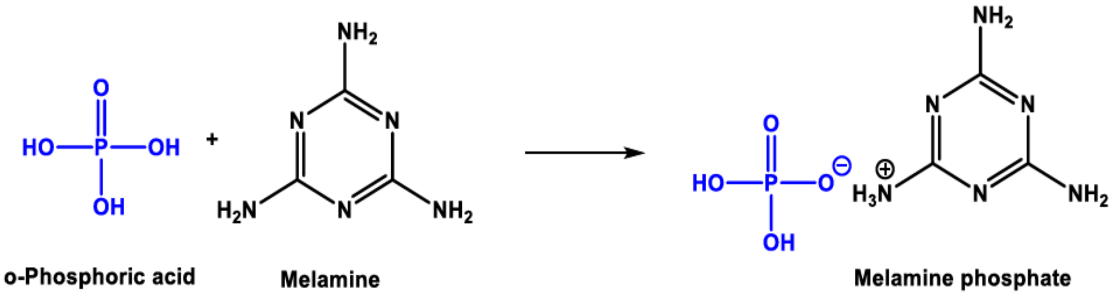


Figure 13. The chemical reaction of melamine phosphate.

Table 4. The formula for rigid polyurethane foams along with FR. (All the weights are listed in grams).

Compounds								
Jeffol-522	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
M-2ME-Polyol	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
Tegostab B-8404	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40
Niax-A1	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14
T-12	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
Water	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80
MDI	35.81	35.81	35.81	35.81	35.81	35.81	35.81	35.81
Flame Retardant	0.00	0.50	1.50	3.00	5.00	8.00	10.00	12.00
Wt. % of FR	0.00	0.86	2.55	4.98	8.03	12.27	14.88	17.34

2.5 Synthesis of rigid polyurethane foams (RPU)

All the selected materials and the detailed weight of compositions for the preparation of rigid polyurethane foams are listed in **Table 4**. First, a half replacement of commercial polyol (Jeffol 522) and myrcene-based polyol were mixed into a cup and stirred continuously (3000 rpm) for 20 seconds. Then, catalyst, surfactant, blowing agent, and flame retardant were added into the cup and stirred vigorously to mix them well. An equal molar ratio of isocyanate was added to the obtained mixture and immediately was stirred until the foaming process took place. The obtained polyurethane foams were named based on the weight of flame retardants. Foams were kept at room temperature for a week to complete the curing process and finish the growth forming.

2.6 Characterization methods for bio-polyol and RPU

The synthesized bio-polyol was analyzed with standard characterization methods and techniques as follows.

2.6.1 Hydroxyl value

Phthalic anhydride pyridine (PAP) is one of the proven and standard methods among different measuring methods for hydroxyl content. PAP is an international standard technique based on ASTM-D-4274. A hydroxyl reagent was prepared via phthalic anhydride (148 g) and imidazole (8 g) into pyridine (1000 mL). Then, a sample (0.3-0.4 mg) and the prepared hydroxyl reagent (10 mL) were added into a glass bottle by using a pipette. The mixture was capped and kept in an oven over 100 °C for 70 minutes and shaken every quarter-hour. Next, the mixture was cooled down to room temperature. Then, water (10 mL) and isopropanol (20 mL) (HPLC grade) were inserted into the cooled mixture, and the mixture was stirred for about 10 minutes. In the last step, phenolphthalein (3-5 drops) were added to the mixture and shaken vigorously, which was considered as the reference volume of the initial solution (V_0). Further, the obtained solution was slowly titrated with 1.0 N sodium hydroxide (NaOH) till the solution became pink in color. Finally, the hydroxyl value of the sample was calculated via the following equation:

$$Theoretical\ \#OH = \frac{56.11 \times N \times (V_0 - V)}{w} \qquad (mg\frac{KOH}{g})$$

Whereas; (V_0-V) is referred to the volume of before and after titration in milliliter units, and (w) is related to the weight of sample in grams.

2.6.2 Viscosity

Viscosity (η) is a classical and main method to analyze the resistance to flow. The viscosity of fluid reflects the transmission of friction force amid particles or shows the resistance to flow. The dynamic viscosity of the prepared polyol was measured using an AR 2000 dynamic stress rheometer (TA Instruments, USA) as shown in **Figure 14**. The analysis occurred at room temperature with shear stress linearly and ramp rate between 1 to 2,000 Pa. The dynamic viscosity measurement was performed using a 2° cone angle and 25 mm diameter of a plate.

Figure 14. AR 2000 dynamic stress rheometer.

2.6.3 Fourier transform infrared (FT-IR) spectroscopy

FT-IR analysis is a common analytical test to examine the chemical structures regarding the functional groups of organic and inorganic polymeric materials. FT-IR is a traditional development of infrared spectroscopy with more advantages including high accuracy of wavenumber and greater sensitivity to noise ratio. Moreover, FT-IR can be used in all three states of matter: gas, liquid, and solid. FT-IR sends infrared rays in the ranges of 10,000 to 500 cm^{-1}. All the unique features have been detected between 4000 to 500 cm^{-1} through the absorbed energy in molecules. In fact, each molecule will show an individual spectral signature, which makes the FT-IR analysis a useful instrument for the identification of chemicals. A PerkinElmer Spectrum Two^{TM} spectrophotometer (**Figure 15**) was used to check the functional groups of chemical components.

Figure 15. PerkinElmer Spectrum Two FT-IR Spectrometer.

2.6.4 Gel permeation chromatography (GPC)

Chromatography is known as the most versatile and precise method for analyzing chemicals and polymeric materials. Gel permeation chromatography is a reliable analytical technique that separates molecules in polymers on the basis of size. GPC is a size-exclusion technique and can determine significant parameters like the molecular weight distributions for a complex polymer. This analysis is carried by dissolving a sample in a solvent (mobile phase) via passing through a porous column. Then, the separation mechanism of molecules happens when a molecule has a stronger connection with the stationary phase: it takes a longer time to separate and leave it. In this experiment, the molecular weight of the polyol was measured using a 1260 Infinity HPLC with a system by Agilent (Santa Clara, CA). This instrument is shown in **Figure 16**, which is equipped with four 300 × 7.8 mm Phenogel 5 μm columns with pore sizes of 50, 102, 103, and 104 Å. Tetrahydrofuran was used as an effluent solvent, and the experiment was performed with a flow rate of 1 mL per min at 30 °C for 90 minutes.

Figure 16. Gel permission chromatography.

2.6.5 Apparent density of foams

Density is a key parameter affecting the physicomechanical properties and performances of foam. Apparent density can be calculated by the division of mass over the volume. Foam density is impacted by the internal volume of pores distributed throughout the cross-linked matrix. Here, foams were cut in a cylinder shape with a diameter and height of 45×30 mm, respectively to calculate the density of foams based on the ASTM D1622.

2.6.6 Closed-cell content of foams (CCC)

Classification of foams is dependent on the cell structure, which is either an open or closed-cell structure. Polyurethane foams are characterized by trapping air on the pore structure. In the open-cell foam, the pores are formed with irregular shaped-cells that are connected together. Because the cells are not completely encapsulated gas, water and other liquids are easily absorbed. Closed-cell foam, in contrast, is made of regular, uniform cells which prevents from a large amount of air or gas from entering. Rigid polyurethane foam is one of the most popular types of closed-cell content. In this measurement, an ultrapycnometer (Ultrafoam 1000) shown in **Figure 17**, was used to measure closed-cell content according to the ASTM D2856. This instrument contains two interconnected sections: a chamber: and, a pressure-temperature sensor. First, the volume of the empty chamber was measured by opening the valve of nitrogen gas which moved into the chamber. Then, a cylindrical sample, of known dimensions and mass, was placed into the chamber to measure closed-cell content.

Figure 17. Ultrapycnometer (Ultrafoam 1000).

2.6.7 Scanning electron microscopy (SEM) of foams

Scanning electron microscopy captured surface image with beam electrons. The sample was irradiated with a high-energy electron beam or ionized atoms on top of the surface through the releasing of electrons. Due to the interaction between the electron beam and sample, different signals are produced, which displayed the ultimate image. SEM represents that the morphological structure contained important information about the specimen surface. There are two steps to take images of the foam samples. First, the top area of foams was cut in cubical shapes with dimensions of 0.5 cm for each length. Samples were placed into a magnetron sputtering instrument to be coated with a very thin layer of gold over their surface. The gold sputtering instrument is shown in **Figure 18** (Kurt J. Lesker Company); it is essential that the instrument be used prior to capturing images to conduct the specimen surface. Second, when the top of the polyurethane foam samples was coated with a thin conductive gold layer, the images were taken by a thermo scientific phenom pure desktop SEM, which came from the Sioux company in the Netherlands.

Figure 18. Gold layer sputtering (left), thermo scientific phenom (right).

2.6.8 Compressive strength measurement of foams

Compressive strength is defined as the maximum force applied over a material's surface. The foam is compressed between the parallel plates of the instrument by a gradually applied load. The compressive strength test was analyzed by a universal electronic tensile tester named "Q test 2-tensile machine", based on the ASTM D 1621 as shown in **Figure 19**. To prepare samples for the compressive strength measurement, foams were cut in a rectangle shape, with the dimension of 50 × 50 × 25 mm^3 (width × length × height). Each sample of polyurethane foam was placed between two parallel compression platens from a larger surface. The compressive strength of foams was measured at 10% strain, before its failure.

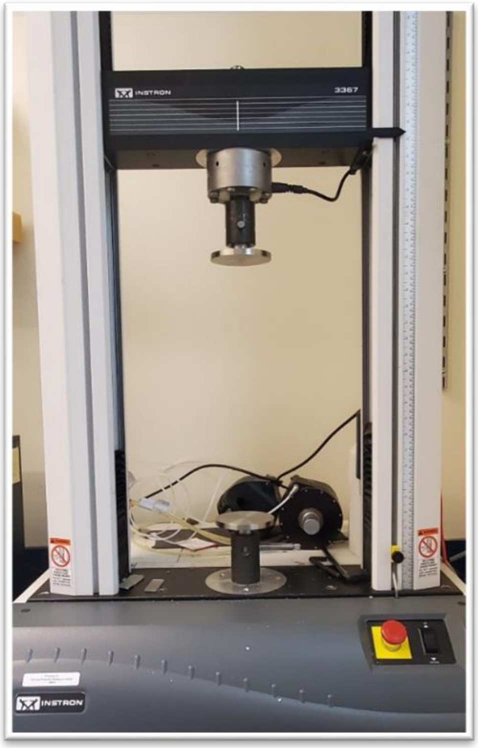


Figure 19. Q test 2-tensile machine.

2.6.9 Thermogravimetric analysis (TGA) of foams

Thermogravimetric analysis is an analytical technique to determine thermal stability of materials by heating at a constant rate, and the weight change of a sample is monitored as a function of temperature. The thermal behavior and decomposition of rigid polyurethane foams were studied by using a TA instrument (TGA Q-500) as shown in **Figure 20**. Around 8-10 mg samples were put onto the platinum pan and were heated at a ramp rate of 10 °C/min, and the temperature increased up to 800 °C under a nitrogen or air atmosphere.

Figure 20. Thermogravimetric analysis instrument.

2.6.10 Horizontal burning test of foams (HBT)

The characteristics of the horizontal burning test of rigid polyurethane foams were determined based on the ASTM D4986-98. Rectangle-shaped specimens were prepared with dimensions of 150 mm (length), 50 mm (width), and 12.5 mm (thickness). The weight of the sample was recorded, and then each foam was exposed to the direct flame for 10 seconds. The self-extinguishing time and weight loss were measured after the foam exposition. The following test was performed within a fume hood under strong ventilation in order to remove vapors generated upon decomposition, as is displayed in **Figure 21**.

Figure 21. Horizontal burning test under the fume hood.

Chapter III

RESULTS AND DISCUSSION

A bio-based polyol was synthesized from myrcene and 2- mercaptoethanol using a photoinitiator. The obtained bio-based polyol was used as an alternative to petroleum-based polyols for preparation of rigid polyurethane foams. Several tests were undertaken to confirm that the bio-based polyol was successfully synthesized and to investigate the physicomechanical and thermal stability of the produced rigid polyurethane foams.

3.1 Interpretation of polyol results

Myrcene-based polyol was analyzed to confirm the success of thiol-ene reaction. Hydroxyl value, iodine number, and viscosity of the obtained polyol were compared with myrcene in section 3.1.1. Sections 3.1.2 and 3.1.3 report the results of FT-IR and GPC, respectively.

3.1.1 Physicochemical properties of bio-polyol

Hydroxyl value shows the number of reactive OH functional groups present in the polyol. It is described as the number of milligram KOH equivalent to the number of OH functional groups. Unsaturated double bonds in myrcene are converted into polyol through reacting with thiol-containing functional groups. The thiol functional bonds are cleaved under ultraviolet radiation to promote the formation of radicals, which can reconnect to dihydrogen and disulfide *(39)*. The experimental hydroxyl value of the synthesized polyol was 466 mg KOH/g, while the theoretical hydroxyl value was 461 mg KOH/g. Since these two hydroxyl values are consistent, it indicates a successful synthesis between myrcene and 2-mercaptoethanol.

Iodine value shows the amount of unsaturation in fatty acids and vegetable oils. The iodine value reflects the number of double bonds in vegetable oils. A higher iodine value indicates a greater unsaturation and a greater tendency to oxidative transformations *(40)*. The iodine value for the prepared polyol was almost zero, which indicates all three double bonds in myrcene were consumed.

The viscosity was measured to determine the ease of flow for myrcene and polyol. The viscosity of myrcene was 0.00436 Pa.s at room temperature. However, the viscosity of the prepared polyol was 1.52 Pa.s, which indicates that the polyol has a higher molecular weight and more hydroxyl groups. This is another confirmation that synthesis was successful. Since the viscosity of polyol is low, it allows a facile synthesis of rigid polyurethane foams.

3.1.2 FT-IR for bio-polyol

FT-IR was performed to identify the chemical bonds of each molecule as displayed in **Figure 22**. The observed peaks and functional groups are shown in **Table 5** for myrcene, 2-ME, and polyol. Several peaks characteristic of myrcene such as 3089 cm^{-1}, 1632 cm^{-1}, 1595 cm^{-1}, 989 cm^{-1}, and 890 cm^{-1} are absent and the alkyl thiol functional group corresponding to 2-ME at 2551 cm^{-1} is also absent *(41) (42)*. Each wavenumber is referred to a specific functional group as shown in **Table 5**. This indicates that both functional groups were consumed and confirms a successful synthesis for the functionalization of myrcene.

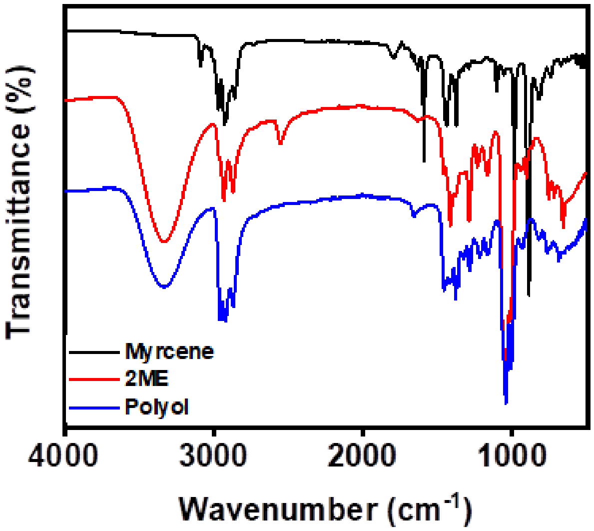


Figure 22. FT-IR for starting materials and polyol.

Table 5. The observed peaks for myrcene and 2-ME.

Functional Group	Wavenumber (cm^{-1})
Myrcene	
Alkenyl C-H stretching (w)	3089
Alkyl CH_3 & CH_2 C-H stretching (m)	2968-2858
C=C stretching (w)	1632
C=C vibration (m)	1595
Alkyl C-H bending (m)	1442
CH_3 & C-H bending (m)	1377
Monosubstituted alkenyl C-H bending (m)	989
Symmetric disubstituted alkenyl C-H bending (s)	890
2-ME	
H-bonded O-H stretching (s, broad)	3333
CH_2 C-H stretching (m)	2929 and 2872
S-H stretching (w)	2551
C-O (primary alcohol) stretching (s)	1049

3.1.3 GPC for polyol

The collected chromatograms in **Figure 23** show that both starting materials have been consumed. The starting materials, myrcene and 2-ME, have lower molecular weights which require a longer time to be consumed. Myrcene and 2-ME are eluted at 40 min and 46 min, respectively. The polyol contains higher molecular weight and displays a shorter retention time of nearly 36 min. The presence of a trimodal distribution in the polyol peak is attributed to the possibility of the formation of dimers and/or trimers. According to the other report *(43)*, there is likely a general thiol-ene side reaction that occurs in which radical carbon species ($C^{\bullet}$) may connect to another $C^{\bullet}$ in place of an $H^{\bullet}$. Therefore, a GPC test also confirmed the functionalization of myrcene via thiol-ene coupling reaction.

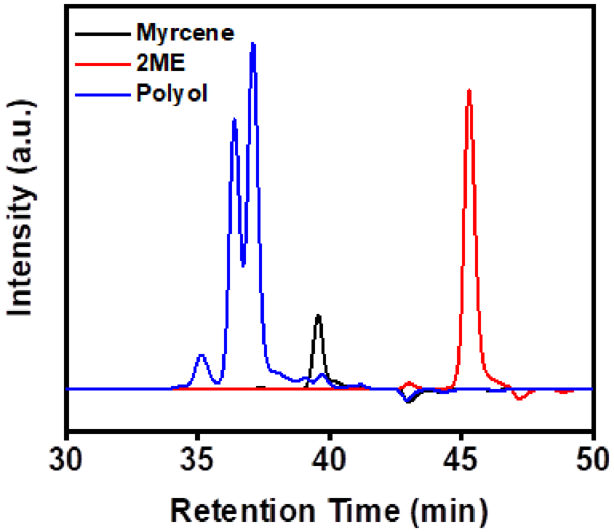


Figure 23. Gel permeation chromatograph for starting materials and polyol.

3.2 Interpretation of melamine phosphate results

After synthesis, FT-IR was used to confirm the interaction between melamine and phosphoric acid. TGA was also used to evaluate the thermal stability of the flame retardants befor being added to the foams. Further explanation is provided in sections 3.2.1 and 3.2.2.

3.2.1 FT-IR for MP

FT-IR was used to analyze the chemical bonds of the ME and the synthesized MP which are shown in **Figure 24**. According to Xiaomin Fu et al. *(44)*, the characteristic absorption peaks of ME are 3468 cm^{-1}, 3418 cm^{-1}, 3130 cm^{-1}, 1651 cm^{-1}, 1549 cm^{-1}, 1427 cm^{-1}, and 1020 cm^{-1}. The absorption bands related to phosphoric acid are 3475 cm^{-1}, 1647 cm^{-1}, 1229 cm^{-1}, and 914 cm^{-1}. Also, there are some new peaks 3364 cm^{-1}, 1515 cm^{-1}, 1408 cm^{-1}, 1241 cm^{-1}, and 954 cm^{-1} which are attributed to the chemical bonding of MP*(45)*,*(46)*. The absorption peaks related to melamine and MP are shown in **Table 6**.

Table 6. The observed peaks for melamine and MP.

Functional Group	Wavenumber (cm^{-1})
Melamine	
Asymmetrical (s) and symmetrical (m) of primary amine	3468 and 3418
Secondary amine (w)	3314-3130
NH_2 deformation(s) and 1,3,5,s-triazine ring (s)	1651 and 1549
C−N stretching (m)	1250-1020
N–H wag (primary and secondary amines)	910-665
MP	
N-H stretching (m) (Aliphatic primary amine)	3400-3300
NH_2 stretching (w) (secondary amine)	3148
C–N stretch (aromatic amines)	1640
N-H bending	1550-1510
C=N stretching	1537-1448
P-OH bending	1404 and 954
P=O bending	1250
Ring breathing type of vibration	1036-924

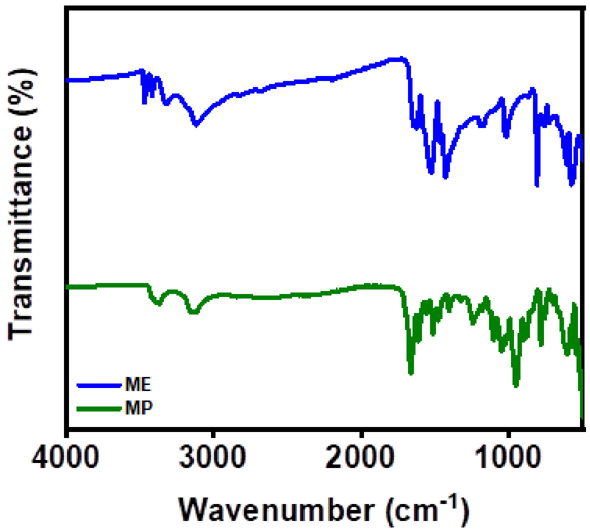


Figure 24. FT-IR for the synthesized MP.

3.2.2 TGA for MP

The thermal behavior of each flame retardant was studied as displayed in **Figure 25** and **Table 7**. The behavior of melamine (ME) is described via condensation reaction with deamination at high temperatures. The blue solid line in the TGA curve shows that the degradation of melamine starts at ~250 °C with 5 wt.% weight loss and reaches ~280 °C with 50 wt.% loss. Melamine undergoes endothermic decomposition and absorbs heat. Degradation of melamine occurs with the release of ammonia and the forming of other derivates like melam and melem with higher thermal stability (~350 °C, 450 °C), respectively. The further condensation of melamine leads to the formation of melon in a higher temperature range (~600 °C) *(47)*. Melamine cyanurate (MC) has higher thermal stability than ME due to the strong intermolecular interaction. MC undergoes an endothermic process, absorbing energy to break down the intermolecular hydrogen bonding and be converted into ME and cyanuric acid. Also, the release of ammonia continued through the entire temperature range. Degradation started at ~306 °C with 5%

weight loss and 50% weight loss was achieved at ~340 °C *(48)*. In contrast to ME and MC, MP shows the first decomposition at ~45 °C. That is likely due to the presence in the mixture of phosphoric acid, which can be liberated in the form of vaporous products. The decomposition temperature at 50% weight loss was ~452 °C and by increasing temperature, a compact layer, which is estimated around 20% residue, was formed to shield the surface of the foam against degradation. According to the research from Sandia National Laboratory *(49)*, MP has the best effectiveness for thermal resistance in comparison to ME and MC.

Table 7. Decomposition temperatures and residue for all three flame retardant additives.

ME Powder			MC Powder			MP Powder		
$T_{d5\%}$ (°C)	$T_{d50\%}$ (°C)	Residue (%)	$T_{d5\%}$ (°C)	$T_{d50\%}$ (°C)	Residue (%)	$T_{d5\%}$ (°C)	$T_{d50\%}$ (°C)	Residue (%)
247.94	279.64	0	306.29	337.30	0	44.67	452.43	20.16

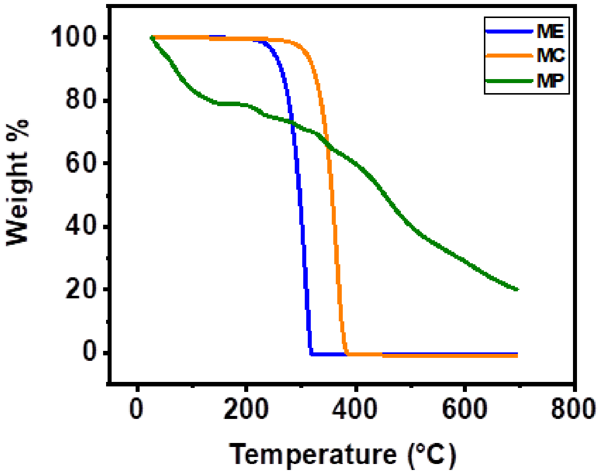


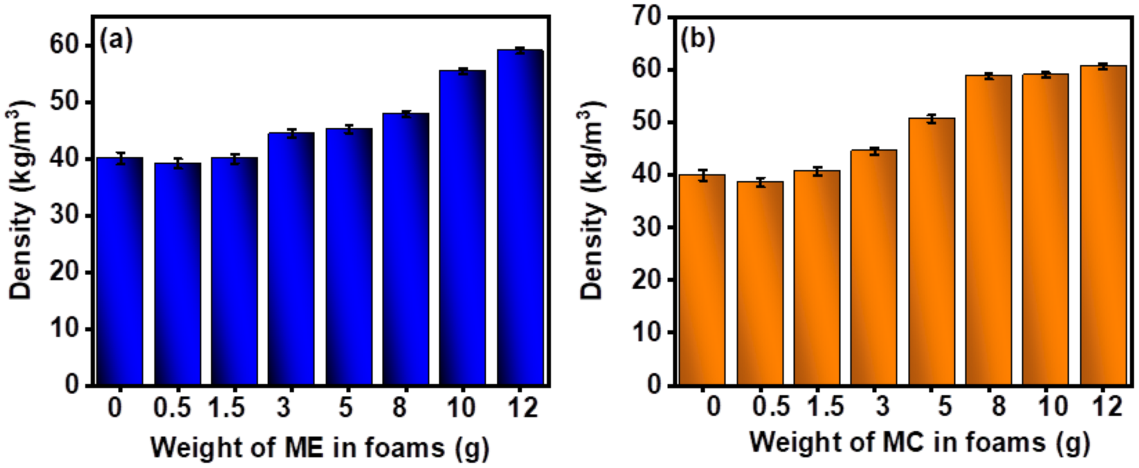
Figure 25. TGA curves for ME, MC, and MP powders under nitrogen.

3.3 Interpretation of foam results

Different experiments were carried out to study the characteristics of rigid polyurethane foam. The experimental results for the physicomechanical performance, thermal behavior, and burning time for the synthesized rigid polyurethane foams are explained in the following sections.

3.3.1 Apparent density of foams

Density may affect the mechanical and thermal properties of the rigid foams. As shown in **Figure 26**, the density of each foam increased by adding a similar amount of different FR into the foam. The higher density leads to better mechanical properties and shorter burning time. The average density of ME foams and MC foams are in the ranges of 39-58 kg/m^3 and 38-60 kg/m^3, respectively. However, MP foams become denser than ME and MC, and their average density is in the range of 37-67 kg/m^3. The gain in density is related to the reaction between phosphoric acid and melamine which causes a slow rising time during the processing of the foam. All in all, the densities of the obtained rigid polyurethane foams are in the acceptable standard range to be used in industrial applications such as construction and building *(50)*.



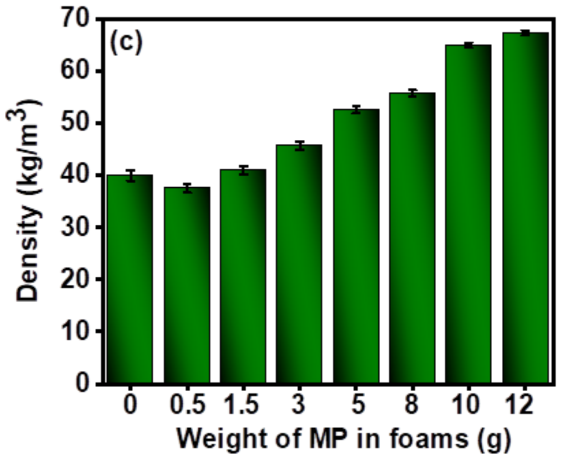


Figure 26. Apparent density of the obtained rigid PU foams with different weights of (a) ME, (b) MC, and (c) MP as flame retardants.

3.3.2 Closed-cell content

A high percentage of closed-cell content provides excellent insulating properties for rigid polyurethane foams. The closed-cell content for the rigid foams with different flame retardants was measured (**Figure 27**). Incorporating flame retardants into the foam caused a slight increase in CCC compared to the neat foam. The average ranges of closed-cell content for all three sets of foams are between 93-95%, which suggests minimal air transmission in the void sections and limited interconnection of cell structures. Hence, the presence of flame retardants provides good insulating properties by inhibiting the fast movement of heat and thermal energy between the cells. Indeed, high closed-cell content acts as a thermal barrier during the burning time which insulates foams from readily accessible oxygen *(51)*. As a result, the prepared data indicates the addition of ME, MC, and MP into the rigid polyurethane foams building high closed-cell content foams.

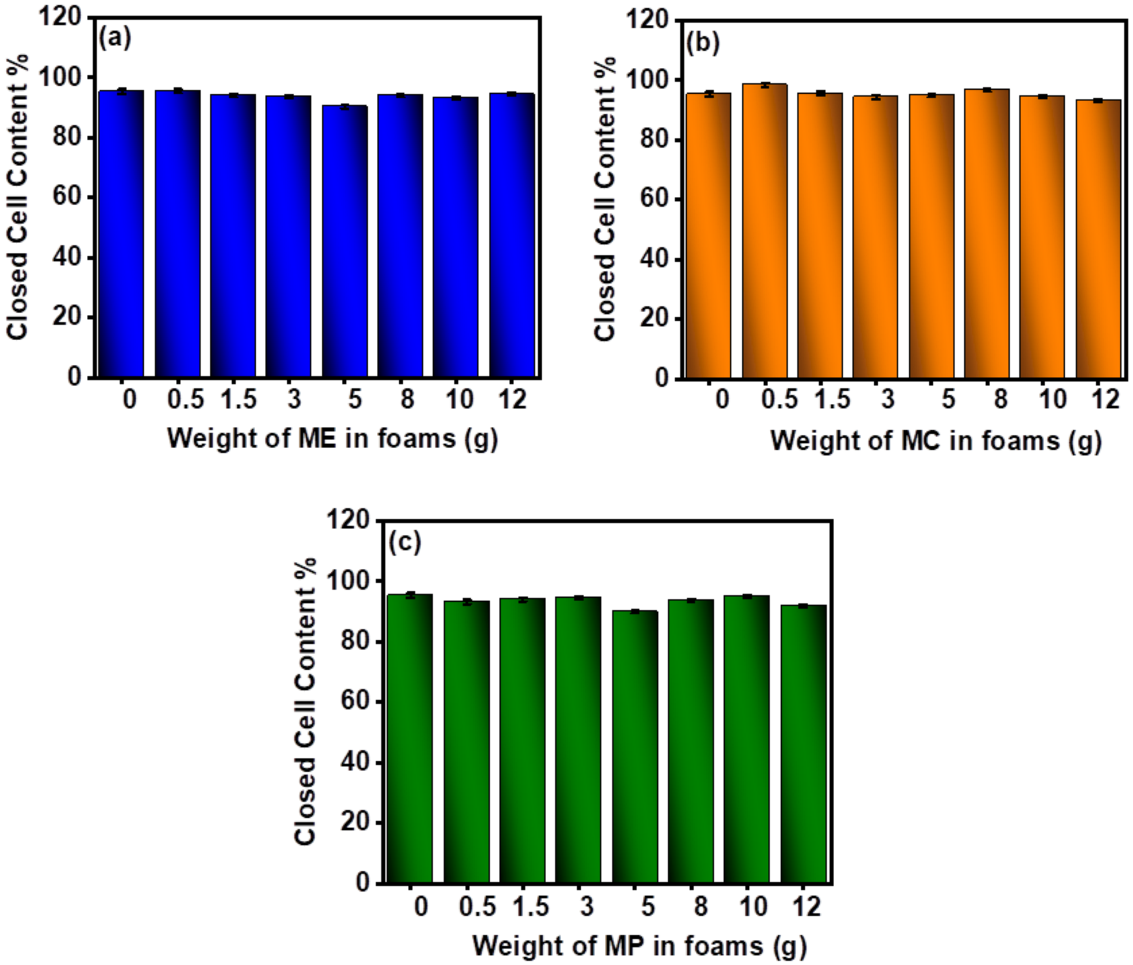
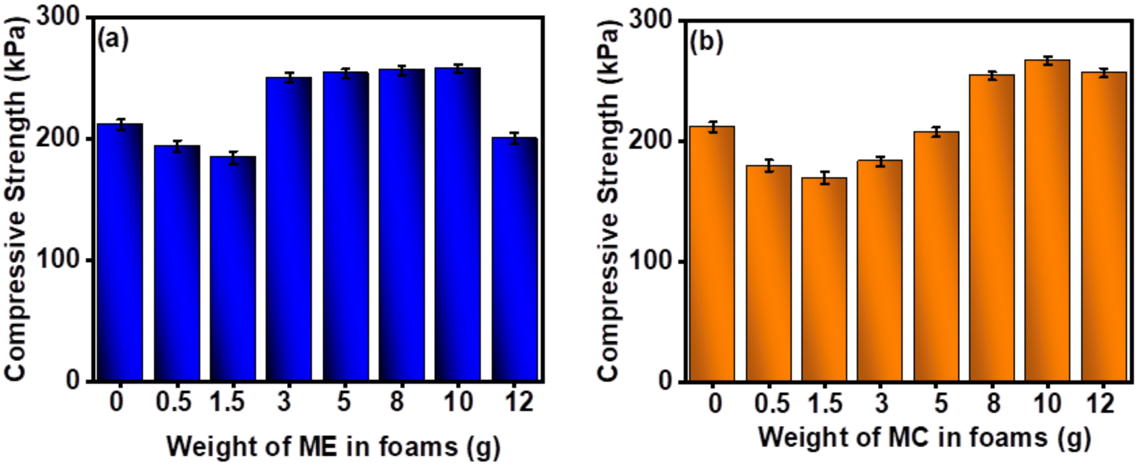


Figure 27. Closed-cell content of the obtained rigid PU foams with different weights of (a) ME, (b) MC, and (c) MP as flame retardants.

3.3.3 Compression strength measurements

Mechanical properties are among the significant parameters for the applications of rigid polyurethane foams. The specific compressive strength depends highly on the density and cell morphology of foams along with good dispersion of solid particles into the foam matrix *(52)*. **Figure 28** displays the compressive strength of rigid foams with three different flame retardants. The results of compressive strength do not show any particular trends which may be related to the incompatible interaction between solid particles and matrix. The compressive strength of the pristine foam is ~211 kPa. The addition of ME particles into the foams showed an increasing trend in compressive strength and stiffness effect *(53)*. Noticeably, the same trend was observed for MC foams as well. The overall ranges of compressive strength of ME and MC foam were 184-257 kPa and 170-267 kPa, respectively. In both cases, the compressive strength increased and reached the maximum point when 10 grams of each ME or MC particle were added. Therefore, it indicates that the presence of each solid particle (ME and MC) within the foam matrix resulting in the foam's strength increasing *(54)*. However, the highest compressive strength of MP foam containing 3 grams MP particles reached ~221 kPa. At concentrations above 3 grams, the compressive strength of MP foams declined. This may be because at higher concentrations dispersed MP particles likely possess high interaction that insufficiently provides strong support as opposed to an applied force *(55)*. The highest specific compressive strengths were 257 kPa, 267 kPa, and 221 kPa when 10 g ME, 10 g MC, or 3 g MP were added, respectively. Although the results show fluctuation, the compressive behavior of all the cases is increased to the optimal levels, and also comparable with the results of other reports.



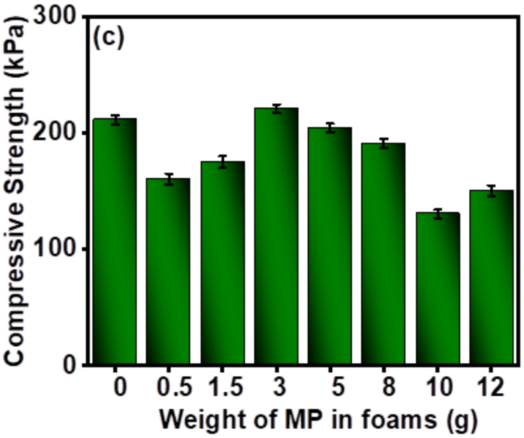
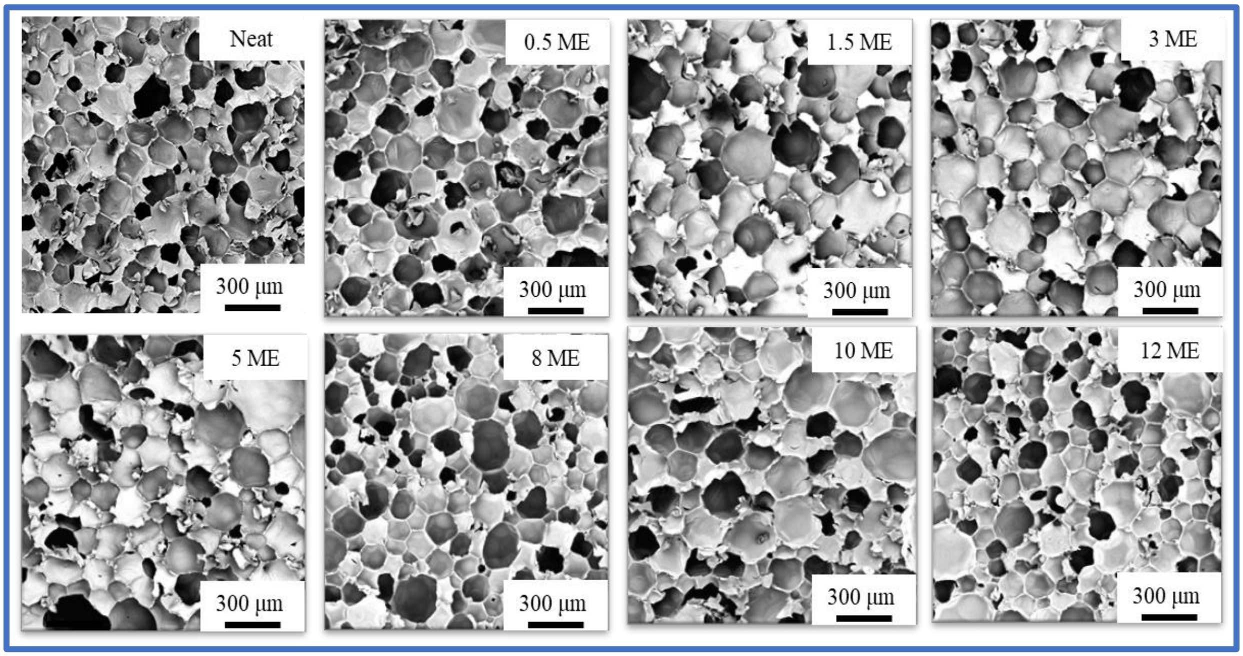


Figure 28. Compressive strength of rigid foams with different weights of (a) ME, (b) MC, and (c) MP-based flame retardants.

3.3.4 Scanning electron microscopy

The morphology of polyurethane foams is influenced by mechanical properties and density. The cell structure of foam species can explain the fluctuation in mechanical properties although the density of each set of foam was improved by increasing the amounts of flame retardants *(27)*. SEM images of all foams are shown in **Figure 29**. The average cellular size for neat foam was ~165 μm. However, the size of rigid foam cells changes when flame retardant is added. Regarding ME foam, the addition of 0.5 g and 1.5 g ME produced a slight increase in cell size. Hence, the number of cells decreased, which resulted in weak compressive strength and less support in opposition to an applied force on top of the foam's surface. On the other hand, the presence of a higher concentration of ME (over 3 grams ME) produced a gradual decrease in the average cell size of ME foam in a range of 128-140 μm approximately. Therefore, the mechanical property of ME foam increased from 3 ME to 10 ME due to the increasing number of foam cells. A strange pattern occurred at 12 ME, where not only the average cell size decreased to 120 μm, but also the compressive strength was reduced. This effect is probably related to the formation of bubbles during the foaming process. Hence, the bubbles occupied large volumes which caused a failure of the mechanical property as well as made small cells *(56)*. For the other case, the cell morphology of MC foam showed a more organized arrangement. The average cell size of MC foam first increased when 0.5 g and 1.5 g MC was added; then it decreased over the higher loading of MC particles. The average cell size reduced in the ranges of 110-135 μm, which most likely suggests a higher number of cells. Therefore, MC foam was able to provide better support under compression. This effect may be attributed to a stronger particle engagement and closer interaction within the foam matrix. As was expected for MP foam, the smallest cell size is related to the 3 MP because the highest mechanical property was observed for this one. In contrast, the other MP foam samples presented erratic and irregular cell structures. The average cell size for MP set was between 195-240 μm, which was larger than ME and MC foam samples *(57)*.



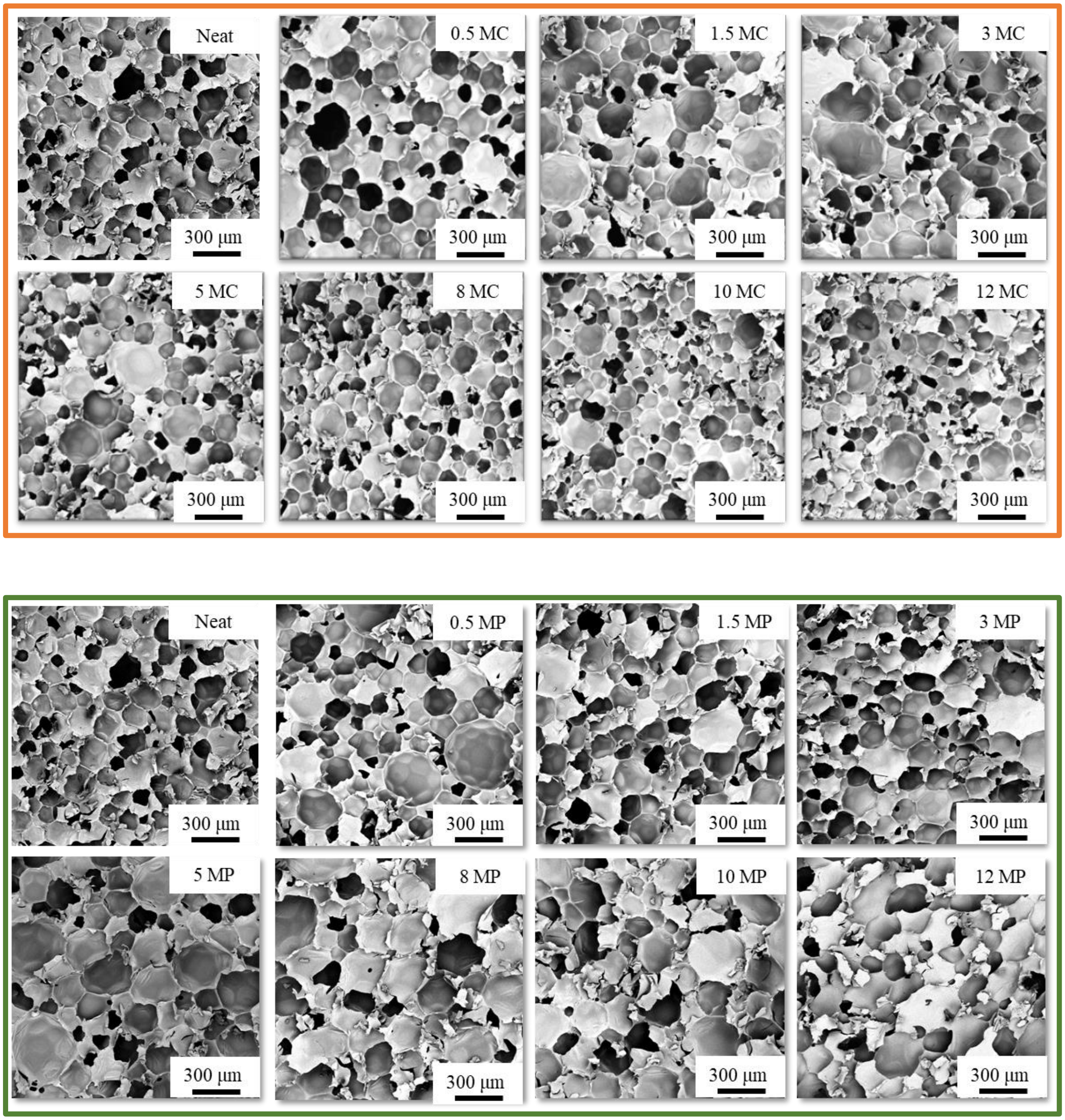


Figure 29. Morphological analysis of cellular structure for rigid foams with different weights of (a) ME (b) MC and (c) MP by SEM images.

3.3.5 Thermogravimetric analysis

The thermal stability for the prepared rigid polyurethane foam containing different flame retardants was analyzed under N_2 atmosphere as illustrated in **Figure 30**. Also, the data related to degradation temperatures at 5 wt.% and 50 wt.% weight loss and char residue are summarized in **Table 8**. TGA is commonly used to review the behavior pattern of thermal stability and degradation. The range of thermal degradation is dependent on several items such as the chemical structure of components, test conditions, heating rate, etc. In general, the first and second degradation steps of rigid foam were observed at 200–350 °C and 480–700 °C, respectively *(58) (59)*. It is expected that better thermal stability will be observed once the flame retardant is present in foams. Melamine interferes with fire during the combustion process and absorbs heat through a condensation reaction in which ammonia and nitrogen gas are released. This process inhibits combustion by reducing the temperature of the substance and by diluting the combustible gases and oxygen *(24) (53)*. The average range of degradation temperature for all ME foams was shown ~234 °C at 5 wt.% and ~310 °C at 50 wt.% weight loss.

Both ME and MC undergo endothermic processes but MC showed higher thermal stability due to the network structure and hydrogen bonding. The decomposition of MC happens around 320-415 °C with a negligible residue. MC breaks down to melamine and cyanuric acid which both generally evaporate during combustion. On heating, melamine releases ammonia to form stable products as melam, melem, and melon at 350 °C, 400 °C, and 450 °C, respectively *(48)*. The initial degradation temperature was at ~240 °C when there was only 5 wt.% weight loss, and then climbed to ~320 °C at 50 wt.% weight loss. Hence, the heat resistance of rigid polyurethane foams increased when the concentration of MC particles increased *(60)*.

Regarding the MP-based foams, it showed $T_{d5\%}$ and $T_{d50\%}$ around ~247 °C and ~365 °C which were higher than ME and MC foams. The second transition happened between 400-500 °C, which showed a significant enhancement in the thermal behavior. The synergetic effect between nitrogen and phosphorus caused the formation of char residue on the surface of the foam. If a foam produces a carbonaceous layer when burned, the thermal stability is improved *(31)*. Therefore, a larger concentration of MP led to the formation of more residue, which inhibits further ignition *(61)*. For example, adding 12 grams of flame retardants resulted in char residue around 11.54%, 0.436%, and 0.286 for MP, MC, and ME foams, respectively.

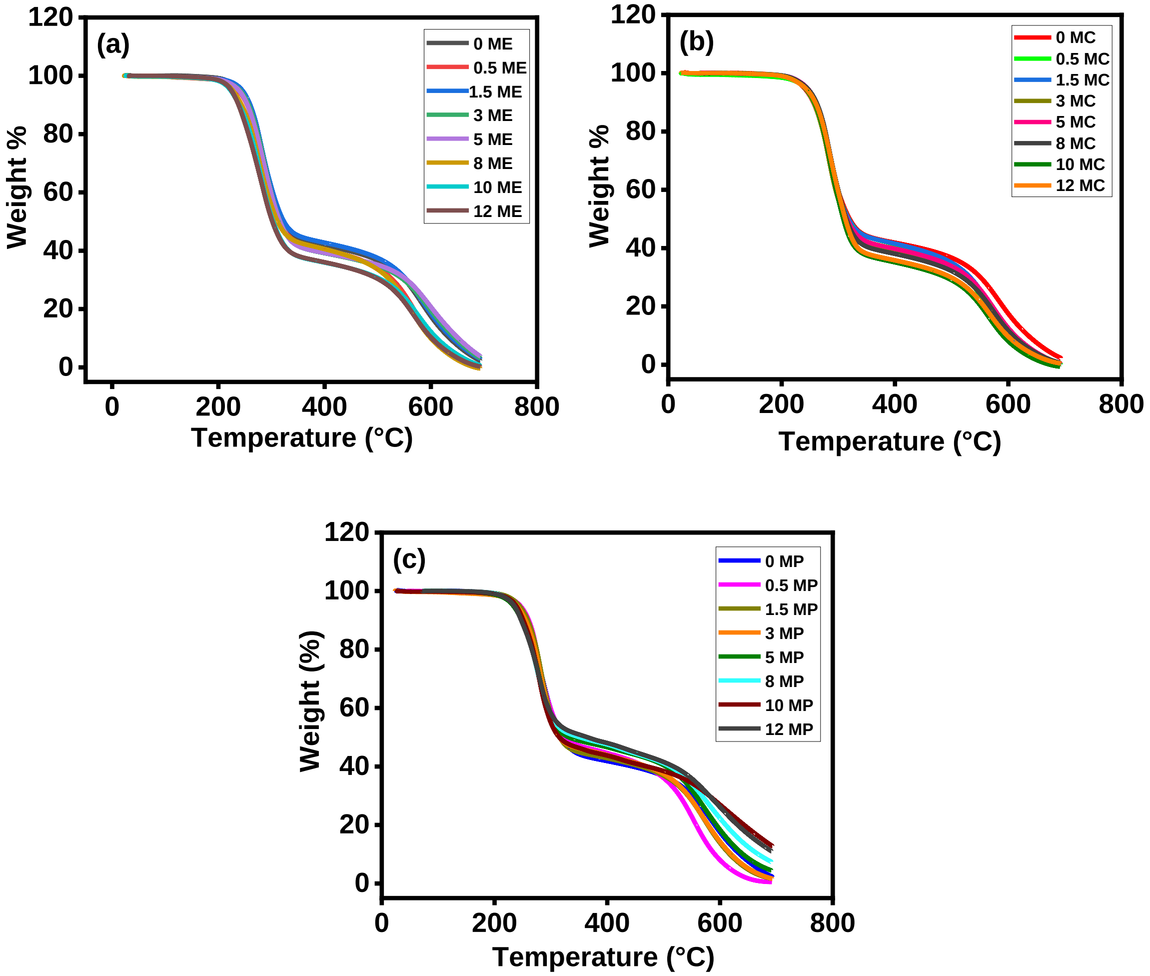


Figure 30. TGA plots of three sets of polyurethane foam with different amounts of (a) ME, (b) MC, and (c) MP under nitrogen.

Table 8. Degradation temperatures at $T_{d5\%}$, $T_{d50\%}$, and residue for ME, MC, and MP based polyurethane foams under nitrogen.

	ME			MC			MP		
Amount of FR	$T_{d5\%}$ (°C)	$T_{d50\%}$ (°C)	Residue (%)	$T_{d5\%}$ (°C)	$T_{d50\%}$ (°C)	Residue (%)	$T_{d5\%}$ (°C)	$T_{d50\%}$ (°C)	Residue (%)
0	240.22	320.02	0	240.22	320.02	0	240.22	320.02	0
0.5	237.41	315.40	0	240.77	310.68	0.181	245.88	327.91	0.476
1.5	245.49	323.38	2.981	245.16	312.40	0	244.18	335.03	1.686
3	240.76	320.27	3.196	247.82	313.83	0.562	246	340.51	1.640
5	239.31	318.76	3.839	248.15	316.03	0.499	248.84	346.89	4.470
8	226.88	314.29	0	249.16	315.52	0.678	249.66	353.83	7.429
10	223.23	313.63	0.792	241.76	317.13	0	251.47	358.30	12.790
12	224.69	315.30	0.286	244.35	320	0.436	253.99	364.98	11.054

Table 9. Degradation temperatures at $T_{d5\%}$, $T_{d50\%}$, and residue for ME, MC, and MP based polyurethane foams under air atmosphere.

	ME			MC			MP		
Amount of FR	$T_{d5\%}$ (°C)	$T_{d50\%}$ (°C)	Residue (%)	$T_{d5\%}$ (°C)	$T_{d50\%}$ (°C)	Residue (%)	$T_{d5\%}$ (°C)	$T_{d50\%}$ (°C)	Residue (%)
0	221.04	307.37	0.542	221.04	307.37	0.542	221.04	307.37	0.542
0.5	237.42	389.60	0.314	242.96	380.33	0.439	244.42	380.33	0
1.5	237.34	375.60	0.401	241.15	370.85	0.336	244.43	409.56	0.668
3	234.19	353.30	0.320	2397.5	363.99	0	241.95	408.83	0.794
5	229.61	347.80	0	239.31	356.94	0.270	235	435.13	1.856
8	224.66	345.50	0	242.81	342.34	0.404	234.52	434.40	1.640
10	217.95	310.18	0.949	240.04	332.10	0.591	239.32	439.93	1.912
12	221.04	307.37	0.542	240.77	329.18	0	232.73	448.29	2.768

In this research, the thermal decomposition of rigid foams was studied in both nitrogen and air atmosphere. In comparison to TGA plots under nitrogen, the thermal decomposition of rigid foam occurs in three steps under air as shown in **Figure 31** Additionally, **Table 9** shows the degradation temperatures at $T_{d5\%}$ and $T_{d50\%}$ and amount of residue produced under air. The behavior of thermal degradation of ME, MC, and MP rigid polyurethane foam under air is similar to the above explanation under nitrogen gas. MP-based foam has higher stability compared to the ME and MC foam. The amount of char residue for all three cases is negligible, but a large improvement in thermal stability is shown when the concentration of flame retardants is increased.

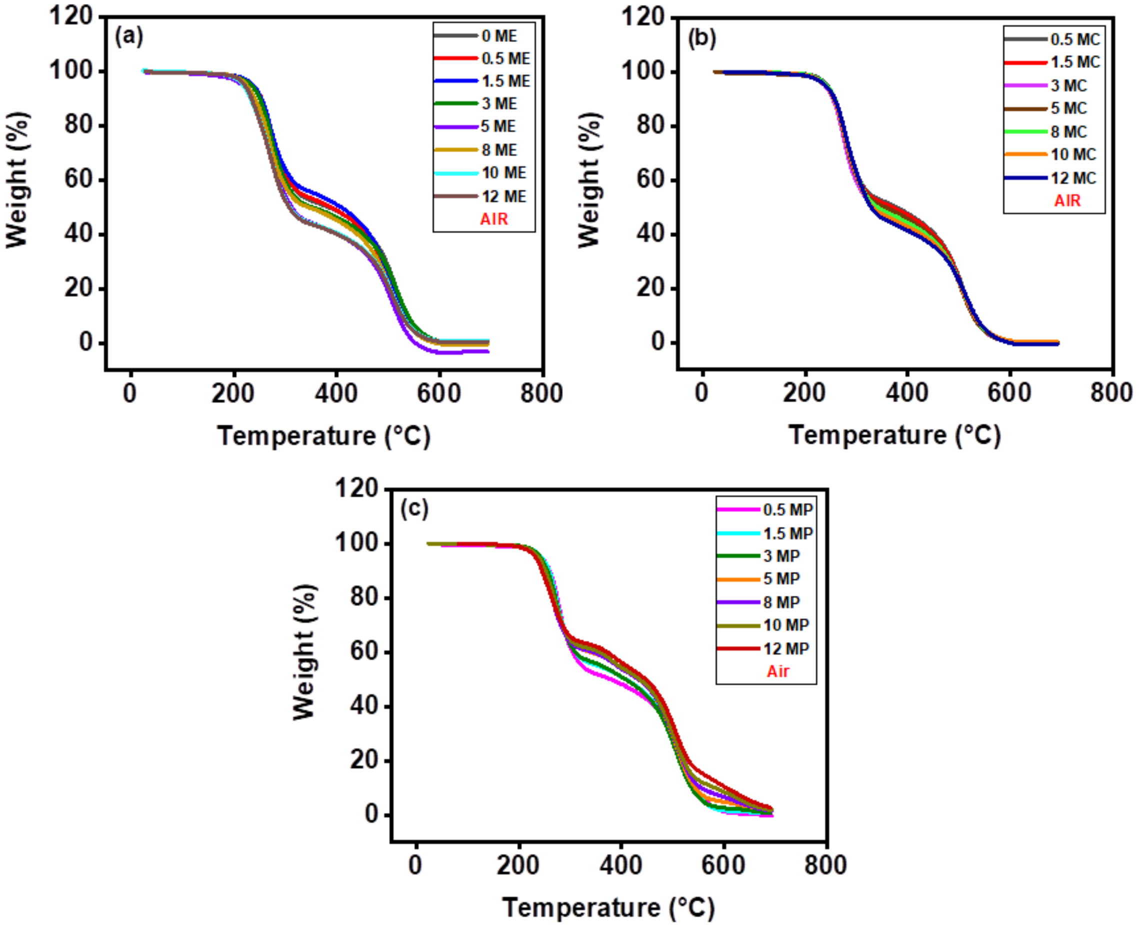


Figure 31. TGA plots of three sets of polyurethane foams with different amounts of (a) ME, (b) MC, and (c) MP under air atmosphere.

3.3.6 Horizontal burning test

The results of the horizontal burning test for ME, MC, and MP-based foams are displayed in **Figure 32**. The pictures of foam samples before and after the burning test are shown in **Figure 33**. The neat foam was burned around 75 seconds and the total weight loss was ~40%. It was predicted that the addition of flame retardant would decrease burning time as well as weight loss. In the ME polyurethane foams, the best result was observed in 12 ME foam, which contained 17.3 wt.% melamine and self-extinguished at 14 seconds with 2.5% weight loss. In the MC polyurethane foams, the best performance was observed in 12 MC foam which contains a similar weight percentage to melamine. Hence, 17.3 wt.% MC extinguished the fire at 21 seconds with 4.1% weight loss. The best achievement for diminishment in ignition time found in the MP set of foams. The lowest burning time and weight loss results were at 11 seconds and 3.3%, respectively in the sample containing 12.27 wt.% (8 MP).

The differences in the fire resistance of melamine derivates may be attributed to the mechanism and mode of action of each flame retardant *(62)*. Melamine as a nitrogen-based flame retardant may either release non-flammable gases such as ammonia and nitrogen into the gas-phase or undergo a condensation reaction that causes deamination and formation of non-soluble products and compact derivates such as melam, melem, and melon *(53)*. These condensed products form a char layer and lead to blocking the airflow passage and any other reactive radical groups that may increase the rate of the fire. Moreover, the decomposition of melamine proceeds endothermically which means it absorbs a significant amount of heat to decrease the temperature of the foam’s surface. According to Thiruma et al., melamine cyanurate acts endothermically *(31)*. The decomposition of MC particles may absorb a larger amount of heat released from the flame region compared to melamine. Also, MC is able to lower the fire temperature as well as reduce fire speed because MC contains a network structure and strong hydrogen bonding between melamine and cyanuric acid. However, in this experiment, MC flame retardant did not perform as well as ME. Flames continued to flicker on the surface of the polyurethane foams treated with MC for a few seconds longer than on the ME treated foam *(54)*. Because MP is a combination of a nitrogen source from melamine and an acid source from phosphoric acid, MP foams showed a satisfactory result compared to ME and MC-foams. The mechanism of MP includes both gas and condensation phases which undergo a condensation reaction, chain separation, and crosslinking or networking reaction during the process of combustion because the interaction between nitrogen-based and phosphorus-based sources brings about the synergism effect. The decomposition of MP could form several intermediate products including radical-scavenge species, and inert gases, and stable residue. The free radicals scavenger of phosphoric acids is $HPO^\bullet$, $PO^\bullet$, or $PO_2^\bullet$ which can react quickly with $H^\bullet$ and $OH^\bullet$. Hence, the deletion of highly reactive free radicals may quench the flame sooner. Additionally, the produced inert gases may weaken fuel concentration and oxygen content. The formation of a thick and stable char layer causes heat insulation, limitation of oxygen transfer, and lengthening the liberation of degradation fragments *(55) (63)*. Therefore, MP improved the flame behavior due to the synergetic effect compared to pristine melamine and melamine cyanurate.

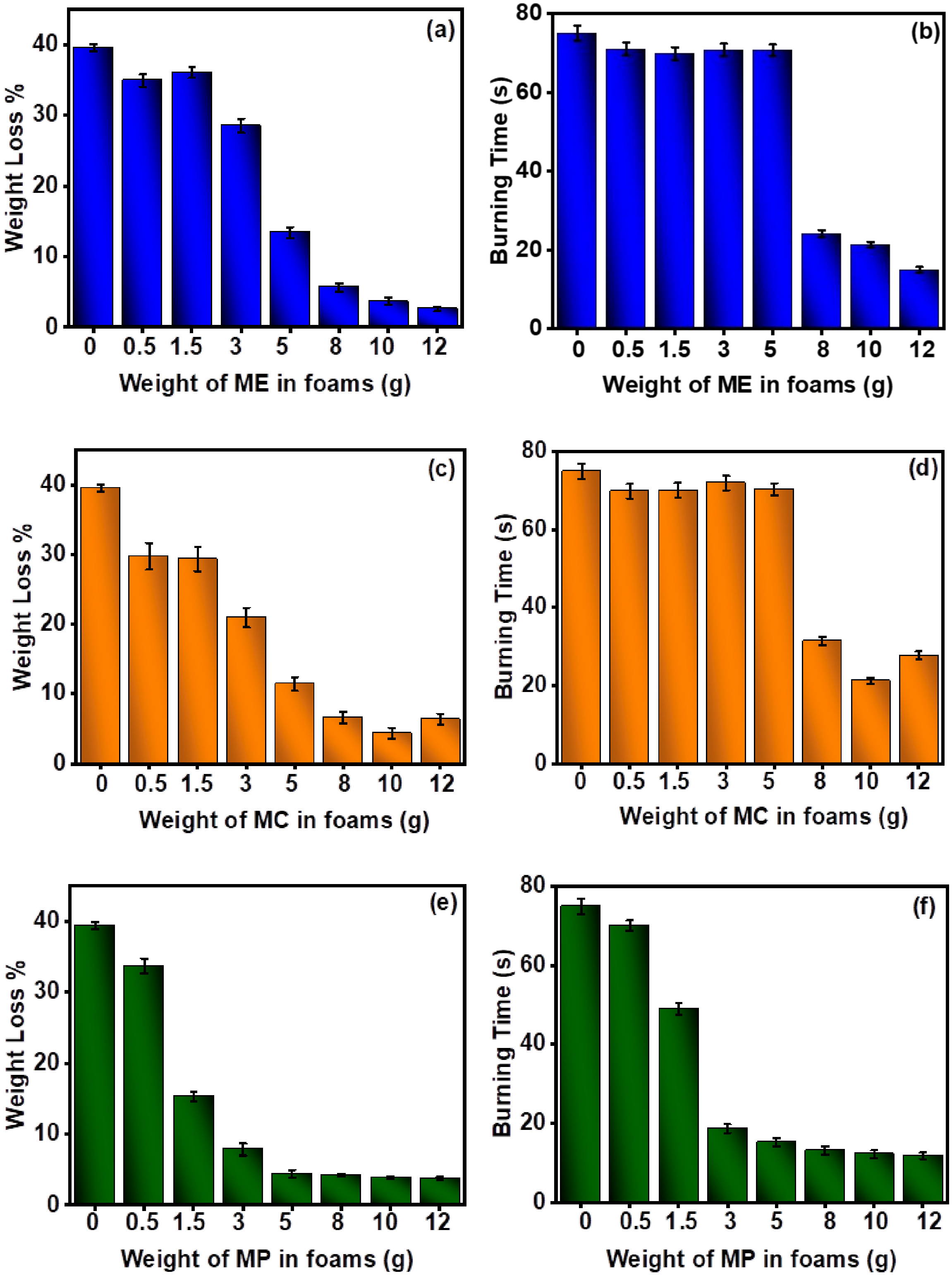
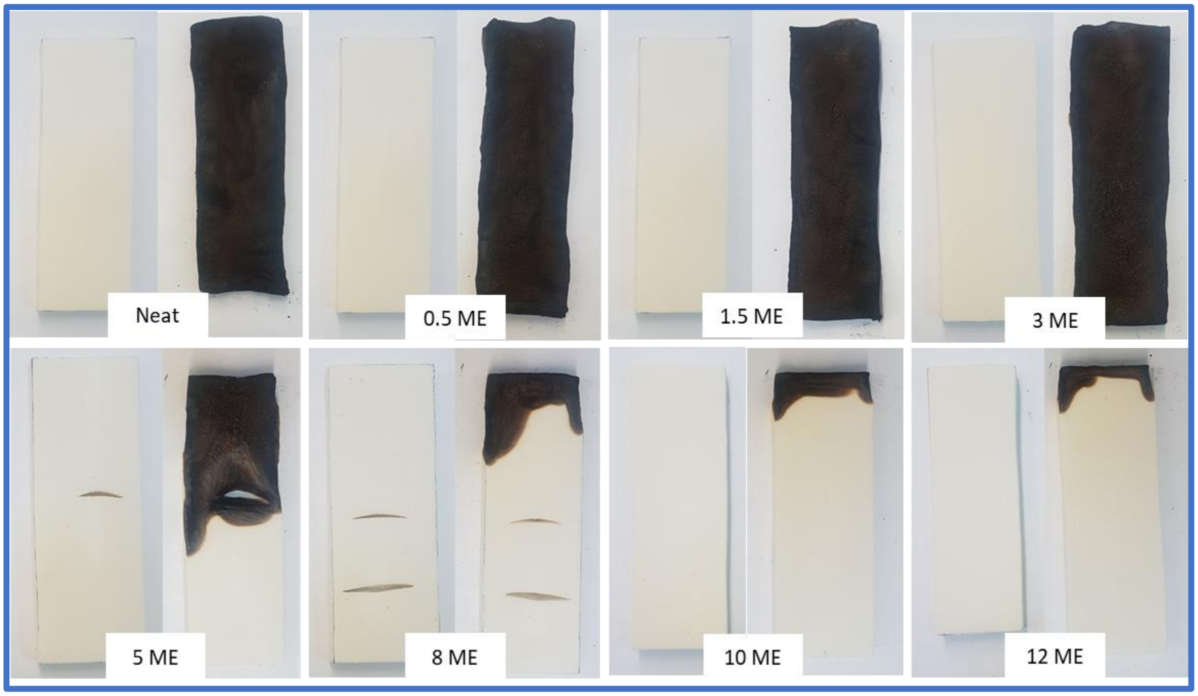


Figure 32. Comparisons of weight loss percent and burning time with different weight of ME (a-b), MC (c-d), and MP (e-f).


Neat
0.5 ME
1.5 ME
3 ME
5 ME
8 ME
10 ME
12 ME


Neat
0.5 MC
1.5 MC
3 MC
5 MC
8 MC
10 MC
12 MC

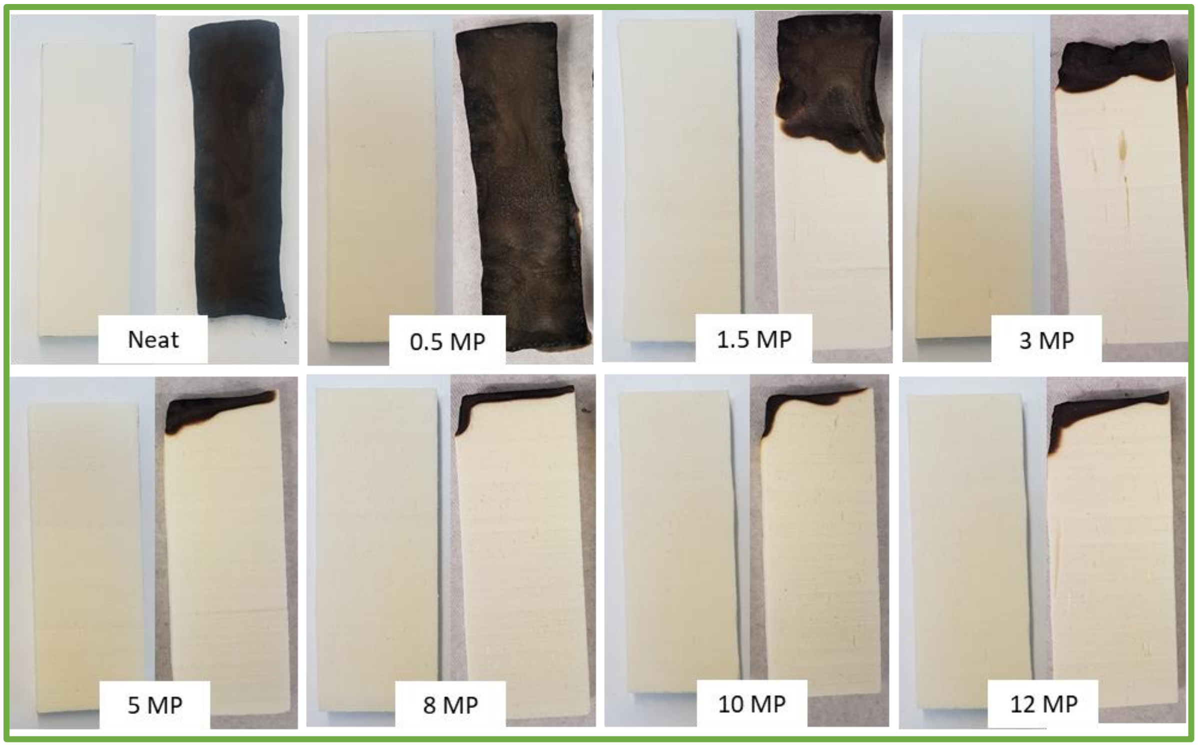


Figure 33. Before and after pictures of the horizontal burning test from Polyurethane foam with different concentration of ME, MC, and MP.

Chapter IV

CONCLUSIONS

In this work, a new bio-based polyol was successfully synthesized from myrcene oil via thiol-ene click chemistry procedure. The synthesis of bio-based polyol proceeded with a one-step reaction in a solvent-free environment at room temperature. The obtained bio-polyol was used for the synthesis of rigid polyurethane foams. Since polyurethane foam is highly flammable, halogen-free flame retardants were chosen as effective additive flame retardants.

From the category of nan-halogenated flame retardants, nitrogenous compounds like melamine and its derivates are very popular and eco-friendly due to low toxicity gases and smoke. The mechanism of nitrogen-containing flame retardants occurs in both gas-phase and solid-phase and causes the formation of a stable char layer. Melamine cyanurate and melamine phosphate as the nitrogen-based flame retardant led to enhanced thermal stability of polyurethane foam. Therefore, during the synthesis of rigid polyurethane foam, melamine and its derivatives were mixed separately into the mixture.

The presence of melamine-based flame retardants showed an overall improvement in the physicomechanical properties of the foam. By increasing the concentration of each flame retardant, the average ranges of foam density and closed-cell content increased and reached around 60-70 kg/m^3 and 90-95%, respectively. These values were in the standard industrial range and caused improvement in the thermal insulation. Also, the mechanical properties of each set of foams increased.

The highest compressive strength of ME foam was 257 kPa when 14.8 wt.% (10 ME) was added. With a similar amount added, MC foam reached the highest compression strength around 267 kPa. In the case of MP foam, with only 4.98 wt.% (3 MP), it showed the highest mechanical strength of about 221 kPa. Hence, the addition of each flame retardant improved the mechanical strength of polyurethane foams.

Moreover, melamine-based flame retardants performed excellently in minimizing the risk of fire. The shortest burning time and lowest weight loss percent of each foam were shown at 17.34 wt.% (12 ME), 14.87 wt.% (10 MC), and 12.27 wt.% (8 MP), and these foams self-extinguished the fire within 14, 21, and 11 sedonds along with 2.5 , 4, and 3 wt.% loss, respectively. In comparison to all samples, the most impressive fire resistance was shown for MP foam containing 12.27 wt.% (8 MP) as it had the shortest self-extinguishment time with the lowest weight loss. Superior flame-retardant properties in MP flame retardant were due to the synergistic effect of nitrogen and phosphorus components that can act in both the solid and gas phases. The formation of a compact char layer leads to blocking the airflow passage in contact with the undersurface of polyurethane in the solid-phase. Also, the liberation of ammonia and nitrogen gas can dilute oxygen and free radical scavenger species in gas-phase.

This study indicates that adding melamine-based materials to rigid polyurethane foams increased the foam's flame resistance where the flame was suppressed in a short time with low production of smoke and toxic gases. Also, rigid polyurethane foams made from bio-based materials including myrcene and nitrogen-based flame retardants offer viable alternatives to petroleum-based products.

V. REFERENCES

1. Bayer O, E. Müller, S. Petersen, Piepenbrink HF, Windemuth E (1950) New Types of Highly Elastic Substances, Vulcollans. Rubber Chem Technol 23:812–835
2. Seymour RB, Kauffman GB (1992) Polyurethanes: A class of modern versatile materials. J Chem Educ 69:909
3. Mark F. Sonnenschein (2014) Introduction. In: Polyurethanes Science, Technology, Markets, and Trends, 1st. John Wiley & Sons, Inc., MI, USA
4. Akindoyo JO, Beg MDH, Ghazali S, Islam MR, Jeyaratnam N, Yuvaraj AR (2016) Polyurethane types, synthesis and applications-a review. RSC Adv 6:114453–114482
5. Borowicz M, Paciorek-Sadowska J, Isbrandt M (2020) Synthesis and application of new bio-polyols based on mustard oil for the production of selected polyurethane materials. Ind Crops Prod 155:112831
6. Gama N V., Ferreira A, Barros-Timmons A (2018) Polyurethane foams: Past, present, and future. Materials (Basel) 11:1841
7. Niranjan Karak (2017) Biobased Hyperbranched Polyurethane. In: Biobased Smart Polyurethane Nanocomposites: From Synthesis to Applications. Royal Society of Chemistry, India, pp 1–40
8. Gama N V, Soares B, Freire CSR, Silva R, Neto CP, Barros-timmons A, Ferreira A (2015) Bio-based polyurethane foams toward applications beyond thermal insulation. J Mater Des 76:77–85
9. Deng Y, Dewil R, Appels L, Ansart R, Baeyens J, Kang Q (2020) Reviewing the thermo-chemical recycling of waste polyurethane foam. J Environ Manage 278:111527
10. Sonnenschein MF (2014) Polyurethanes: Science, Technology, Markets, and Trends. In: Polyurethanes: Science, Technology, Markets, and Trends, 1st. John Wiley & Sons, Inc., MI, USA, pp 255–293
11. Schollenberger CS, Stewart FD (1971) Thermoplastic polyurethane hydrolysis stability. J Elastoplast 3:28–56
12. Sonnenschein MF (2015) Polyurethane Flexible Foams. In: Polyurethanes: Science, Technology, Markets, and Trends, 1st. John Wiley & Sons, Inc., MI, USA, pp 207–234
13. Bryan D. Kaushiva (1999) Structure-property relationships of flexible polyurethane foams. Virginia Polytechnic Institute and State University
14. Bîrca A, Gherasim O, Grumezescu V, Grumezescu AM (2019) Introduction in thermoplastic and thermosetting polymers. In: Grumezescu AM, Grumezescu V (eds) Materials for Biomedical Engineering: Thermoset and Thermoplastic Polymers. Elsevier Science, Romania

15. Sonnenschein MF (2015) Polyurethane Elastomers: Manufacture, Applications, Markets, and Trends. In: Polyurethanes: Science, Technology, Markets, and Trends, 1st. John Wiley & Sons, Inc., MI, USA, pp 294–335

16. Singh H, Jain AK (2008) Ignition, Combustion, Toxicity, and Fire Retardancy of Polyurethane Foams : A Comprehensive Review. J Appl Polym Sci 111:1115–1143

17. Liu X, Hao J, Gaan S (2016) Recent studies on the decomposition and strategies of smoke and toxicity suppression for polyurethane based materials. RSC Adv 6:74742–74756

18. Morgan AB, Wilkie CA (2000) Polymeric, An Introduction to Flame Retardancy, Its Role in Materials Science, and the Field, Current State of the. In: Wilkie CA, Morgan AB (eds) Fire Retardancy of Polymeric Materials, 2nd. CRC Press, NY, USA

19. Lewin M, Weil ED (2001) Mechanisms and modes of action in flame retardancy of polymers. In: Horrocks AR, Price D (eds) Fire Retardant Materials. Woodhead Publishing Ltd, NY, USA, pp 31–68

20. Salmeia KA, Fage J, Liang S, Gaan S (2015) An overview of mode of action and analytical methods for evaluation of gas phase activities of flame retardants. Polymers (Basel) 7:504–526

21. Troitzsch J (1993) Flame retardant polymers current status and future trends. Makromol Chemie Macromol Symp 74:125–135

22. Beard A, Angeler D (2010) Flame Retardants: Chemistry, Applications, and Environmental Impacts. In: Lackner M, Winter F, Agarwal AK (eds) Handbook of Combustion. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, pp 415–440

23. James W. Mitchell (2014) The History and Future Trends of Non-halogenated Flame Retarded Polymers. In: Morgan AB, Wilkie CA (eds) Non-Halogenated Flame Retardant Handbook. John Wiley & Sons, Inc., MA, USA, pp 1–16

24. Horacek H, Grabner R (1996) Advantages of flame retardants based on nitrogen compounds. Polym Degrad Stab 54:205–215

25. Bann B, Miller SA (1958) Melamine And Derivatives Of Melamine. Chem Rev 58:131–172

26. Klatt M (2014) Nitrogen-based Flame Retardants. In: Morgan AB, Wilkie CA (eds) Non-Halogenated Flame Retardant Handbook. John Wiley & Sons, Inc., MA, USA, pp 143–168

27. Hawkins MC, Toole BO, Jackovich D (2005) Cell Morphology and Mechanical Properties of Rigid Polyurethane Foam. J Cell Plast 41:267–285

28. Neisius NM, Liang S, Mispreuve H, Gaan S, Gallen C-S, Ag FN, Wolfhausen C- (2012) Recent Developments in Flame Retardancy of Flexible Polyurethane Foams. In: Morgan AB, Wilkie CA, Nelson GL (eds) In Fire and polymers vi: New advances in flame retardant chemistry and science. American Chemical Society, Washington,

DC, USA, pp 251–270

29. Tao W, Li J (2018) Melamine cyanurate tailored by base and its multi effects on flame retardancy of polyamide 6. Appl Surf Sci 456:751–762

30. Levința N, Vuluga Z, Teodorescu M, Corobea MC (2019) Halogen-free flame retardants for application in thermoplastics based on condensation polymers. SN Appl Sci 1:1–19

31. Thirumal M, Khastgir D, Nando GB, Naik YP, Singha NK (2010) Halogen-free flame retardant PUF: Effect of melamine compounds on mechanical, thermal and flame retardant properties. Polym Degrad Stab 95:1138–1145

32. Modesti M, Lorenzetti A (2002) Flame retardancy of polyisocyanurate-polyurethane foams: Use of different charring agents. Polym Degrad Stab 78:341–347

33. Laoutid F, Bonnaud L, Alexandre M, Lopez-cuesta J, Dubois P (2009) New prospects in flame retardant polymer materials : From fundamentals to nanocomposites. Mater Sci Eng R Reports 63:100–125

34. Singh I, Samal SK, Mohanty S, Nayak SK (2020) Recent Advancement in Plant Oil Derived Polyol-Based Polyurethane Foam for Future Perspective: A Review. Eur J Lipid Sci Technol 122:1900225

35. Maisonneuve L, Chollet G, Grau E, Cramail H (2016) Vegetable oils: A source of polyols for polyurethane materials. OCL - Oilseeds fats, Crop Lipids 23:1–10

36. Grosse Y, Loomis D, Guyton KZ, El Ghissassi F, Bouvard V, Benbrahim-Tallaa L, Mattock H, Straif K (2017) β-Myrcene. In: Heidi Mattock (ed) Some chemicals that cause tumours of the urinary tract in rodents. International Agency for Research on Cancer, France, p 1003

37. Behr A, Johnen L (2009) Myrcene as a natural base chemical in sustainable chemistry: A critical review. ChemSusChem 2:1072–1095

38. Mihail Ionescu, Radojcˇic´ D, Wana X, Petrovic´ ZS, Upshaw TA (2015) Functionalized vegetable oils as precursors for polymers by thiol-ene reaction. Eur Polym J 65:439–448

39. Desroches M, Caillol S, Lapinte V, Auvergne R, Boutevin B (2011) Synthesis of biobased polyols by thiol-ene coupling from vegetable oils. Macromolecules 44:2489–2500

40. Adekunle KF (2015) A Review of Vegetable Oil-Based Polymers: Synthesis and Applications. Open J Polym Chem 5:34–40

41. Silverstein RM, Webster FX, Kiemle D (2014) Spectrometric identification of organic compounds, 7th Editio. John Wiley & Sons, Inc.

42. Lin-Vien D, Colthup NB, Fateley WG, Grasselli JG (1991) Alkanes. In: The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules.

Elsevier, pp 9–28

43. M. de Souza F, Choi J, Bhoyate S, Kahol PK, Gupta RK (2020) Expendable Graphite as an Efficient Flame-Retardant for Novel Partial Bio-Based Rigid Polyurethane Foams. C — J Carbon Res 6:27

44. Taylor P, Fu X, Liu Y, Wang Q, Zhang Z, Wang Z, Zhang J, Fu X, Liu Y, Wang Q, Zhang Z, Wang Z (2011) Novel synthesis method for melamine polyphosphate and its flame retardancy on glass fiber reinforced polyamide 66. Polym Plast Technol Eng 50:1527–1532

45. Yang H, Song L, Tai Q, Wang X, Yu B, Yuan Y, Hu Y, Yuen RKK (2014) Comparative study on the flame retarded efficiency of melamine phosphate, melamine phosphite and melamine hypophosphite on poly (butylene succinate) composites. Polym Degrad Stab 105:248–256

46. Chen Y, Wang Q (2007) Reaction of melamine phosphate with pentaerythritol and its products for flame retardation of polypropylene. Polym Adv Technol 18:587–600

47. Costa L, Camino G (1988) Thermal behaviour of melamine. J Therm Anal 34:423–429

48. Sangeetha V, Kanagathara N, Sumathi R, Sivakumar N, Anbalagan G (2013) Spectral and Thermal Degradation of Melamine Cyanurate. J Mater 2013:262094

49. Abelow AE, Nissen A, Massey L, Whinnery L (2017) Effectiveness of Flame Retardants in TufFoam. Albuquerque, USA

50. Hawkins MC, O'Toole B, Jackovich D (2005) Cell morphology and mechanical properties of rigid polyurethane foam. J Cell Plast 41:267–285

51. Gravit VM, Ogidan O, Znamenskaya E (2018) Methods for determining the number of closed cells in rigid sprayed polyurethane foam. MATEC Web Conf 193:03027

52. Zhu H, Xu S (2020) Preparation of Flame-retardant Rigid Polyurethane Foams by Combining Modified Melamine–formaldehyde Resin and Phosphorus Flame Retardants. ACS Omega 5:9658–9667

53. Członka S, Strąkowska A, Strzelec K, Kairytė A, Kremensas A (2020) Melamine, silica, and ionic liquid as a novel flame retardant for rigid polyurethane foams with enhanced flame retardancy and mechanical properties. Polym Test 87:106511

54. Sut A, Metzsch-Zilligen E, Großhauser M, Pfaendner R, Schartel B (2019) Synergy between melamine cyanurate, melamine polyphosphate and aluminum diethylphosphinate in flame retarded thermoplastic polyurethane. Polym Test 74:196–204

55. Li TT, Xing M, Wang H, Huang SY, Fu C, Lou CW, Lin JH (2019) Nitrogen/phosphorus synergistic flame retardant-filled flexible polyurethane foams: Microstructure, compressive stress, sound absorption, and combustion resistance. RSC Adv 9:21192–21201

56. Kageoka M, Tairaka Y, Kodama K (1994) Effects of melamine particle size on flexible polyurethane foam properties. J Cell Plast 33:219–237

57. Wang C, Wu Y, Li Y, Shao Q, Yan X, Han C, Wang Z, Liu Z, Guo Z (2018) Flame-retardant rigid polyurethane foam with a phosphorus-nitrogen single intumescent flame retardant. Polym Adv Technol 29:668–676

58. Bhoyate S, Ionescu M, Kahol PK, Gupta RK (2018) Sustainable flame-retardant polyurethanes using renewable resources. Ind Crop Prod 123:480–488

59. He J, Jiang L, Sun J, Lo S (2016) Thermal degradation study of pure RPU in oxidative and non-oxidative atmospheres. J Anal Appl Pyrolysis 120:269–283

60. Nhung HT, Linh PD, Hanh NT, Nhan NT, Oanh HT, Tuyen ND, Van Tuyen N, Ha HM (2019) Effect of the incorporation of organoclay and melamine cyanurate on the flame retardancy and mechanical property of polyurethane foam. Vietnam J Chem 57:368–374

61. Jiang H, Bi M, Ma D, Li B, Cong H, Gao W (2019) Flame suppression mechanism of aluminum dust cloud by melamine cyanurate and melamine polyphosphate. J Hazard Mater 368:797–810

62. Tawfik SY (2017) Flame Retardants : Additives in Plastic Technology. In: Palsule S. (ed) Polymers and Polymeric Composites: A Reference Series. Springer, Berlin, Heidelberg

63. Wang G, Bai S (2017) Synergistic effect of expandable graphite and melamine phosphate on flame-retardant polystyrene. J Appl Polym Sci 134:45474