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HIGHLY FLAME RETARDANT AND BIO-BASED RIGID POLYURETHANE FOAMS DERIVED FROM ORANGE PEEL OIL

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HIGHLY FLAME RETARDANT AND BIO-BASED RIGID POLYURETHANE FOAMS DERIVED FROM ORANGE PEEL OIL

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

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Pittsburg, Kansas

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An Abstract of the Thesis by
Chunyang Zhang

Polyurethane is an important class of polymer which is being used for various industrial applications in the form of rigid foams, flexible foams, thermoplastic, elastomer, coating, and adhesive. Especially there is a huge market for rigid polyurethane foams for their applications as thermal insulating material in building and housing. In general, polyurethanes are prepared using polyols and diisocyanates. Most of the polyols used by industries are petrochemical based. In this project, a novel polyol from an orange peel oil-based derivative, limonene dimercaptan, was synthesized using one step photochemical thiol-ene reaction. The synthesized polyol was used to prepare flame retardant polyurethane foams using dimethyl methyl phosphonate (DMMP) as an additive flame retardant (AFR) and a new bromine containing reactive flame retardant (RFR) derived from 2,4,6-tribromophenol. The foams using DMMP with phosphorus loading of 0, 0.23, 0.45, 0.90, 1.3, and 1.7 wt% and bromine-polyol with a bromine content of 0, 4.0, 4.5, 5.0, 5.5, and 6.0 wt% were prepared and analyzed. Our results suggest that prepared polyurethanes showed moderate density and high closed cell content. Both flame retardants lead to rigid polyurethane foams with excellent physicomechanical properties with a short self-extinguishing time and low weight loss after burning test. The reactive bromine-polyol leads to rigid polyurethanes with better physicomechanical

properties than those of foams based on AFR, but the flame retardant properties of foams prepared using AFR are superior to the foams prepared using bromine-polyol (RFR). From the overall observations, the bio-based polyurethane foams showed efficient flame retardant properties and can be used as flame retardant foam for various applications.

TABLE OF CONTENTS

CHAPTER PAGE

LIST OF TABLES

TABLE PAGE

LIST OF FIGURES

CHAPTER I

INTRODUCTION

1.1. Bio-based Polymers

Polymers are high molecular weight compounds that are repeatedly linked by covalent bonds from many identical and simple structural units. Compared to other materials, such as wood, glass, and steel, polymers have been used in substantial quantities for only five to seven decades.[1] However, their development speed and wide applications are far greater than these traditional materials. Now polymers are no longer a substitute for traditional materials but have become increasing important in the fields of agriculture, industry, national defense, science, and technology.[1]

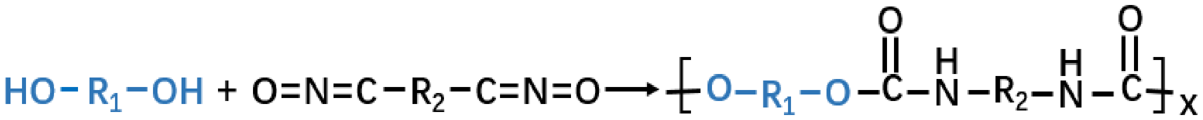
Most polymers are synthesized using chemicals from petrochemical industries. For example, olefins and aromatics, as the building blocks for various kinds of polymers, are obtained by catalytic cracking of petroleum or natural gas liquids like ethane and propane.[2] With rapid developments in global polymer industries, the amounts of olefins and aromatics consumed for polymers has dramatically ballooned. As a result, the excessive use of petroleum creates situations where people face energy shortage and an exhausting surfeit carbon dioxide, climate changing, acid rain, air pollution, and other environmental issues.

Using bio-based chemicals instead of petrochemicals based chemicals is considered a promising way to offset the non-renewable energy use and greenhouse gas emissions of the petroleum-chemical industry. Therefore, increasing attention has been paid to bio-based polymers synthesized by bio-based chemicals. In recent years, European Chemicals Agency (ECHA) and U.S. Environmental Protection Agency (EPA) have greatly promoted greener approaches for preparing polymers.[3,4] In the approaches, several bio-resources such as vegetable fats, oils, starch were successfully used.[5-7] Because of bio-based polymers derived from natural materials, they also have the merit of bio-degradability which is environmentally friendly.[7] Additionally, some of bio-based polymers have advantageous socio-economic effects and demonstrate performance benefits over petroleum-derived polymers.[6]

1.2. Bio-based Polyurethanes

Polyurethanes are the polymers containing recurring urethane [-NH-CO-O-] groups in the main chain. Polyurethanes have wide applications in industries in the form of foams, castings, elastomers, adhesives, and much more.[8-13] For examples, Polyurethanes can be used in the manufacture of microcellular foam seals and gaskets, rigid foam insulation panels, durable elastomeric wheels for shopping cart and elevator, high performance adhesives, surface coatings and surface sealants, synthetic fibers, hard-plastic parts for electronic instruments. Polyurethane industries had a market of 54 billion dollars in 2015, which is expected to continuously grow at the rate of about 7%.[14]

In general, polyurethanes are produced by the reactions of a polyol containing multiple hydroxyl [-OH] groups with a diisocyanate [-C=N=O] group to form a repeating urethane group (Figure 1.1). The use of different types of polyols and isocyanates will form polyurethanes with a wide range of properties. For example, polyols with high functional groups will produce polyurethanes with high mechanical strength. Therefore, the design and synthesis of novel polyols are highly significant for the development of high-performance polyurethanes.



$$HO-R_1-OH + O=N=C-R_2-C=N=O \longrightarrow \left[O-R_1-O-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-R_2-\overset{H}{N}-\overset{O}{\overset{\|}{C}} \right]_x$$

Figure 1.1: Reaction of isocyanate with a polyol to form a polyurethane

Bio-based polyols for polyurethanes have gained considerable attention to reduce dependence on petroleum and to be more environmentally friendly. Bio-based polyols using vegetable oils for polyurethanes has initiated wide research for sustainability issues.[15] In general, multiple hydroxyl groups were generated at the double bonds of the vegetable oils making them suitable to react with the isocyanates for polyurethanes. The number of hydroxyl groups generated in the vegetable oils control the crosslinking and mechanical properties of the polyurethanes.[16] Soybean oil, castor oil, canola oil, corn oil, sunflower oil, cashew-based derivatives and many other sources were used to synthesize polyols for polyurethanes.[16-31]

1.3. Flame Retardant Rigid Polyurethanes Foams

Rigid polyurethane foams are considered as a prime candidate for thermal insulation and filling material in the construction industry due to their excellent electrical and thermal resistance, high compressive strength, and dense closed-cell structure.[32,33] About half of the polyurethanes are being used for construction, appliances, and furniture.[14] However, polyurethane foams suffer from the disadvantage of high flammability which is amplified due to the higher surface with respect to the mass density of the product. Moreover, high oxygen, carbon, and hydrogen content in the polyurethanes readily allows ignition even with a small glint of fire causing serious fire hazards.[9,34] According to the National Fire Protection Association most fires are structural fires.[35-39] Table 1.1 displays some of the data for the fire damage in the United States. As evident from the Table 1.1, the structural fires have always accounted for a large proportion of fires and have caused significant loss. Since polyurethanes are being used for the structural applications, the fires could be prevented if current polyurethanes are replaced by flame retardant polyurethanes. Thus, development of flame retardant polyurethanes is very important. The importance could be further enhanced if we used polyols from the bio-resources to prepare flame retardant polyurethanes for structural applications.

Table-1.1: Fire loss in the United States.

Year	Structure fires during the year	Civilian deaths	Civilian injuries	Property damage (in Billions $)	% of total fire property
2012	480,500	2,470	14,700	9.8	35
2013	487,500	2,855	14,075	9.5	39
2014	494,000	3,275	15,775	9.8	38
2015	501,500	2,685	13,000	10.3	37
2016	475,500	2,950	12,775	7.9	74

1.4. Objective of the Thesis

The primary objective of this thesis is to study the physicomechanical and flammability of the flame retardant polyurethanes. The polyol for the polyurethanes was synthesized using limonene dimercaptan, an orange peel oil-based derivative, through an easy one step photochemical thiol-ene reaction. Flame retardancy in the polyurethanes was introduced by adding a new bromine containing polyols as reactive flame retardant and phosphorous containing compound as an additive flame retardant. Structural, thermal, flame retardancy, and mechanical properties of these polyurethane foams were evaluated to study the effects of addictive and reactive flame retardants on the properties of polyurethane foams.

CHAPTER II

EXPERIMENTAL DETAILS

2.1. Starting Materials

The details of the starting materials are given below:

2.1.1. Polyols

In polyurethane manufacturing, polyols are defined as low molecular weight compounds containing at least two hydroxyl groups. Several types of polyols can be used for polyurethane foams, such as polyether polyols, polyester polyols, and hydroxyl-terminated polyolefins. Among them, polyether polyols are most widely used for polyurethane foams.[40] The properties of polyols, including molecular weight, chemical structure, and acid value play an important role in determining the properties of the polyurethane foams such as density, flexibility, and thermal stability.

Limonene-dimercaptan and bromine-based polyols were synthesized. The details are given in **section 2.2**. Jeffol SG-360, a sucrose-based polyether polyol, was purchased from Huntsman, USA and used without further purification. Jeffol SG-360 has a molecular weight of 730 g/mol, an OH content of 360 mg KOH/g, functionality of 4.7, an equivalent weight of 156, and viscosity of 3,500 cps at 25 ^{o}C.

2.1.2. Isocyanate

Isocyanate is a compound which contains N=C=O (NCO) groups. This group reacts with the hydroxyl group of the polyol to make polyurethanes. Isocyanate is another important component in polyurethane manufacturing as the properties of the polyurethanes can be altered using different isocyanates. The major isocyanates produced in the market are diisocyanate (TDI), diisocyanate-diphenylmethane (MDI) and their derivatives.

In this work, Rubinate M isocyanate which is methylene diphenyl diisocyanate (MDI) was used. MDI was purchased from Huntsman, USA and used as received. The chemical structure of MDI is shown in Figure 2.1**.** Rubinate M isocyanate has an equivalent weight of 135, NCO content of 31%, and viscosity of 210 cps at 25 ^{o}C.

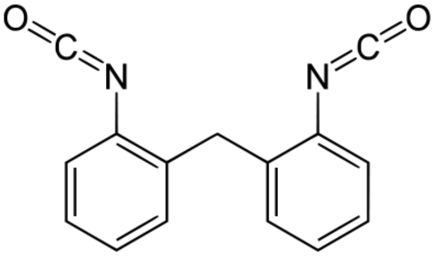


Figure 2.1: Chemical structure of methylene diphenyl diisocyanate.

2.1.3. Water

In the preparation of polyurethane foams, water is added as a blowing agent. Water reacts with isocyanate to produce carbon dioxide. This carbon dioxide comes out as gas bubbles during polymerization process to form foams. The water-isocyanate reaction is given below.[40]

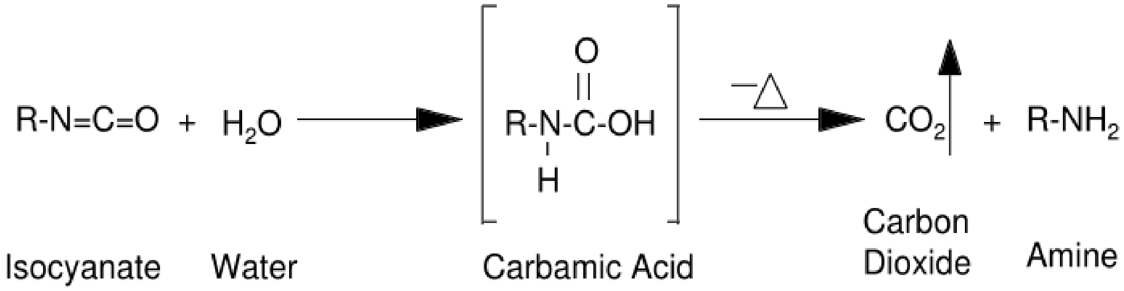


Figure 2.2: Water-isocyanate reaction

2.1.4. Catalysts

The isocyanate group reacts relatively slowly with polyols and water. The reaction is accelerated by the addition of catalysts. Therefore, catalysts are very important for the preparation of polyurethanes. There are different types of catalysts. Catalysts used for the gelling reaction of isocyanate with polyols are called “gelling catalysts”. The catalysts used for the blowing reaction of isocyanate with water are called “blowing catalysts”. Tertiary amines and organometallics (primarily tin-containing compounds) catalysts are the most common catalysts and are used for blowing reaction and gelling reaction, respectively. For tertiary amines, a strong nucleophile provided by the extra electron pair on the nitrogen atom can attack the carbon of the isocyanate group.[39] Organometallics catalysts such as organotins play an important role in the isocyanate reactions. They act as powerful electrophilic catalysts.[42,43] Tertiary amines and organometallics are generally considered as blowing and gelation catalysts, respectively, but they also work in another reaction and tend to catalyze both the isocyanate-water and the isocyanate-polyol reactions.[41, 42]

In this work, DABCO® T-12 catalyst obtained from Air Products, USA which is mainly dibutyltin dilaurate and Niax™ catalyst A-1 which contains 70 percent bis(2-dimethylaminoethyl) ether from OSi Specialties, USA were used as catalysts.

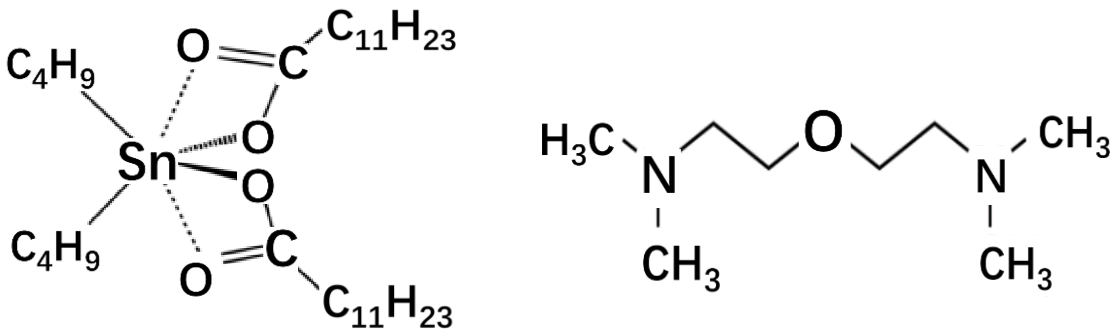


Figure 2.3: Chemical structure of dibutyltin dilaurate and bis (2-dimethyl-aminoethyl) ether.

2.1.5. Surfactant

A surfactant takes a crucial role in reducing surface tension, emulsifying incompatible ingredients, promoting bubble nucleation, stabilizing the rising foam, and reducing the defoaming effect. Among these, the most important to foam production is to mix the incompatible components in the polymerizing mixture. Surfactants also help to control the foam cells by stabilizing the gas bubbles formed in the process. They prevent growing cells from coalescing and combining together until those cells have sufficient strength to become self-supporting during polymerization. The growing foams probably have a risk of collapse in the absence of the surfactants.[41, 44]

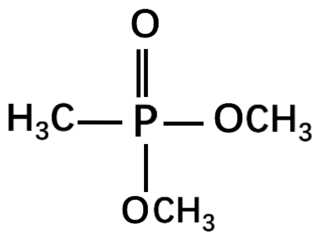
Tegostab B-8404, which is a silicone-based surfactant, was used as obtained from Evonik, USA.

2.1.6. Flame Retardants

Flame retardants are the compounds which can inhibit flame growth. Flame retardants have different mechanisms which depend on their type. For example, phosphorus-based fire retardants generate PO•, PO_2•, HOPO•, and $HOPO_2$• radicals in the gas phase which terminate the highly active flame-propagation radicals (HO• and H•). In addition, they make a char layer on the substrate surface which cuts off the oxygen supply to the surface making them suitable for flame retardancy applications.[45,46] For endothermic flame retardants, including some metal hydroxides and mineral carbonates, their endothermic decomposition cools the condensed phase, slowing down degradation, or taking away heat that would lead to fuel release. In this work, we explored the flame retardant characteristics of bio-based polyurethanes using phosphorus-based and bromine-based flame retardants, which can be very effective at low loadings compared to other flame retardants such as expandable graphite and endothermic flame retardants.[9,13]

Based on the mechanism, flame retardants can be broadly classified into two types: additive and reactive flame retardants. The additive flame retardants are the compounds containing chlorine, bromine or phosphorus without the reactive groups such as -OH, -NH_2 or -NCO to get involved in the polyurethane reaction. These compounds are directly added to the polyurethane to prevent the growth of fire and are not part of the polyurethane structure. The reactive flame retardants are the compounds which participate in reaction during polyurethane formation and act as flame retardant too. Most reactive flame retardants are polyols containing halogens, phosphorus, silicone and nitrogen. Normally reactive flame retardants can assure a permanent flame retarding effect and stable physical properties in the long term due to the strong chemically bond between flame retardants and polyurethane structure.[40] In this work, the effect of additive and reactive flame retardants on the physicomechanical properties and flammability of bio-based polyurethanes are studied. Phosphorus-based additive flame retardant and bromine-based reactive polyols were used.

Dimethyl methyl phosphonate (DMMP) was used as additive flame retardant. DMMP was purchased from Sigma-Aldrich, USA. The structure of the DMMP is given below:



$H_3C{-}P(=O)(OCH_3){-}OCH_3$

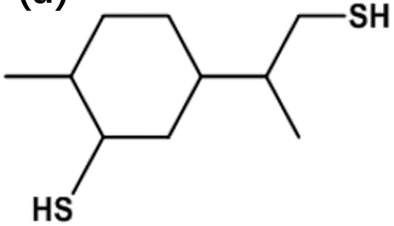
Figure 2.4: Chemical structure of dimethyl methyl phosphonate (DMMP)

The details for the reactive flame retardant polyol which was synthesized is given in **section 2.1.7.**

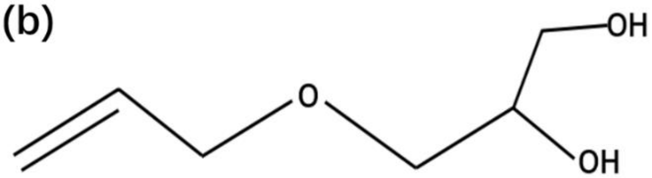
2.1.7. Chemical Compounds for Limonene-dimercaptan and Bromine-based Polyol

Limonene dimercaptan, also called dipentene dimercaptan, is mercaptenized limonene, a major component of orange peel. Limonene dimercaptan from Chevron Philips, USA and glycerol-1-allyl ether from Acros Organic, USA were obtained and used as received. Starting materials for the synthesis of bromine-based polyol 2,4,6-tribromophenol (2,4,6-TBP) and glycidol (GLY) were purchased from Sigma-Aldrich, USA. Ethylene oxide (EO) was purchased from ARC specialist products, USA. 2-hydroxy-2-methylpropiophenone as a photo-initiator for limonene-based polyol and tetra-methylguanidine (TMG) as the catalyst for the synthesis of bromine-based polyol were obtained from Sigma-Aldrich, USA. The chemical structures of the above stated compounds are given below:

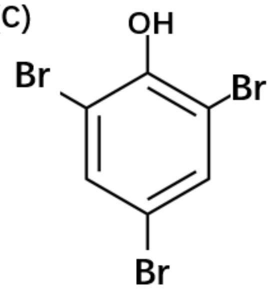
(a)



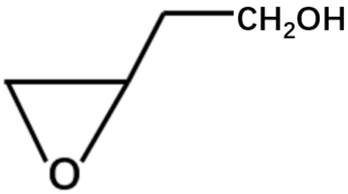
(b)



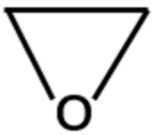
(C)



(d)



(e)



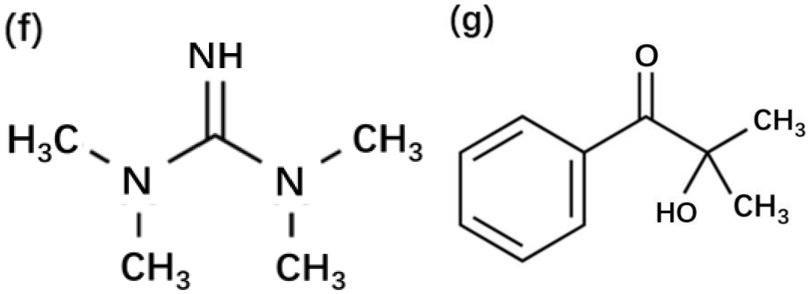


Figure 2.5: Chemical structure of (a) dipentene dimercaptan (b) glycerol-1-allyl ether (c) 2,4,6-tribromophenol (d) glycidol (e) ethylene oxide (f) tetra-methylguanidine (g) 2-hydroxy-2-methylpropiophenone.

2.2. Synthesis of Polyols

2.2.1. Synthesis of Limonene-dimercaptan based Polyol

Limonene-dimercaptan based polyol (LDM-GAE) was synthesized by using limonene dimercaptan and glycerol-1-allyl ether. In a typical synthesis, 51 g of limonene dimercaptan was added to react with 66 g of glycerol-1-allyl ether (in a molar ratio of 1:2). The thiol-ene reaction was carried out at room temperature for 6 h under 365 nm ultraviolet radiation in the presence of 2.5 wt% of 2-hydroxy-2-methyl propiophenone as the photo-initiator. The reaction mixture was stirred constantly using a magnetic stirrer at 300 rpm during the entire reaction period. The schematic of the overall setup for the thiol-ene reaction is given in Figure 2.6.

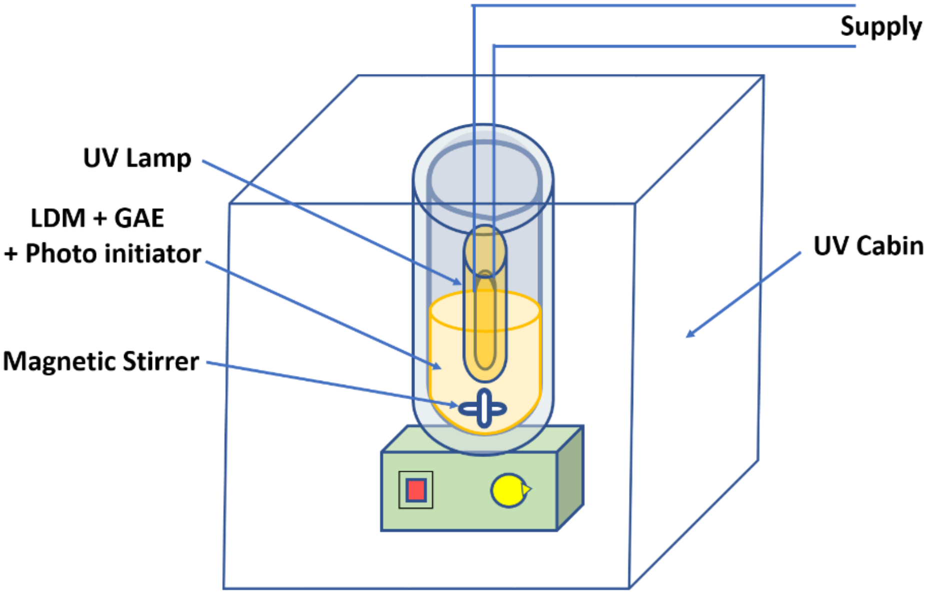


Figure 2.6: Schematic of overall Setup of the reactor for synthesis of polyol using thiol-ene reaction.

The corresponding reactions and mechanism are shown in Figure 2.7 and Figure 2.8. The process is a typical chain reaction started with initiation and then propagated. First, with the help of the photo-initiator, a thiyl radical, (-S•) was formed from a thiol (-S-H) under irradiation.[48] Then the thiyl radical reacted to the C=C bond to generate an intermediate carbon-centered radical which transferred to another thiol to form a new thiyl radical to propagate the reaction. The thiol-ene addition product, limonene-dimercaptan-based polyol was obtained after intermediate carbon-centered radical transferring.[48,49]

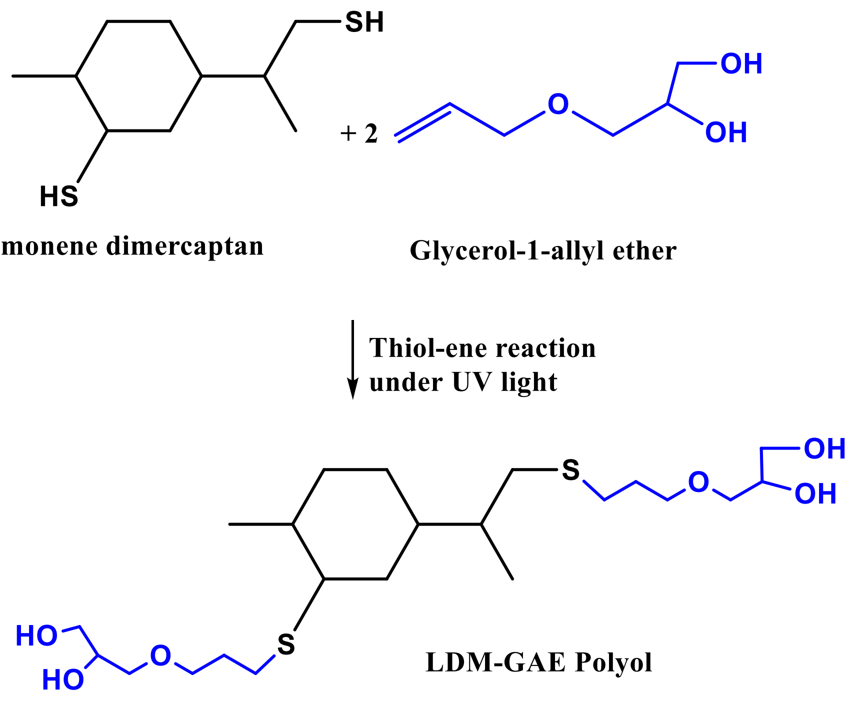


Figure 2.7: Reaction showing the synthesis of polyol using thiol-ene chemistry.

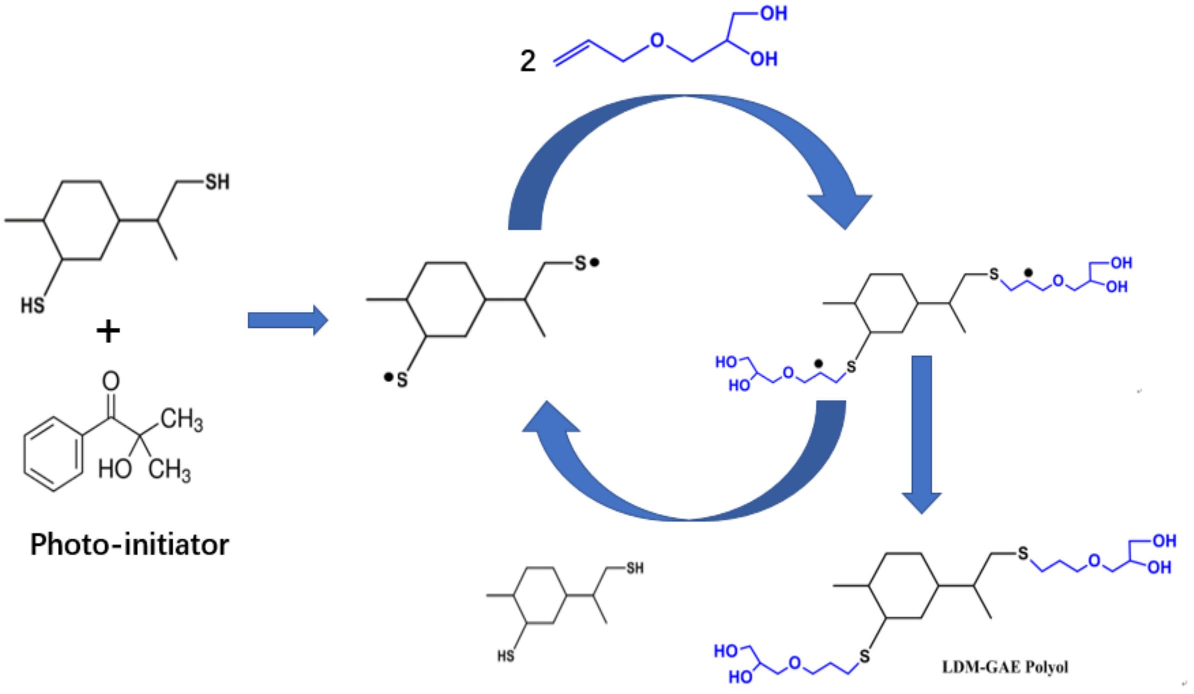


Figure 2.8: The mechanism showing the synthesis of polyol using thiol-ene chemistry.

2.2.2. Synthesis of Bromine-based Polyol

Bromine-based polyol was synthesized by reacting 0.2 mol of 2,4,6-tribromophenol with 0.4 mol of glycidol in the presence of 0.5 wt% tetramethylguanidine as a catalyst. The reactor was first purged with nitrogen several times followed by a steady pressure flow of 10-15 psi. The reaction was carried out at 105-110 ^oC. Water cooling was used to maintain the temperature due to the exothermic nature of the reaction. After 1.5 h of reaction, when exothermicity of the reaction reduces and the temperature approached about 110 ^oC, 0.4 mol of ethylene oxide was added to the mixture. The reaction was continued for further 2 h to ensure completion of the reaction. The compound was purified using vacuum distillation at 90-100 ^oC under a vacuum of 60-65 mmHg. The resulting bromine-polyol was light brown and viscous in nature. The reaction and the structure of the bromine-based polyol are given in Figure 2.9. And the mechanisms for the reactions could be the attack of the phenol group or hydroxyl group on the protonated glycidol or ethylene oxide.[50,51]

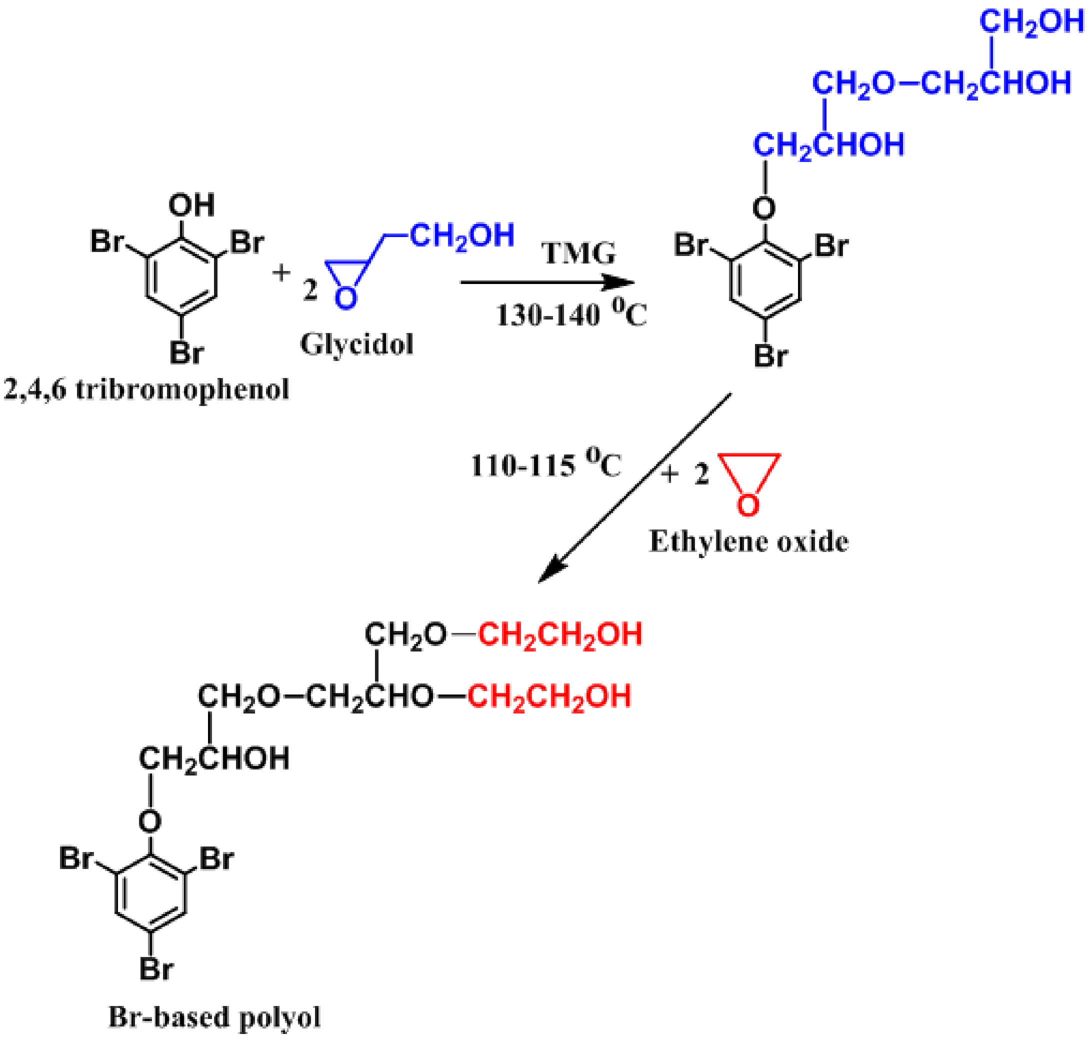


Figure 2.9: Reaction showing the synthesis of bromine-based polyol.

2.3. Characterization of Polyols

2.3.1. Phthalic Anhydride/Pyridine (PAP) Method

The hydroxyl number (OH number) of the polyols was determined by the phthalic anhydride/pyridine (PAP) method (ASTM-D 4274). Hydroxyl reagent was 2N phthalic anhydride solution in pyridine (1,000 ml), which was prepared by dissolving 148 g of phthalic anhydride and 4 g of imidozole in pyridine. First, a sample weight of 0.4 mg and 10 ml OH reagent was measured accurately and added to a 100 ml glass bottle with a magnetic bar. The bottles were capped and placed in an oven at 100 ^oC for 70 min (shaking every 15 mins) and cooled down to room temperature. Then 10 ml of water (HPLC grade), 20 ml of isopropanol (HPLC grade) and 3-5 drops of the phenolphthalein indicator (10 g/l) was added and stirred. The volume was recorded as v_o. This was titrated with 1.0 N NaOH until the color of solution turned pink and recorded the volume used as v. The OH number was calculated by the equation:

$$\text{OH\#}= \frac{56.11\times1.00\times(\text{vo}-\text{v})}{\text{w}} \text{ (mg KOH/g)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

2.3.2. Acid Value

The acid value was determined according to IUPAC2.201 standard (indicator method). For this, about 3 g of the test portion was weighed and put into a 125 ml conical flask. This was dissolved in about 30 ml of the solvent mixture prepared by using 500 ml isopropanol, 500 ml toluene, and 3 ml Phenolphthalein indicator (10 g/l in 95% isopropanol). This was titrated with 0.1N KOH to the endpoint of the indicator (pink color for at least 10 sec). The acid value of polyols can be calculated using the following expression:

$$\text{Acid Value} = \frac{56.11 \times 0.100 \times \text{V}}{\text{w}} \text{ (mg KOH/g)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

2.3.3. Viscosity Measurements

Viscosity is defined as the resistance to flow for a material. The viscosity of polyol was measured using a AR 2000 dynamic stress rheometer (TA Instruments, USA) at 25 ^{o}C with shear stress increasing from 1 to 2,000 Pa linearly. The rheometer has a cone plate with an angle between 28 and a cone diameter of 25 mm.

2.3.4. Gel Permeation Chromatography (GPC)

The progress of the reaction and molecular weight of the polyols was analyzed using gel permeation chromatography by Waters (Milford, MA, USA). It was composed of four 300 × 7.8 mm phenogel 5 µ columns with different pore sizes of 50, 102, 103, and 104 A˚. Eluent solvent was tetrahydrofuran and eluent rate was 1 ml/min at 30 ^{o}C.

2.3.5. Fourier Transform Infrared Spectroscopy (FT-IR)

FTIR was used to study for the reaction proceedings through a change in peaks of the functional groups in a FTIR spectroscopy. Shimadzu IR Affinity-1 spectrophotometer was used to record the FT-IR spectrum of the polyol at room temperature.

Figure 2.10: Pictures of (a) AR 2000 dynamic stress rheometer, (b) Gel permeation chromatography, and (c) Shimadzu IR Affinity-1 spectrophotometer.

2.4. Preparation of Flame Retardant Rigid Polyurethane Foam

Flame retardant polyurethane foams were prepared using polyols with different weight ratio, isocyanate, catalysts, surfactant, and water. The weight of isocyanate to polyols and distilled water was calculated based on the following equation:

$$w_i = Ew_i\left(\frac{Wp1}{Ewp1} + \frac{Wp2}{Ewp2} + \cdots + \frac{Wwater}{Ewwater}\right) \ldots\ldots\ldots\ldots\ldots (3)$$

where w_i, w_{p1}, w_{p2} and w_{water} are the weights of isocyanate, limonene polyol, bromine polyol and water, respectively; Ew_i, Ew_{p1}, Ew_{p2} are the equivalent weights of isocyanate, limonene polyol, bromine-polyol, respectively. Addictive flame retardant polyurethane foams were prepared using LDM-GAE polyol and commercial polyol SG-360. Reactive flame retardant polyurethane foams were prepared using LDM-GAE, SG-360 polyols and bromine-based polyol.

2.4.1. Additive Flame-retardant (AFR) Polyurethane Foams

All the ingredients were added according to Table-2.1 to prepare polyurethane foams with different concentration of phosphorus and were designated accordingly. All the ingredients except MDI were added to a 500 ml cup and stirred vigorously (3,000 rpm) to mix completely. After complete mixing, 32.07 g of MDI was added into the mixture and stirred at 3,000 rpm to make AFR-polyurethane foams designated as P-0%, P-0.2%, P-0.45%, P-0.9%, P-1.3%, and P-1.7%, respective to the percentage of phosphorus added. Then the mixture was allowed to rise at room temperature until it stopped growing and became rigid. Foams were kept at room temperature for more than a week to complete the curing process.

Table-2.1: Formulation for preparation of phosphorus-containing polyurethane foams

Compounds	P-0%	P-0.2%	P-0.45%	P-0.9%	P-1.3%	P-1.7%
Jeffol-360	10	10	10	10	10	10
LDM-GAE	10	10	10	10	10	10
DMMP	0	0.5	1	2	3	4
Tegostab B-8404	0.4	0.4	0.4	0.4	0.4	0.4
Niax-A1	0.12	0.12	0.12	0.12	0.12	0.12
T-12	0.04	0.04	0.04	0.04	0.04	0.04
Water	0.8	0.8	0.8	0.8	0.8	0.8
MDI	32.07	32.07	32.07	32.07	32.07	32.07

All weights are in gram.

2.4.2. Reactive Flame-retardant (RFR) Polyurethane Foams

Reactive flame retardant polyurethane foams were synthesized using the above method but having a various concentration of bromine-based polyol along with LDM-GAE polyol. The formulation is given in Table-2.2. The foams were designated as Br-4%, Br-4.5%, Br-5%, Br-5.5%, and Br-6% representing the bromine content in overall foams.

Table-2.2: Formulation for preparation of bromine containing polyurethane foams

Compounds	Br-4%	Br-4.5%	Br-5%	Br-5.5%	Br-6%
Jeffol-360	10	10	10	10	10
LDM-GAE	10	10	10	10	10
Br-Polyol	6.8	7.85	9	10.2	11.57
Tegostab B-8404	0.56	0.56	0.56	0.56	0.56
Niax-A1	0.16	0.16	0.16	0.16	0.16
T-12	0.06	0.06	0.06	0.06	0.06
Water	1.01	1.01	1.01	1.01	1.01
MDI	42.84	43.82	44.9	46.02	47.55

All weights are in gram.

2.5. Characterization of the Rigid Polyurethane Foams

Polyurethane foams were characterized using various methods. The details are given below:

2.5.1. Apparent Density

The apparent density of the polyurethane foams was determined according to a standard test method for apparent density of rigid cellular plastics (ASTM D 1622). The apparent density of each of the foams was calculated as an average of the densities of the top and middle portions of the foam in the direction of the rising foam. For this, a cylindrical foam with a diameter of about 45 mm and a height of about 30 mm was cut out. The weight of the foam was measured on a balance of ± 5 mg precision. After the dimensions were measured to ± 0.1 mm precision, the density of synthesized foams was calculated.

2.5.2. Closed Cell Content

The closed-cell content of the foams was measured using Ultrapycnometer, Ultrafoam 1000 according to ASTM 2856 standard method.

2.5.3. Compression Strength

The compression strength of the foams was determined using a foam with a dimension of 50 mm × 50 mm × 25 mm (length × width × height). The compressive strength at 10% strain was determined by using a Q-Test 2-tensile machine (MTS, USA) according to ASTM 1621 standard method. The compressive force rising with a strain rate of 30 mm/min was applied parallel to the direction of the foam.

2.5.4. Thermogravimetric Analysis (TGA)

A TA instrument (TGA Q500) was used to study the thermal behavior of the foams. Thermogravimetric analysis was performed under a nitrogen atmosphere by heating the foams from room temperature to 600 ^{o}C with a heating rate of 10 ^{o}C/min.

2.5.5. Microstructural Characterization of the Foams

Microstructure and cell size distribution of the rigid polyurethane foams were studied using a Phenom G2 Pro scanning electron microscope (Netherlands). Before imaging, foam samples with a sharp-blade shape were attached with conductive carbon tape and gold sputtered to avoid the charging effect during imaging.

2.5.6. Flammability Tests of the Foams

Fire-retardant properties, which are essential properties for flame retardant rigid polyurethane foams, were examined using the test method for horizontal burning characteristics of cellular polymeric materials (ASTM D 4986-98). After exposing specimens of the standard size of 150 mm × 50 mm × 12.5 mm to flame for 10 s, burning time and weight difference (before and after the burn) were recorded.

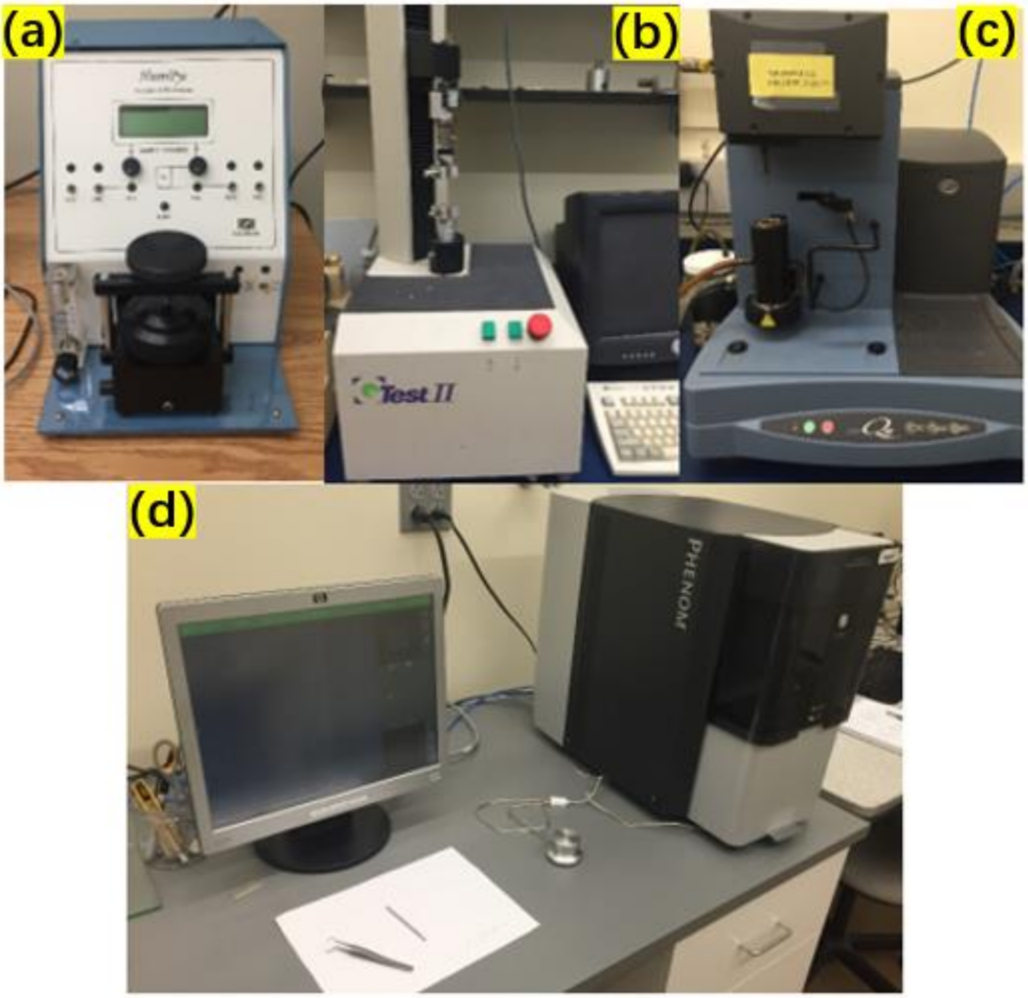


Figure 2.11: Pictures of (a) Ultrapycnometer, Ultrafoam 1000, (b) Q-Test 2-tensile machine, (c) TA instrument, and (d) Phenom G2 Pro scanning electron microscope

CHAPTER III

RESULTS AND DISCUSSION

3.1. Polyol Data and Discussion

3.1.1. Hydroxyl Number and Acid Value

The hydroxyl number (OH number) is an important characteristic which is defined as the number of hydroxyl groups available for the reaction with isocyanate groups. It is defined as the milligrams of potassium hydroxide equivalent to the hydroxyl content in one gram of the polyol. The acid value is the amount of residual acidic material in a polyol which decreases the activity of the catalyst for the gel reaction, by acid-base neutralization.[40] Therefore, it is important to control the acidity of the polyols. The acid value is reported in the same unit as the hydroxyl number (mg KOH/g).

LDM-GAE polyol showed a hydroxyl number of 470 mg KOH/g and an acid value of 0.7 mg KOH/g. Bromine-polyol showed a hydroxyl number and an acid value of 398 and 0.28 mg KOH/g, respectively. Both polyols showed a high hydroxyl number and a low acid value, which ensure a higher degree of reactivity of the polyol during the foaming process to make polyurethanes.

3.1.2. The Viscosity of the Polyols

The viscosity of a polyol can give a good measure of the extent of intermolecular forces present. The higher amount of OH number and larger molecular weight of polyols tend to have a larger viscosity due to the larger intermolecular forces because of hydrogen bonding and entanglement in the large molecules. LDM-GAE polyol showed a viscosity of 6.5 Pa.s while bromine-polyol was solid at room temperature.

3.1.3. Gel Permeation Chromatography

The gel permeation chromatography graph provides the molecular weight distribution behavior of the reacting species and the product, which was used to analyze the proceedings of the reaction. It can be clearly observed from Figure 3.1 that the retention time for LDM-GAE polyol was reduced to 35 min with respect to LDM (39 min) and GAE (38 min). This indicates that a higher molecular weight product has been formed. The sharp peak in the GPC graph of LDM-GAE indicates the narrow molecular weight distribution (polydispersity index of 1.07) of the obtained polyol. It also confirms that only one product was formed during thio-ene reaction. The disappearance of the peaks due to starting materials in the GPC curve of the polyol further confirms the completeness of the reaction. It is reported that the use of non-mercaptanized limonene showed some unreacted starting materials.[32] This problem seems to be resolved by using mercaptanized limonene oil as observed in our study.

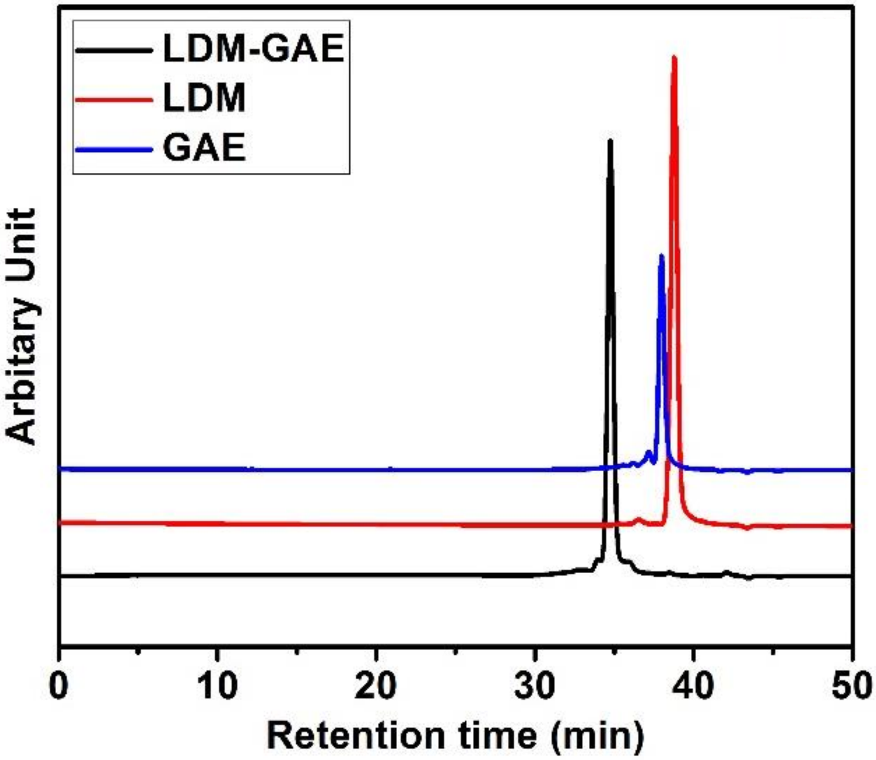


Figure 3.1: GPC graphs for LDM, GAE, and LDM-GAE polyol.

An increase in the molecular weight can be observed by the reduction in retention time of bromine based-polyol compared to other raw materials as seen in the GPC curves (Figure 3.2). GLY shows multiple peaks around 36, 38 and 42 min which could be due to the formation of oligomers due to active monomeric nature.[50-52] Due to the hydroxyl group attached to each glycidol molecule, the activated monomer mechanism results in a probability of higher amorphous structure.[53] Hence, broad molecular weight distribution is observed for the bromine-polyol. Moreover, the peak observed around 37 for 2,4,6 TBP completely disappeared in the final bromine-polyol suggesting the completeness of the reaction.

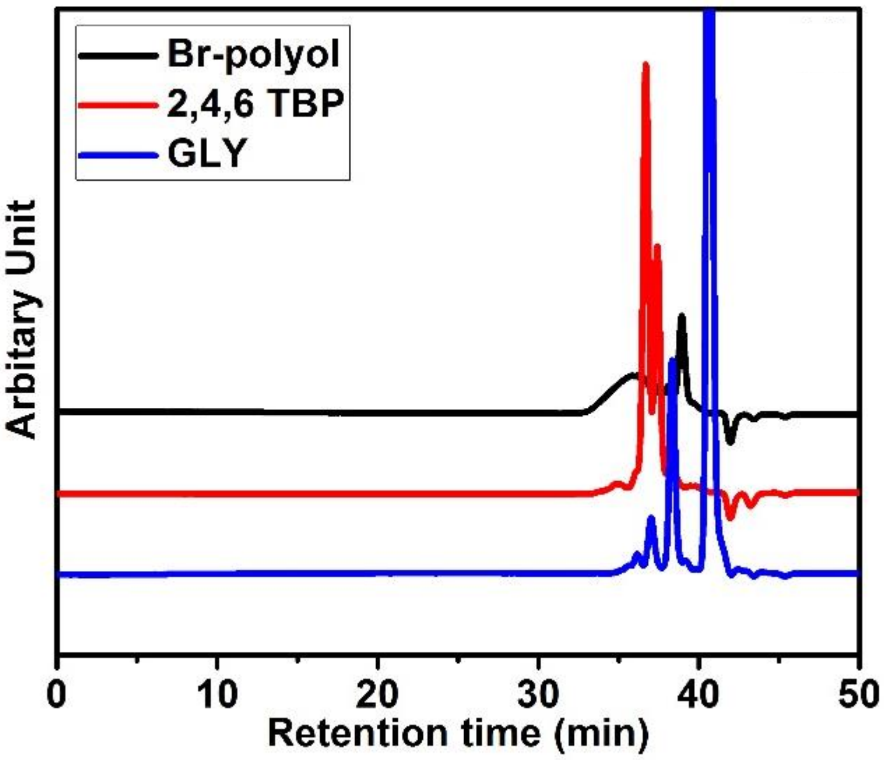


Figure 3.2: GPC graphs for 2,4,6-TBP, GLY, and Br-polyol.

3.1.4. FT-Infrared Spectroscopy

The reaction mechanism for the reacting species was analyzed using infrared-spectroscopy to confirm the desired structure of the LDM-GAE polyol. Figure 3.3 shows the FT-IR spectra of starting materials and the obtained product. As seen in the absorption graphs, the double bond of glycerol allyl ether near 1700 cm^{-1} reacts with the -SH group of LDM at 2550 cm^{-1} to obtain LDM-GAE polyol containing hydroxyl group around 3400 cm^{-1}. There is clear indication of C-S bond formation as desired by the reaction near 1086 cm^{-1} and the disappearance of the peak for -SH group in the LDM-GAE polyol, which ensures that the reaction has proceeded as desired. And the high absorption peak of hydroxyl group around 3400 cm^{-1} confirms the chemical structure of LDM-GAE polyol with a high amount of OH groups. Similar behavior was observed in other resources.[8] Thus, from FT-IR analysis, it can be stated that reaction was complete.

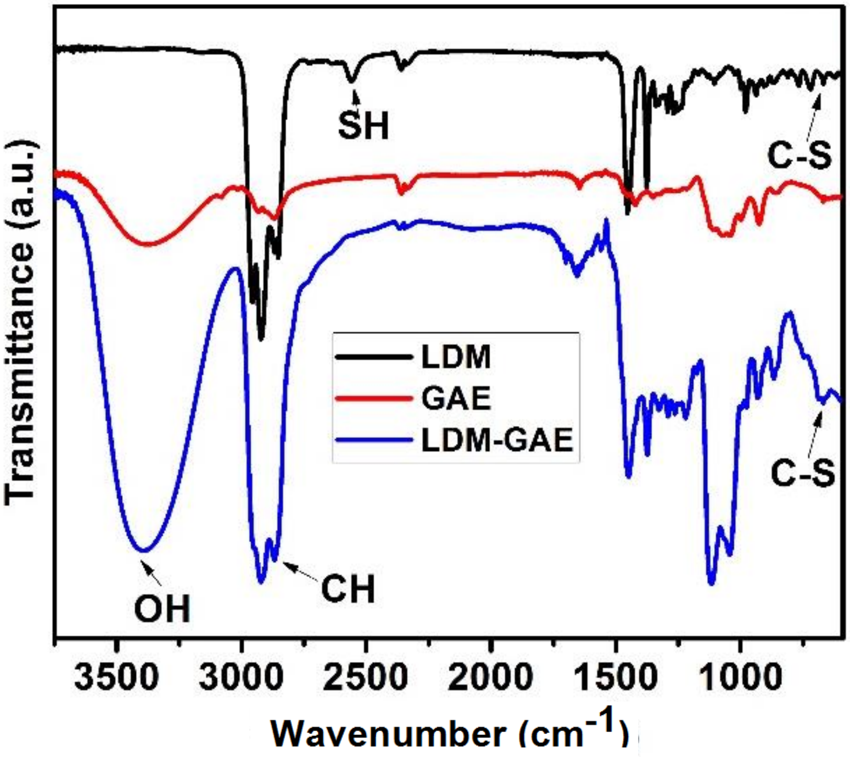


Figure 3.3: FT-IR graphs for LDM, GAE, and LDM-GAE polyol.

Figure 3.4 shows the FT-IR spectra for raw materials and the final product for bromine-polyol. As reaction proceeds between 2,4,6-TBP and GLY, the phenol group represented by the sharp peak at 1159 cm^{-1} is converted to –(C-O-C)- bond observed by a strong broad peak from 1000-1300 cm^{-1}. Further, the peak between 2937-2873 cm^{-1} represents -(CH_2)- bond as observed in GLY and final polyol. The peak at 3070 cm^{-1} which is the characteristic peak of aromatic sp^2-CH stretch can be observed in 2,4,6-TBP and final bromine-polyol. Peaks at 856, 738, 702 and 667 cm^{-1} are the representative peak for substituted benzene group followed by a peak at 675 cm^{-1} which represent C-Br bond. This represents that the compound contains an aromatic ring with bromine substitution. Lastly, the peak at around 3400 cm^{-1} represents the OH group which can be observed in 2,4,6-TBP, GLY and in bromine-polyol. The hydroxyl group is the most important functional group taking part in urethane reaction, whose appearance suggests that bromine-based reactive flame retardant could participate in the reaction with isocyanate. Hence, FT-IR curves represent the effective proceedings for the expected reaction.

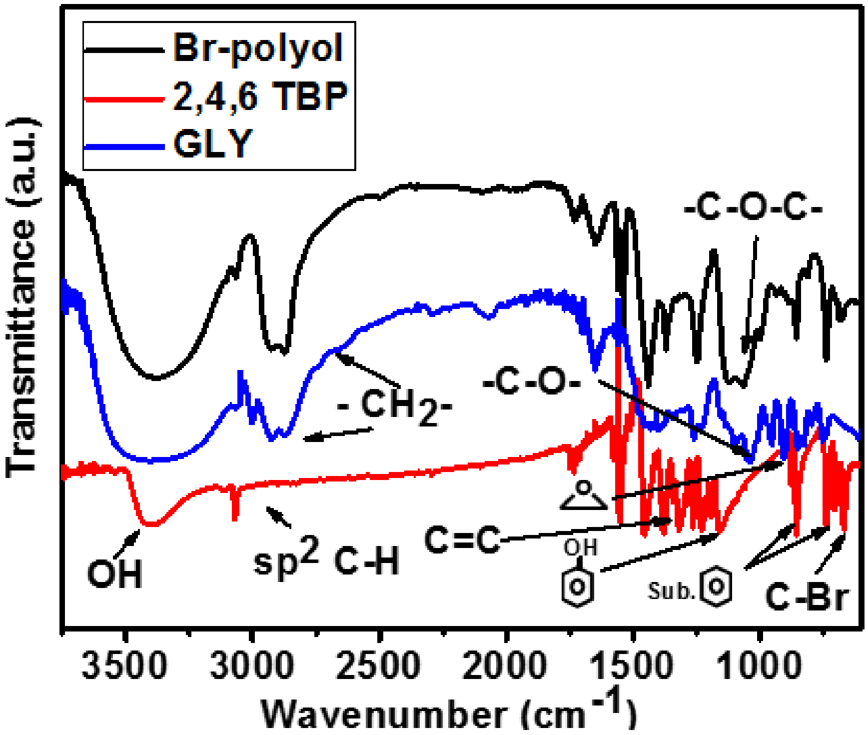


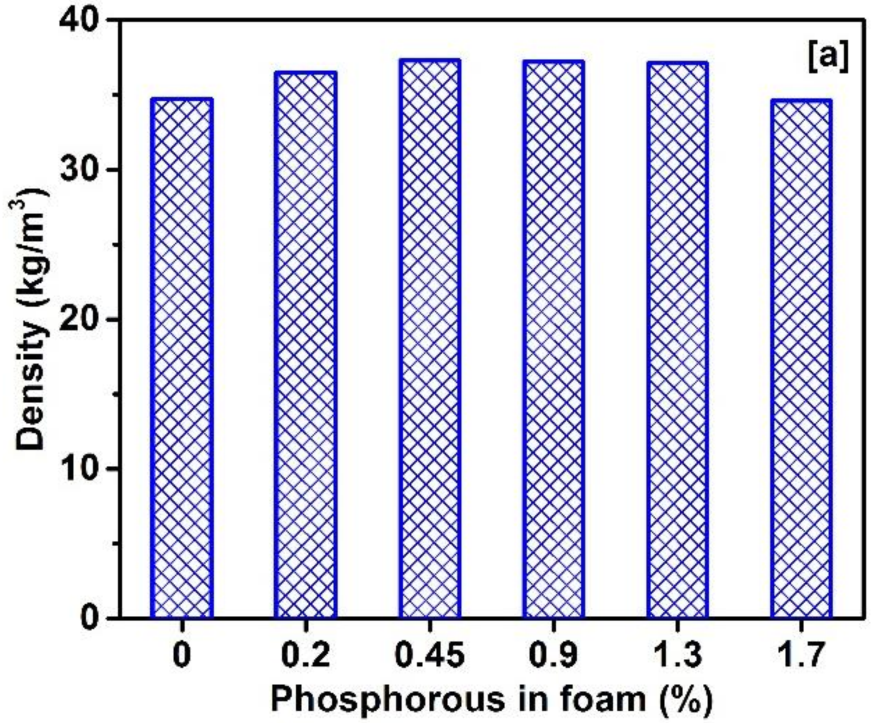
Figure 3.4: FT-IR graphs for 2,4,6-TBP, GLY, and Br-polyol.

3.2. Rigid Polyurethane Foam Data and Discussion

Rigid polyurethane foams were studied using apparent density, closed cell content, compression strength, scanning electron microscopy, and horizontal burning test.

3.2.1. Apparent Density

The density of foams is one of the most important parameters influencing physical and mechanical properties, as well as applications of the foams. The density ranges from 30 to 50 kg/m^3 is the standard for commercial industrial foams.[53] The average density of the polyurethane foams was calculated using the average density of cylindrical and square-shaped test specimens and is shown in Figure 3.5(a, b). It can be observed that the addition of DMMP showed no significant change in density of the AFR-foams, which is between 34-38 kg/m^3. It suggests that the increasing amount of addictive flame retardant DMMP could not considerably affect the formation of polyurethane foams. RFR-foams showed higher average density of about 45 kg/m^3 and significant change in the density with increasing bromine content in the foam. This could be explained as the synthetic effect of the higher bromine-polyol amount in the foams and low OH number compared with LDM-GAE polyols. The average density of RFR-foams was higher compared to AFR-foams which could be due to the larger amount of bromine-polyol and MDI participating in the reactions. For both AFR-foams and RFR-foams, overall observations show that their densities comply with industrial standards enabling its application in commercial foams.[2]



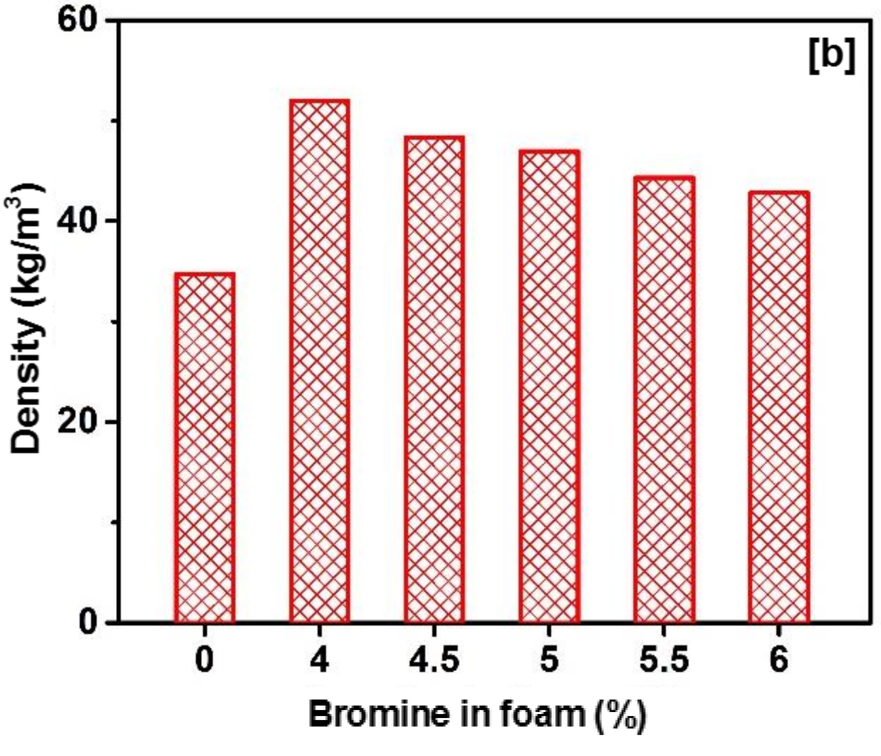


Figure 3.5: Density for (a) AFR-polyurethane foams, and (b) RFR-polyurethane foams.

3.2.2. Closed Cell Content

Closed cell structure provides excellent thermal insulation properties to rigid polyurethane foams with the lowest thermos-conductivity constant of all known materials.[38] Therefore, closed cell content is another property measurement tool to define thermal insulation characteristics of the foams. The AFR foams and RFR foams both showed closed cell content higher than 95%. Figure 3.6 (a, b) shows the percentage closed cell content for all synthesized flame-retardant polyurethane foams. A higher closed cell prevents air flow within the cellular structure preventing easy heat transfer from one cell to another resulting in higher insulation properties as well as restricting easy access to oxygen when subjected to burning. Furthermore, after comparing foams without DMMP and with DMMP, there is no change observed in closed-cell content of the foams, which suggests that the addition of DMMP does not make the closed cell structure of the foams open, unlike other additive flame retardants such as expandable graphite and melamine.[55] Similar behavior of constant high closed cell content was observed for bromine-based foams. The obtained results of AFR foams and RFR foams seem to have highest close cell content to ensure excellent thermal insulation compared to most of the other results.[8, 56, 57]

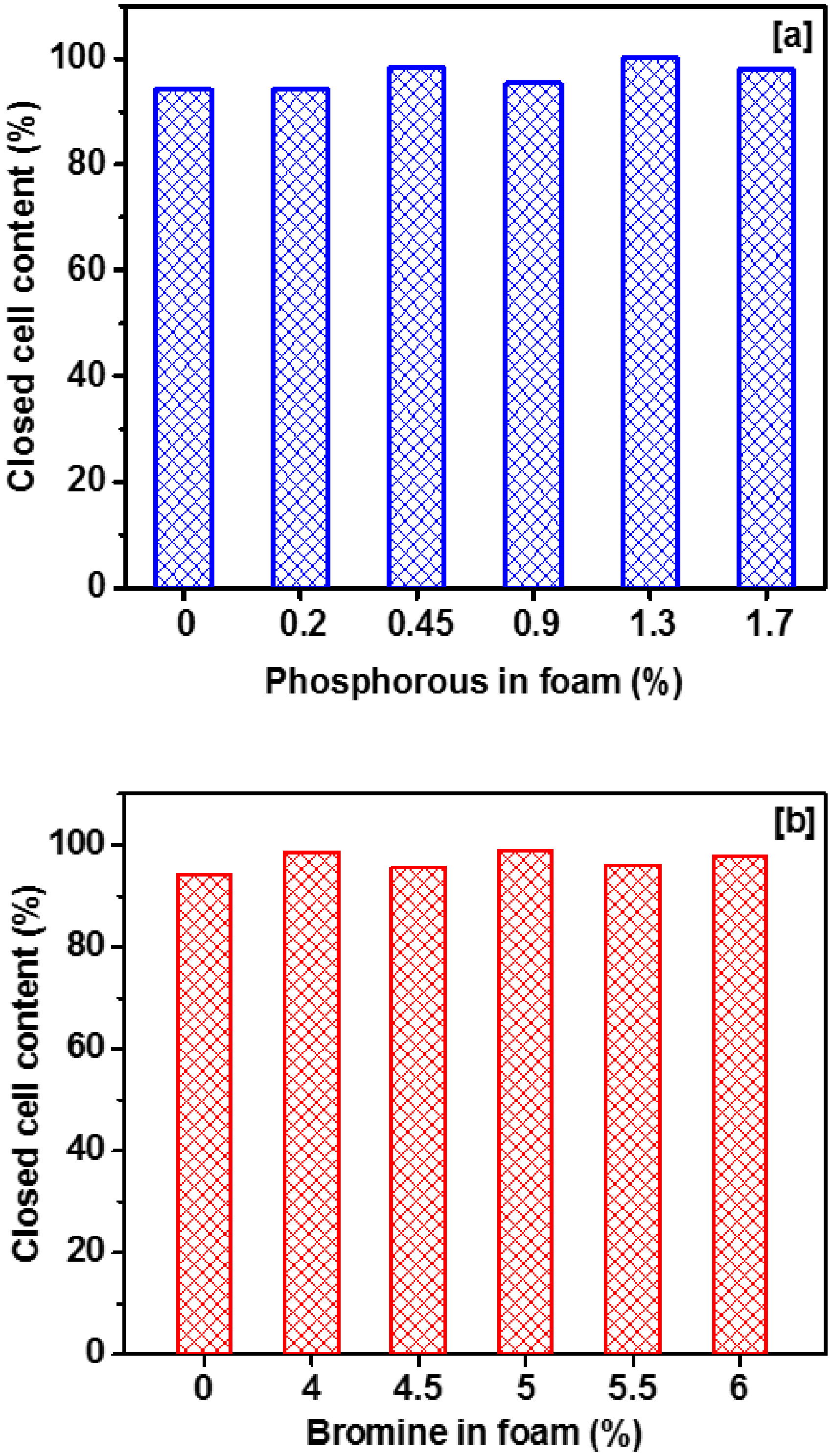


Figure 3.6: Close cell content for (a) AFR-polyurethane foams and (b) RFR-polyurethane foams

3.2.3. Compression Strength

The compression strength of all the foams is displayed in Figure 3.7 (a, b). Our results suggest gradual depreciation in compression strength properties with the addition of DMMP. Foams without DMMP showed the strength of 170 kPa which reduced to 120 kPa when DMMP was added to make a phosphorus content of 1.7 wt%. Obtained results are comparatively higher than some cardanol and castor based foams.[25,58] The observed decrease in mechanical properties could be due to the incompatibility of DMMP within the substrate. Similar behavior was observed in other reports.[34] To overcome this problem generally noticed in additive based FR approach, bromine-based RFR-foams were synthesized and used for polyurethanes. As the concentration of bromine-polyol increases in the composition, there is a respective increase in the compression strength of the RFR-foams. The compression strength increased from 170 kPa to 325 kPa when the concentration of bromine in foams increased from 0 to 6 wt%. This improvement can be due to the crosslinking effect supported by bromine-polyol within the foam structure providing sufficient rigidity to the foams. It was observed that foams from limonene with almost similar density and having higher hydroxyl number improved the number of crosslinking sites within the foams and showed higher results for ideal non-FR foams.[34] Similarly, bromine-based polyol with a higher hydroxyl number of 398 mg KOH/g would have supported in providing sufficient degree of crosslinking within the foams after being added in increased concentration. This suggests rigidity of the foams is directly dependent upon the hydroxyl number of synthesized polyols and the type of additives used for exhibiting the flame retardancy. Hence, obtained foams have a considerable amount of strength with respect to density and hydroxyl number for rigid foam application.

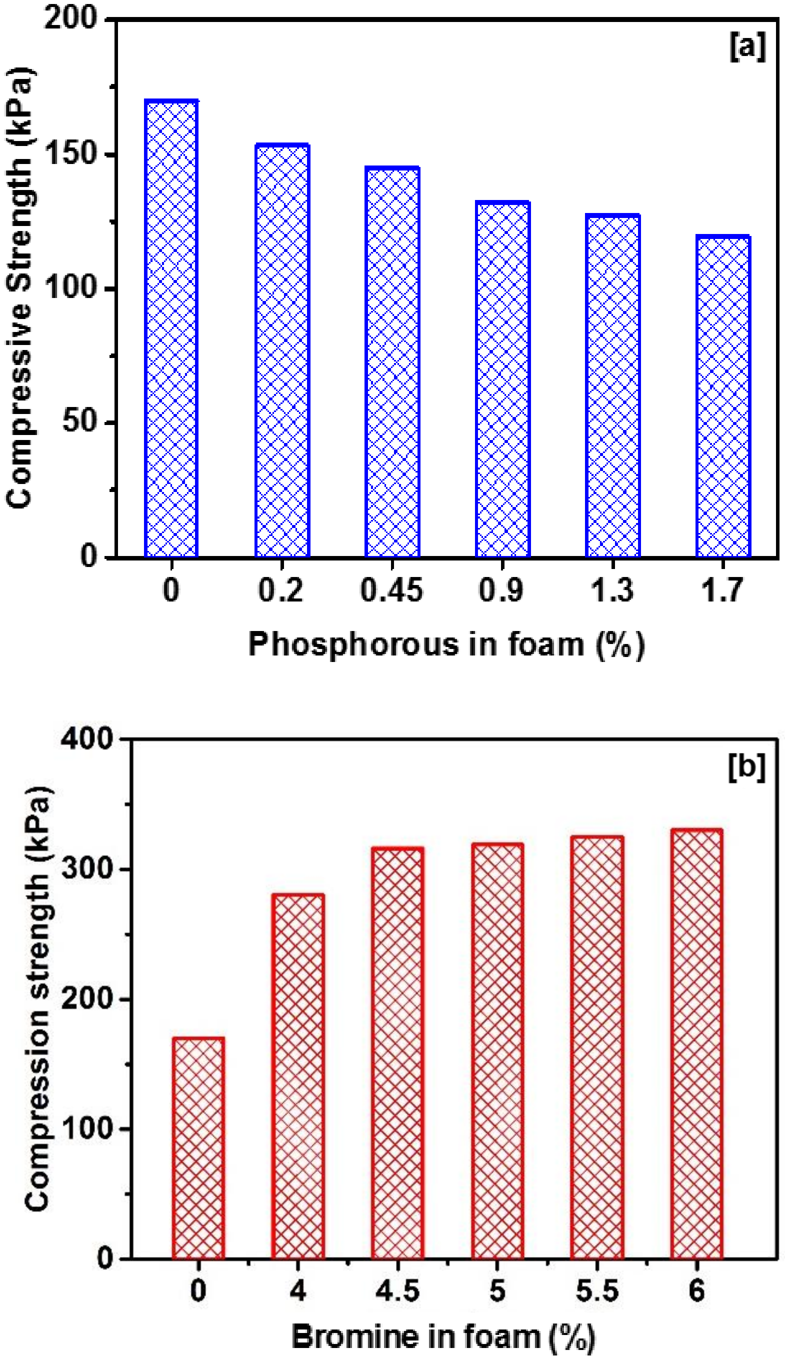


Figure 3.7: Compression strength for (a) AFR-polyurethane foams, and (b) RFR-polyurethane foams.

3.2.4. Microstructural Properties of the Foams

A scanning electron microscope was used to analyze the microcellular structure and its corresponding distribution within the foam. SEM images of all the foams are displayed in Figure 3.8 and 3.9. The overall cell size of LDM-GAE foam without any DMMP showed around 250 µm size. On addition of DMMP, there was a gradual increase observed in the cell size from about 250 to 320 µm. This could be due to the plasticizing effect of DMMP increasing the cell size of the foams. Similar behavior was observed in other reports, showing that additive flame retardants, melamine based flame retardants and expandable graphite tend to destroy the cell structure and increase cell size of foams. However, this problem is nullified in RFR-foams. Due to a higher degree of crosslinking provided by reactive bromine-polyol, the average cell size of RFR-foams is maintained to an average of 225 µm thereby eliminating any possible plasticizing behavior as provided by DMMP, showing no significant changes with the addition of bromine-polyols. Moreover, from the SEM images, all of the prepared AFR-foams and RFR-foams showed uniformly distributed cell structure with excellent density for closed cells, which further confirms the previous results for high compression strength and above 95% closed cell content.

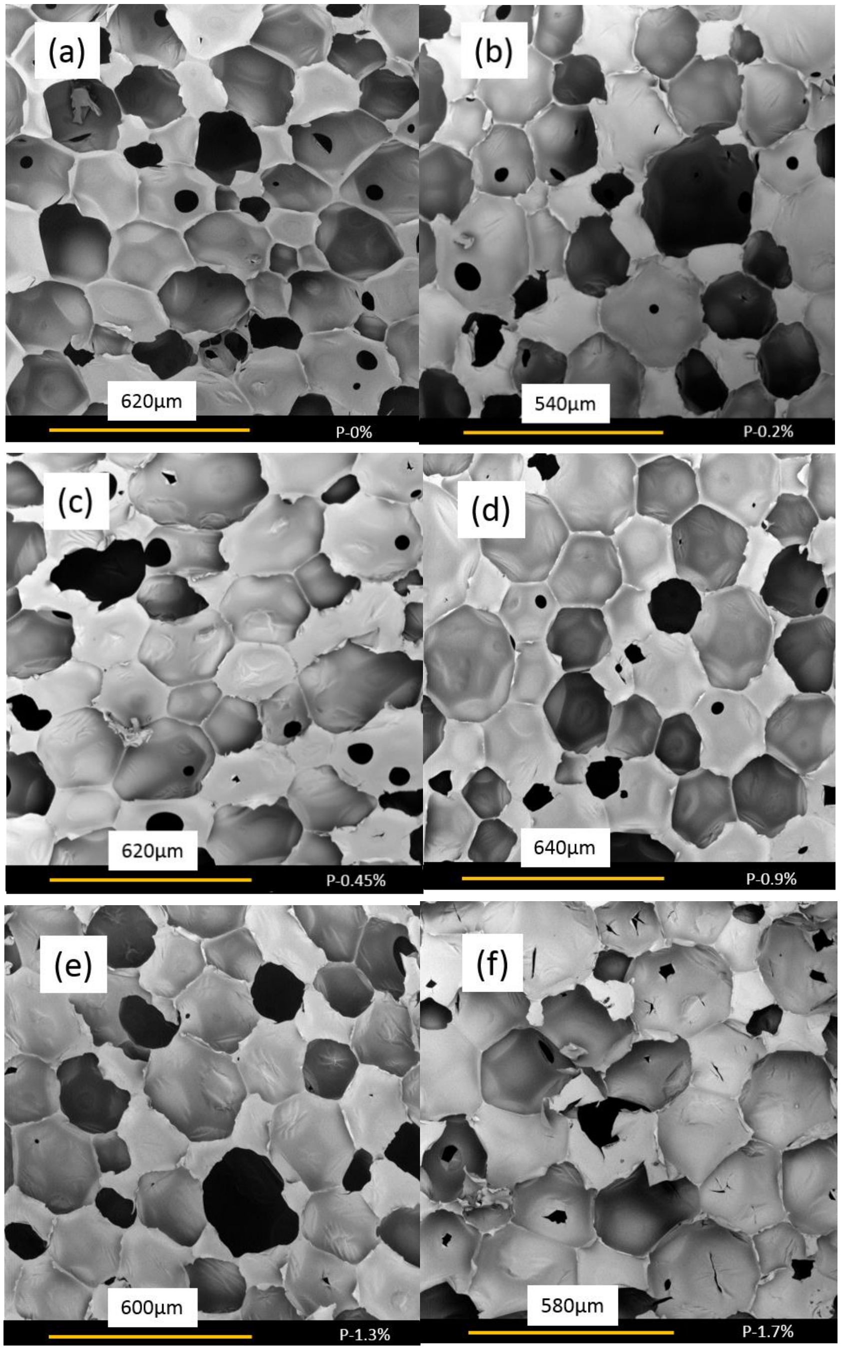


Figure 3.8: SEM images of the AFR-polyurethane foams containing various amount of phosphorus.

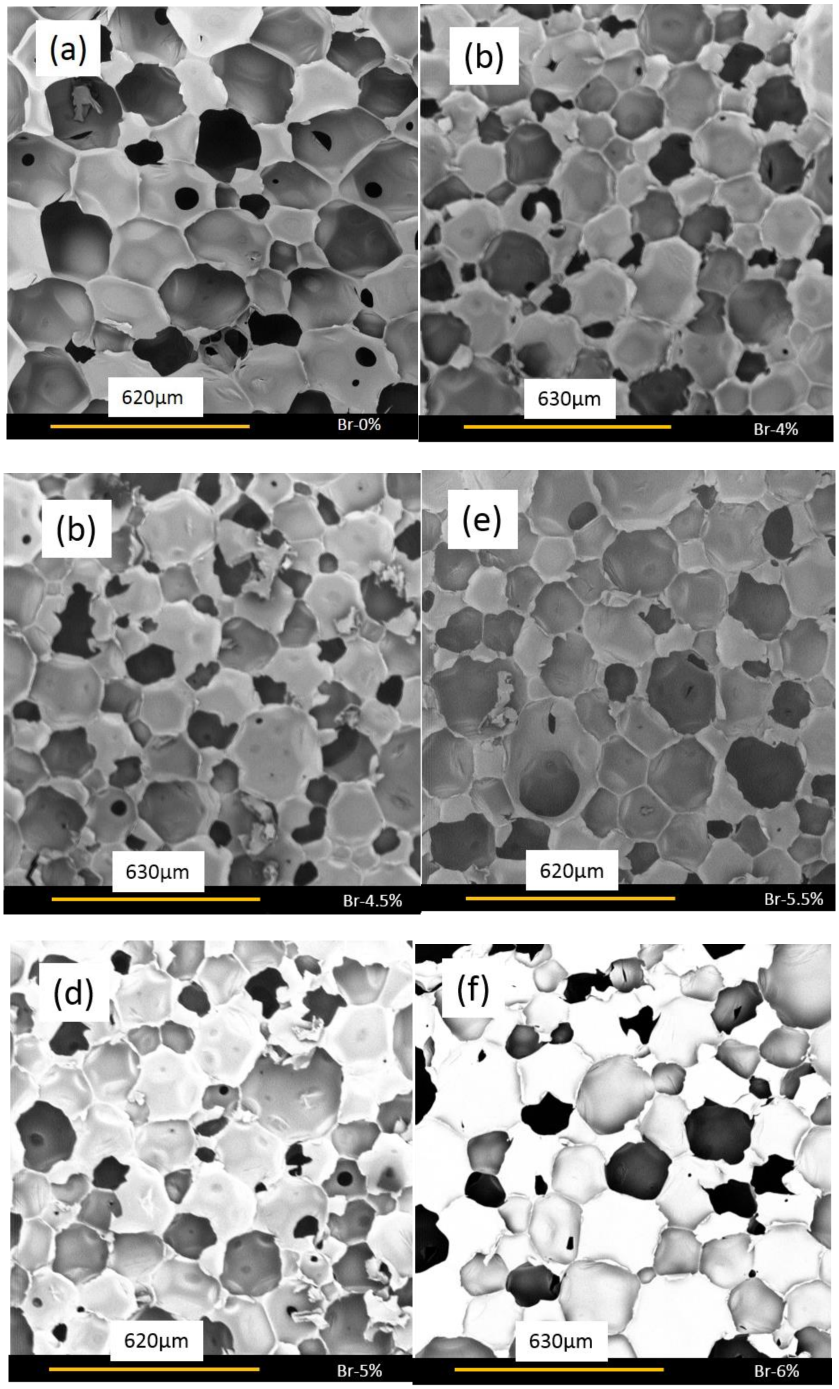
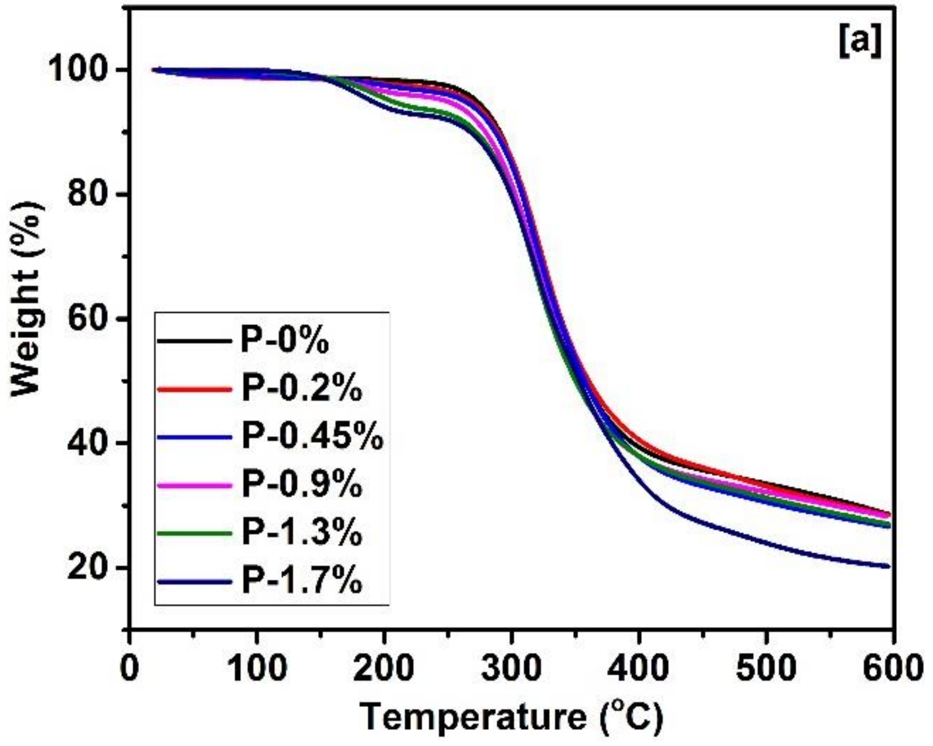


Figure 3.9: SEM images of the RFR-polyurethane foams containing various amount of bromine.

3.2.5. Thermal Degradation Properties

The thermal properties of foams were analyzed using thermo-gravimetric analysis (TGA). The TGA curves in Figure 3.10(a) for AFR-foams suggest that multiple transitions were observed with the addition of DMMP leading to a change in the thermal behavior of the foams. As temperature escalates around 130 ^{o}C, the first transition starts to occur and continues until around 250 ^{o}C. A higher amount of DMMP reduced the weight loss. This behavior was due to the increased amount of volatilization of DMMP with its addition at the elevated temperature thereby forming a better char layer which inhibits fire, consequently reducing the weight loss.[45,59] Moreover, observation suggests that major degradation of the foams occurred between 300-400 ^{o}C leading to chain cleavage and substantial depolymerization of polyurethanes. Similar behavior was observed in other results.[8,34,50] TGA curves from Figure 3.10(b) for RFR-foams showed no such thermal transitions below 300 ^{o}C which suggests no prior release of any volatile compound as seen in AFR-foams. Actual degradation of the foam occurs between 300-400 ^{o}C, during which bromine activates its flame retarding ability in the air. There were no major weight loss transitions in overall foams up to 250 ^{o}C, suggesting that RFR-foams showed thermal stability without releasing any volatiles like DMMP, as in AFR-foams, until thermal temperature reaches to actual degradation phase.



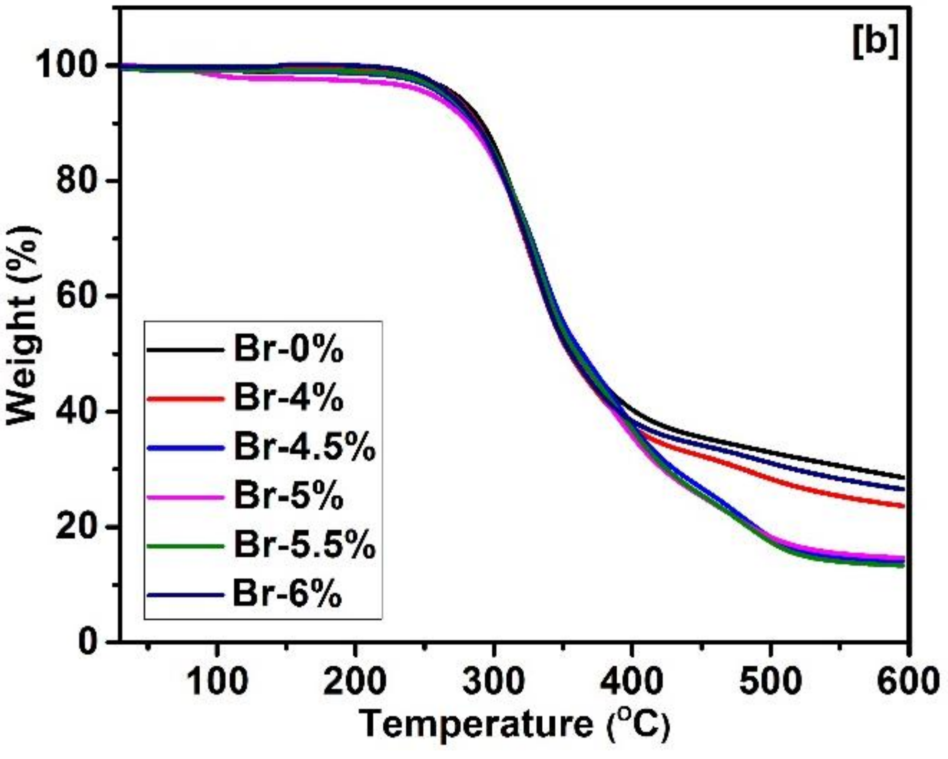
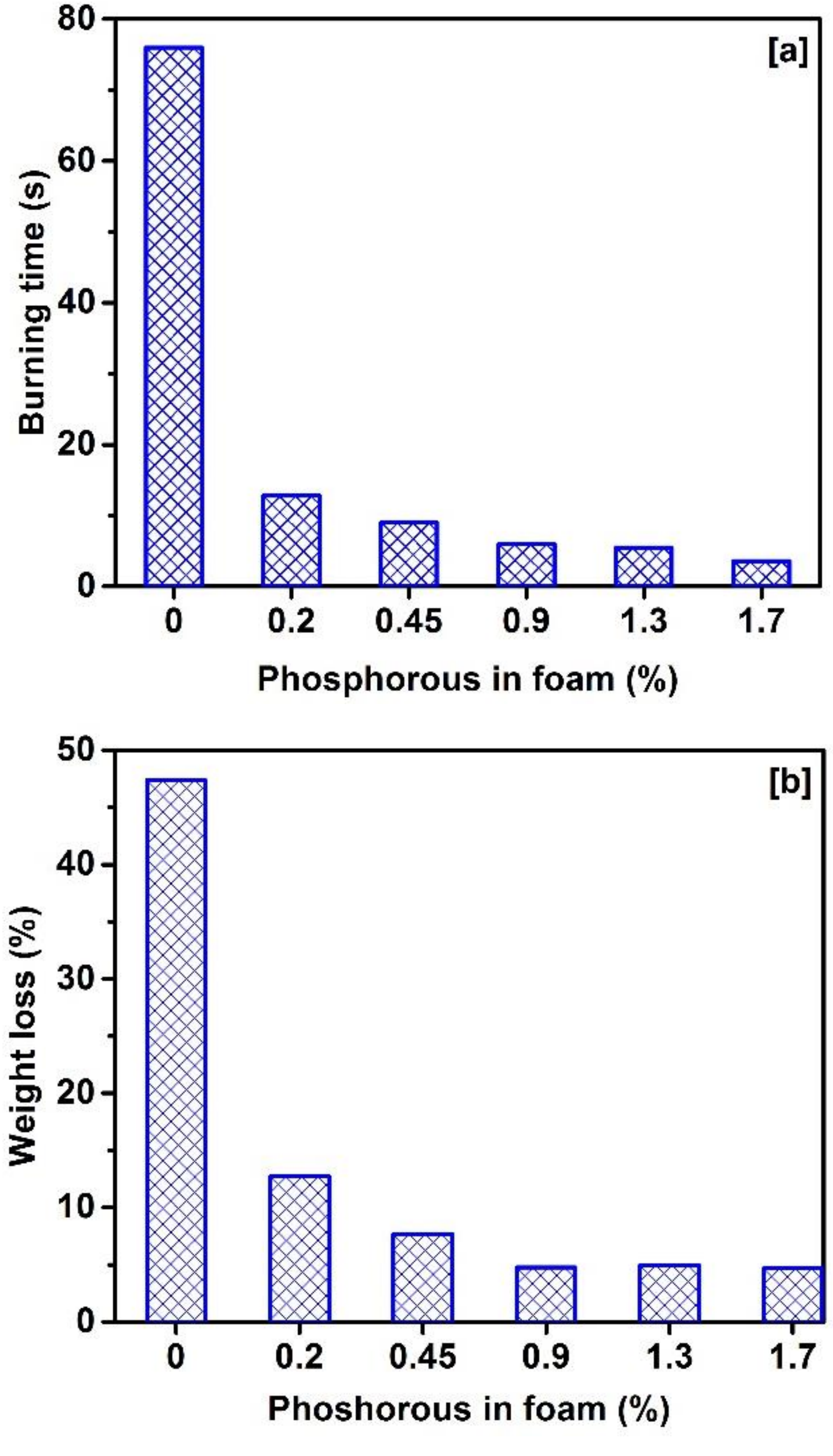


Figure 3.10: TGA curves for (a) AFR-Foams, and (b) RFR-foams.

3.2.6. Flammability Tests of the Foams

Lastly, to analyze the on-field flame retardant characteristics of the foams, the horizontal burning test was performed as per standards (ASTM D 4986-98). Results of the burning test and respective weight loss are shown in Figure 3.11 (a-d). A schematic of the test, shown in Figure 3.12 explains in detail the overall test and flame retardant mechanism for AFR and RFR-Foams. Foams without DMMP resulted in a burning time of 75 seconds with around 48 % weight loss. This time was significantly reduced to 12 seconds when the phosphorus content in AFR-foam was 0.2%. The optimum burning time was reported to be 7.5 seconds with a minimum weight loss of 4.7 % when the phosphorus content of polyol was as low as 0.9 %. All the reported results are among lowest of the overall observed results for the burning test.[6] This significant improvement in flame retardancy was due to the two-way active contribution of DMMP in condensed as well as in vapor phase.[46] Firstly, the formation of the intumescent barrier layer of char over the surface of the foams prevents the combustible media, oxygen and thermal energy to propagate. Secondly, radical phosphorus species such as PO*, PO_2* and OHPO* help in the inhibition of H* and OH*.[44] Hence, the addition of a very small amount of DMMP has led to effective flame retardancy for the polyurethane foams. For RFR-foams, the burning time was reduced from 75 seconds to 12.8 seconds and weight-loss decreased from 48% to 12.6% when bromine content in the foam was 4.5%. Further, with increasing concentration of bromine to 6% the self-extinguishing time went down to merely 7.2 seconds with 6.3% weight loss. Even with a lower concentration of bromine (around 4.5%), significant improvement in flame retardancy was observed, which is comparable to higher preferred concentrations explained in other previously reported descriptions about bromine-based FR-compounds.[60,61] This could be due to effective flame retardancy mechanism of bromine in the air. During combustion, polymers undergo bond scission producing diffused polymer fragments in the air creating combustible fuel which ignites above auto-ignition temperature, liberating heat and maintaining the fire triangle.[46] Various different radicals are produced, including very reactive species H* and HO*. These radicals are likely to react with O_2 in the air and promote the chain reaction, producing more radicals.[56] Exothermicity promotes with this chain reaction. For example, OH* reacts with CO molecule and forms CO_2 giving an exothermic reaction. Hence, Br* released from RFR-foams reacts with active OH* and H* to form less reactive and sometimes inert molecules inhibiting the burning process. Previous reports suggest similar behavior for a bromine-based compound.[46]

Figure 3.11(a, b) shows the actual photographs of various AFR-foams and RFR-foams comparing the burning behavior with increased phosphorus and bromine content, respectively. It can be directly observed that the pure polyurethane foams completely burned from one side to another side. With a little amount of addictive flame retardant DMMP or reactive flame retardant bromine-polyols in foams, there is a significant decrease for the burned surface area, which suggests the addition of DMMP and reactive flame retardant bromine-polyols considerably reduces the burning of the polyurethane foams.

[a]
Burning time (s)
0
20
40
60
80
0
0.2
0.45
0.9
1.3
1.7
Phosphorous in foam (%)
[b]
Weight loss (%)
0
10
20
30
40
50
0
0.2
0.45
0.9
1.3
1.7
Phoshorous in foam (%)

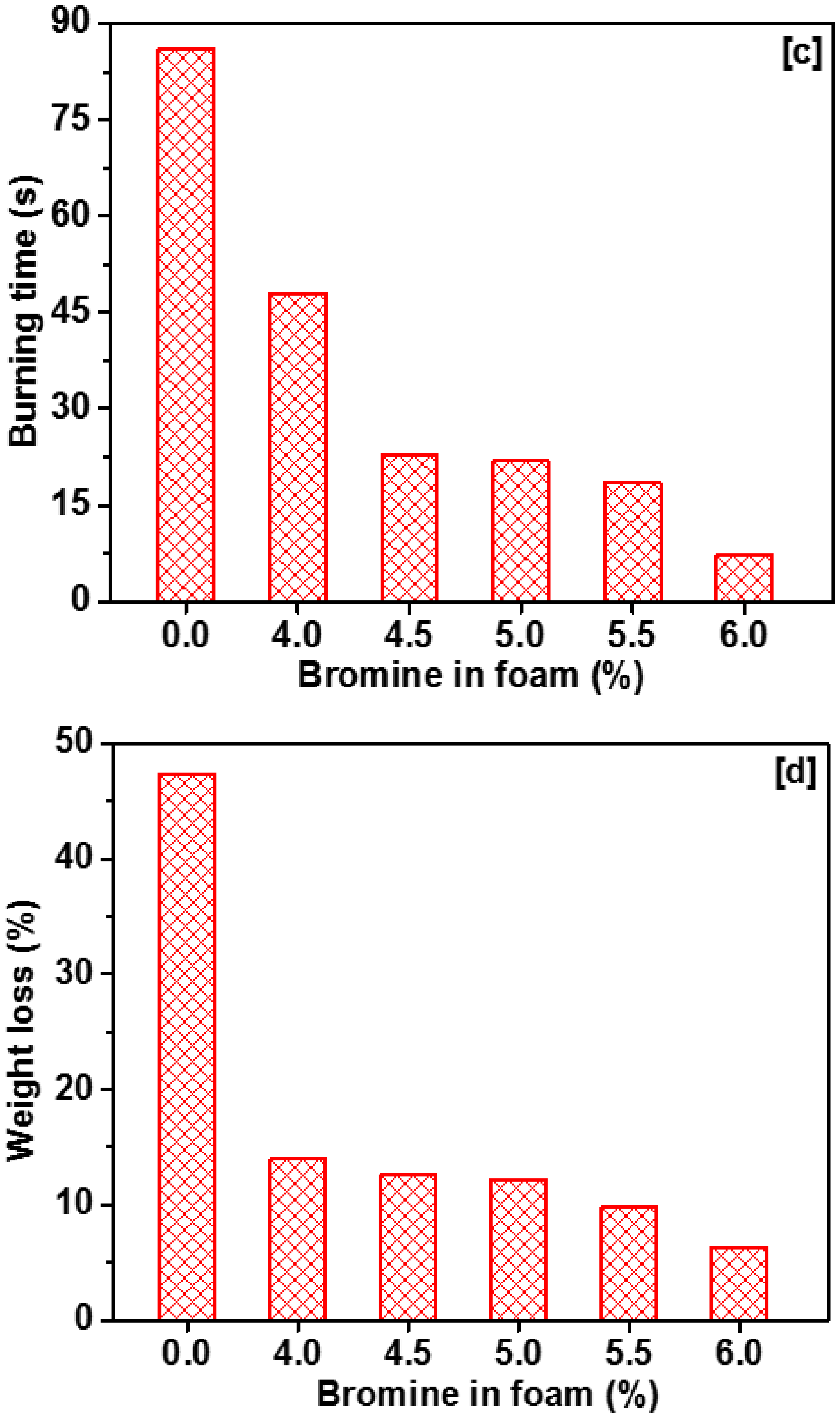


Figure 3.11: Burning time and percentage weight loss for (a, b) AFR-Foams, and (c,d) RFR-foams

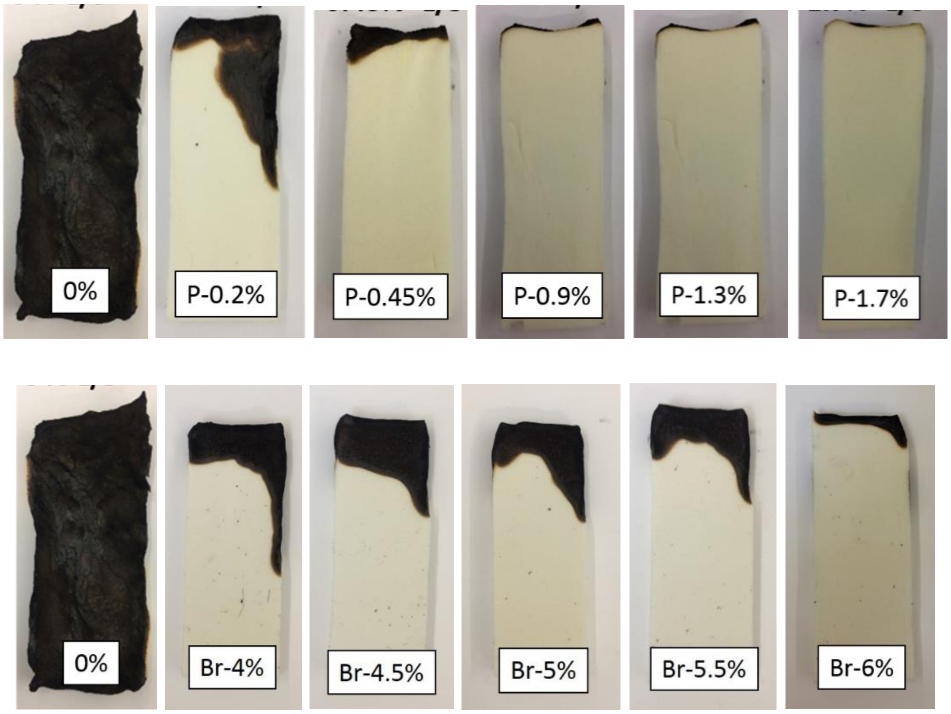


Figure 3.12: Photographs of the foams after the burring test: (a) ARF-Foams; (b) RFR-Foams.

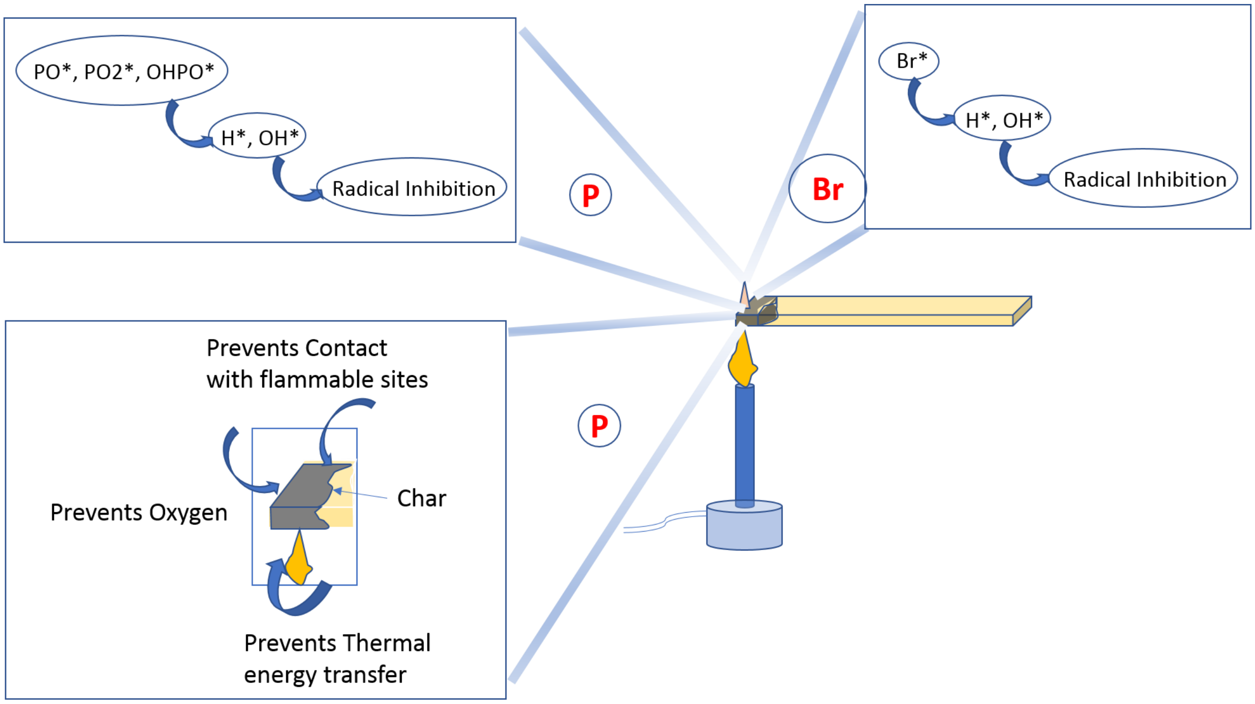


Figure 3.13: Schematic of burning mechanism and flame retarding action by AFR and RFR.

CHAPTER IV

CONCLUSION

From the overall study, it is concluded that high purity bio-based polyol can be obtained by single-step thiol-ene reaction between limonene dimercaptan and glycerol-1-allyl-ether with a low polydispersity index of 1.07. The thiol-ene reaction carried on at room temperature without any side-reactions, showing the great advantages compared to other methods for preparing polyols. The synthesized polyol was used to prepare polyurethanes which showed moderate density, high mechanical strength, and uniformly distributed cell structure with excellent closed cell content above 95%. Flame retardancy was introduced in the foams by the addition of different concentrations of phosphorus and bromine-based compounds. Dimethyl methyl phosphonate and a new bromine containing compound was added as additive and reactive flame retardants, respectively. It was observed that 0.9 wt% phosphorus in AFR polyurethanes and 4.5% bromine in RFR polyurethanes could provide an optimum extinguishing time of 7.5 and 12.8 seconds with weight loss of less than 10%. Flame retardancy in these foams could be due to radical species generated by the phosphorus and bromine in foams as well as the formation of the intumescent barrier layer of char over the surface of the foams. Moreover, with the addition of RFR, bromine-polyol, the mechanical properties of the foams improved significantly, which in contrast depreciated with the addition of AFR. The highest compression strength of 325 kPa was observed with 6 wt% of bromine in the foam while a reduced compression strength of 120 kPa was observed for the foam containing 1.7 wt% of phosphorus. The cellular size of the foams was observed to be gradually increasing with the addition of DMMP which could be due to plasticizing effect while the average cell size of RFR-foams was maintained to an average of 225 µm. Our studies showed that bio-derived polyurethanes can be highly flame retardant. The reported polyurethane foams showed efficient flame retardancy, high mechanical, and thermal properties and can be used for rigid flame retardant foam applications.

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APPENDICES

APPENDICES

APPENDICES A - List of Conference Presentations

1) **Zhang, Chunyang;** Wang, Z.; Bhoyate, S.; Morey, T.; Brooks L. Neria; Vasiraju, Venkata; Gupta, Gautam; Palchoudhury, Soubantika; Kahol, P. K.; Mishra, S. R. Felio Perez; Gupta, R.K. "Polymeric nanofibers decorated with MoS2 as an efficient and stable electrocatalyst for hydrogen generation," 15th Annual Capitol Graduate Research Summit, February 20, 2018.
2) **Zhang, Chunyang;** Bhoyate, Sanket; Ionescu, M.; Wan, X.; Kahol, P. K.; Gupta, R.K. "Highly Flame Retardant and Bio-based Rigid Polyurethane Foams Derived from Orange Peel Oil", 16th Annual K-INBRE Symposium, Overland Park, Kansas, January 16-17, 2018.
3) Bhoyate, Sanket; Ranaweera, C; **Zhang, Chunyang;** Hyatt, M.; Kahol, P. K.; Gupta, R.K. "Tea Leaves Derived Carbon for High Temperature Energy Storage Devices," American Chemical Society Midwest Regional meeting, October 18-20, 2017.
4) **Zhang, Chunyang;** Bhoyate, Sanket; Ionescu, M.; Wan, X.; Kahol, P. K.; Gupta, R.K. "Highly Flame Retardant and Bio-based Rigid Polyurethane Foams Derived from Orange Peel Oil", 2017 ACS Midwest Regional Meeting, Oct 18-20, 2017, Lawrence, KS.
5) Albeladi, N.; **Zhang, Chunyang;** Bhoyate, Sanket; Siam, S. Khamis; Kahol, K. Pawan; Gupta, Ram. "Binger Free Approach to Synthesize Nanostructured Nickel Compounds for Energy Storage Applications," American Chemical Society Midwest Regional Meeting, October 18-20, 2017.
6) Bhoyate, Sanket; **Zhang, Chunyang;** Ranaweera, Charith; Mishra, Sanjay; Kahol, Pawan; Gupta, Ram. "Binder free approach to synthesize flexible nanostructured cobalt oxide electrode for oxygen evolution reaction", 254th ACS National Meeting&Expsition, Aug 20-24, Washington, DC
7) Ranaweera, C.; **Zhang, Chunyang;** Bhoyate, S.; Jimenez, Ashley; Kahol, Pawan; Gupta, Ram. "Fabrication of cobalt oxides embedded carbon nanofibers for high performance energy storage devices", 253rd ACS National Meeting&Expsition, San Francisco, California, April 2-6, 2017.
8) **Zhang, Chunyang;** Bhoyate, Sanket; Ionescu, M.; Wan, X.; Kahol, P. K.; Gupta, R.K. "Bio-based polyols using Limonene for Rigid Polyurethane Foams with Enhanced Flam-Retardancy", PSU Student Research Colloquium, Pittsburg, Kansas, April 6, 2017.
9) Ranaweera, C.; **Zhang, Chunyang;** Bhoyate, Sanket; Jimenez, Ashley; Kahol, P. K.; Gupta, R.K. "High Performance Supercapacitor Device Based on Polymer Derived Carbon Nanofiber with Enhanced Capacity at Elevated Temperatures," 2017 PSU Research Colloquium, April 6, 2017.

10) Bhoyate, Sanket; **<u>Zhang, Chunyang</u>;** Ionescu, M.; Kahol, P. K.; Gupta, R.K. "High-quality Polyurethane Foams and Sheets from Sustainable Natural Resources," 2017 PSU Research Colloquium, April 6, 2017.
11) Bhoyate, Sanket; **<u>Zhang, Chunyang</u>;** Ionescu, M.; Kahol, P. K.; Gupta, R.K. "Polyurethane Foams/cast Sheets Using Polyols from Agro-cultivable Resources," 62nd Annual Oklahoma Pentasectional Meeting of the ACS, March 22-25, 2017.
12) Bhoyate, Sanket; **<u>Zhang, Chunyang</u>;** Ionescu, M.; Kahol, P. K.; Gupta, R.K. "Green Polyurethanes for Industrial Applications Using Eco-renewable Resources," 14th Annual Capitol Graduate Research Summit, March 10, 2017.

APPENDICES B - List of Publications

1) Ranaweera, C. K.; **Zhang, C**.; Bhoyate, S.; Kahol, P. K.; Ghimire, M.; Mishra, S. R.; Perez, F.; Gupta, B. K.; Gupta, R. K. Flower-Shaped Cobalt Oxide Nano-Structures as an Efficient, Flexible and Stable Electrocatalyst for the Oxygen Evolution Reaction. *Mater. Chem. Front.* **2017**, *1*, 1580.(Ranaweera, C. K and **Zhang, C contributed equally**).
2) **Zhang, C**.; Wang, Z.; Bhoyate, S.; Morey, T.; Neria, B.L.; Vasiraju, V.; Gupta, G.; Palchoudhury, S.; Kahol, P.K.; Mishra, S.R.; Perez, F.; Gupta, R.K. MoS_2 Decorated Carbon Nanofibers as Efficient and Durable Electrocatalyst for Hydrogen Evolution Reaction. **C 2017**, **3**, 33.
3) Bhoyate,S.; Ranaweera, C. K.; **Zhang, C.;** Morey, T.; M. Hyatt, P. K. Kahol, M. Ghimire, S. R. Mishra, R. K. Gupta. Eco-Friendly and High Performance Supercapacitors for Elevated Temperature Applications Using Recycled Tea Leaves. Global Challenges **2017**, 1, 1700063.
4) **Zhang, C.;** Bhoyate, S.; Ionescu, M.; Kahol, P. K.; Gupta, R. K. Highly Flame Retardant and Bio-Based Rigid Polyurethane Foams Derived from Orange Peel Oil. Accepted-2018. Polymer Engineering and Science 2018.
5) **Zhang, C.;** Bhoyate, S.; Ionescu, M.; Kahol, P. K.; Ghimire, M.; Mishra, S.R.; Perez, Felio; Gupta, R. K. Highly Efficient and Durable Electrocatalyst based on Nanowires of Cobalt Sulfide for Overall Water Splitting. Under review-2018.ACS Applied Energy Materials 2018.
6) **Zhang C**.; Bhoyate, S.; Kahol, P. K.; Mishra, S. R.; Gupta, R. K., "N/O Doped Flexible Carbon Cloth for Durable Metal Free Catalyst for Water Splitting," Submitted-2018, *Electrochimica Acta* 2018.

APPENDICES C - Published Work on Polyurethanes

Zhang, C.; Bhoyate, S.; Ionescu, M.; Kahol, P. K.; Gupta, R. K. Highly Flame Retardant and Bio-Based Rigid Polyurethane Foams Derived from Orange Peel Oil. Accepted-2018. Polymer Engineering and Science 2018.