EFFECTS OF SOME ADDITIVES ON THE PROPERTIES OF RIGID POLYURETHANE FOAMS: FLAME RETARDANCY, THERMAL CONDUCTIVITY AND COMPRESSIVE STRENGTH

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MSc. Thesis

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ABSTRACT

EFFECTS OF SOME ADDITIVES ON THE PROPERTIES OF RIGID POLYURETHANE FOAMS: FLAME RETARDANCY, THERMAL CONDUCTIVITY AND COMPRESSIVE STRENGTH

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Anadolu University, Graduate School of Science, January 2018

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In this study, rigid polyurethane foam composites containing aluminum trihydrate (ATH), zinc borate (ZnB), triphenyl phosphate (TPhP), and their binary blends were prepared by using one-shot method. Additive amounts were varied from 10% to 50% by polyol weight percentage, and the weight fractions of the binary blends were also fixed at 40%. The flame retardancy, thermal insulation, and mechanical properties of the foam composites were investigated. Limiting oxygen index (LOI), horizontal burning and cone calorimeter tests were performed for flame retardancy. The surface morphology, closed cell content, density, thermal conductivity and compressive strength of the foams are determined. All additives showed increases in the LOI values and decreases in the flame spread rates. Self-extinguishing was observed for the composites of 40% and 50% by polyol weight percentage. In most cases, peak heat release rate and total heat release of composites were less than those of rigid polyurethane foam. Composites with TPhP exhibited the higher amount of carbon monoxide release while composites incorporated with ATH diminished the carbon monoxide production. Composites filled with ATH demonstrated reduced total smoke release and total smoke production. The thermal conductivity values of composites containing ATH and ZnB showed decreases until the level of 7.8% compared to the foam without additives. The compressive strength values of almost all foam composites were observed to be above 120 kPa, which is an acceptable value for most of the applications. All of the results revealed that composites possessing both improved flame retardancy and preserved/improved thermal and mechanical properties can meet the demands from the foam industries.

Keywords: Rigid polyurethane foam, Composite, Flame retardancy, Thermal conductivity, Compressive strength.

ÖZET

BAZI KATKILARIN SERT POLİÜRETAN KÖPÜKLERİN ÖZELLİKLERİ ÜZERİNE ETKİLERİ: ALEV GECİKTİRİCİLİK, ISIL İLETKENLİK VE BASMA DAYANIMI

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Bu tez çalışmasında, alüminyum hidroksit (ATH), çinko borat (ZnB), trifenil fosfat (TPhP) ve bunların ikili karışımlarını içeren sert poliüretan köpük kompozitler tek atış yöntemi kullanılarak hazırlanmıştır. Katkı miktarı, poliole göre ağırlıkça %10'dan %50'ye kadar değiştirilmiştir. İkili karışımlarda ise bu oran poliole göre ağırlıkça %40'a sabitlenmiştir. Kompozitlerin alev geciktiricilik, ısıl yalıtım ve mekanik özellikleri incelenmiştir. Alev geciktiricilik için sınırlayıcı oksijen indeksi (LOI), yatay yanma ve konik kalorimetre testleri yapılmıştır. Köpüklerin yüzey morfolojileri, kapalı hücre içerikleri, yoğunlukları, ısıl iletkenlik ve basma dayanımları belirlenmiştir. Tüm katkılar LOI değerlerini arttırırken, alev yayılma hızlarını düşürmüştür. Poliole göre ağırlıkça %40 ve %50 katkı oranlarında bazı kompozitler için alevin kendiliğinden söndüğü gözlemlenmiştir. Birçok durumda kompozitlerin pik ısı salınım oranları ve toplam ısı salınımları sert poliüretan köpükten daha düşüktür. ATH katkılı kompozitlerin yanması ile toksik karbonmonoksit salınımı azalırken, TPhP içeren kompozitler yüksek miktarda karbonmonoksit salınımına neden olmuştur. Ayrıca, ATH kullanımı toplam duman salınımını da azaltmıştır. ATH ve ZnB içeren kompozitlerin ısıl iletkenlik değerleri katkısız köpüğe göre %7,8'e kadar düşürülmüştür. Neredeyse tüm kompozitlerin basma mukavemet değerleri birçok uygulama için kabul edilir bir değer olan 120 kPa'ın üstünde olduğu belirlenmiştir. Tüm sonuçlar birlikte değerlendirildiğinde, iyileştirilmiş yanma özelliklerinin yanısıra ısıl yalıtım ve mekanik özellikleri de korunmuş/iyileştirilmiş bu kompozitlerin, sert poliüretan köpük endüstrisinin taleplerini karşılayabileceği ifade edilebilir.

Anahtar Kelimeler: Sert poliüretan köpük, Kompozit, Alev geciktiricilik, Isıl iletkenlik, Basma mukavemeti.

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Emre AKDOĞAN
January 2018

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STATEMENT OF COMPLIANCE WITH ETHICAL PRINCIPLES AND RULES

I hereby truthfully declare that this thesis is an original work prepared by me; that I have behaved in accordance with the scientific ethical principles and rules throughout the stages of preparation, data collection, analysis and presentation of my work; that I have cited the sources of all the data and information that could be obtained within the scope of this study, and included these sources in the references section; and that this study has been scanned for plagiarism with "scientific plagiarism detection program" used by Anadolu University, and that "it does not have any plagiarism" whatsoever. I also declare that, if a case contrary to my declaration is detected in my work at any time, I hereby express my consent to all the ethical and legal consequences that are involved.

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ABBREVIATIONS

AHP	: Aluminum hypophosphite
APP	: Ammonium polyphosphate
ATH	: Aluminum trihydrate
CFC	: Chlorofluorocarbon
CFC-11	: Trichlorofluoromethane
DMMP	: Dimethyl methylphosphate
DPPM	: 2,2-diethyl-1,3propanediol phosphoryl melamine
EG	: Expandable graphite
FR	: Flame retardant
H-CFC	: Hydrogen chlorofluorocarbon
H-FC	: Hydrogen fluorocarbon
HFM	: Heat Flow Meter
HRR	: Heat release rate
LOI	: Limiting oxygen index
MARHE	: Maximum average rate of heat emission
MDH	: Magnesium hydroxide
MDI	: Diphenylmethane diisocyanate
OMMT	: Organic modified montmorillonite
ONC	: Organic modified nanoclay
pEG	: Pulverized-EG
php	: Per hundred polyol by weight
pHRR	: Peak heat release rate
pMDI	: Polymethylene polyphenyl diisocynate
PMMA	: Poly(methylmethacrylate)
PU	: Polyurethane
RIM	: Reaction injection molding
RPUF	: Rigid polyurethane foam
RPUFC	: Rigid polyurethane foam composite
SEM	: Scanning Electron Microscope
SNGO	: SiO_2 nanospheres/GO hybrid
t pHRR	: Time peak heat release rate
TDI	: Toluen diisocyanate

TGA : Thermogravimetric analysis
THR : Total heat release rate
TPhP : Triphenyl phosphate
TSP : Total smoke production
TSR : Total smoke release rate
TTI : Time to ignition
UL 94-HB : UL 94 horizontal burning
V : Burning rate
ZnB : Zinc borate

1. INTRODUCTION

1.1. Research Objective

Fire constitutes a tremendous destructive force in the physical world. For instance, at the end of the 2016 in Istanbul, there has been a 12% increase in all fires compared to 2012 (http-1). Fires are extremely challenging to combat and, at times, even impossible to keep under control. They cause extensive damage to human life and property every year. Several industries have been working over a long period of time to prevent or at least to retard the threat fire poses to living beings and livelihood.

Polymeric materials, which are easy to manufacture and employ, are easily combustible because of their organic structure. As in the case of a majority of polymeric materials, rigid polyurethane foam (RPUF) is also easily combustible. As a matter of fact, it is more combustible than other materials as a result of its rigid cellular and organic structure, additionally it contains flammable, explosive gases in its closed cells. During a RPUF burn, toxic gases that are extremely harmful to human health and the environment are released (Levchik and Weil, 2004, p. 1598), thus effectively limiting the use of RPUFs. To reduce the combustibility of RPUFs, various materials referred to as flame retardants (FR) are added during the production stages, such as alumina trihydrate (ATH), expandable graphite (EG), and triphenyl phosphate (TPhP). In such cases, the most important thing is to possess knowledge of the combustion stages of RPUF and select a proper FR accordingly. At the same time, it is essential to ensure that the mechanical and thermal insulation properties are not compromised by the addition of the FR.

The research objective of this project was to investigate, by means of experimentation, the combustion tendency of the RPUFs and produce rigid polyurethane foam composites (RPUFCs) with better thermal resistance compared to RPUFs with the addition of FR blends. One of the best methods toward the reduction of the combustion tendency of RPUFs is to use synergistic FR blends. Furthermore, the composite materials must preserve both the mechanical and the thermal insulation performance of RPUFCs and considerably reduce the production costs. The most effective method to improve thermal insulation is to decrease the cell size of RPUF. The FR additives may also act as agents for decreasing the cell size of RPUF, subsequently improving the thermal insulation and mechanical properties of foam structures.

The obtained composite materials of RPUFs will work to make more time available for the victims of fire to escape and douse the fire. Thus, it can be said that the materials added as FRs will have the potential to limit the loss of life and property. The composites of RPUFs used in home refrigerator industries in particular will have better thermal insulation performances with respect to the neat RPUF, thus reducing the consumption of energy. The new materials are also aimed at the prevention of the loss of energy by the enhancement of thermal insulation.

1.2. The History and Development of Polyurethane

Dr. Otto Bayer and his coworkers were researching for a new material in response to Wallace Carother’s work on polyamides and polyesters, known as nylons. Then, polyurethane (PU) was developed by Dr. Otto Bayer, recognized as the “father of polyurethane” in 1937 at the I.G. Farben Laboratories in Leverkusen, Germany (Szycher, 1999, p. 1). After toluene diisocyanate (TDI) was invented in the 1940s, PUs had begun to be utilized as foams, coatings, and cast elastomers (Fink, 2013, p. 69). The first foams were also based on TDI, and RPUFs were used as the insulation material to cover a beer barrel for the first time in 1948. PU elastomers and rigid foams had begun to be used in adhesives by the 1950s. Steel sandwich building panels were produced with the RPUFs for the first time in the year 1960. RPUFs had started to be employed as spray building insulation by 1979. Today, thermal insulation and construction are the biggest markets in the RPUF industry.

From the day PU was first discovered till today, several different types of PU materials have been discovered. PU is said to be a unique material for consumers owing to its performance and durability. The applications of PU have been depicted in Figure 1.1. PUs can be classified in the following seven main groups based on their application: flexible slab, flexible molded foam, rigid foams, solid elastomers, reaction injection molding (RIM), carpet backing, and two component formulations.

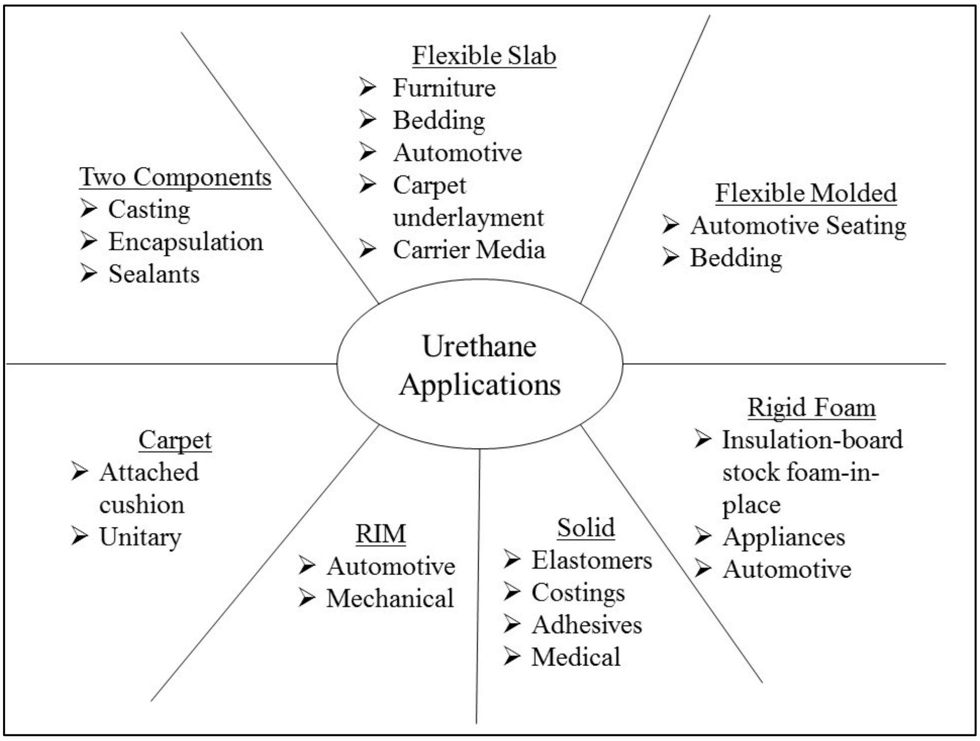


Figure 1.1. *Applications of polyurethanes (Szycher, 1999, p. 3)*

PU has a gigantic market share in the plastic industry, and the demand for rigid and flexible foam is increasing significantly day by day. According to marketing research results, the global market revenue of PU foams was estimated to be worth $40.1 billion in 2012 and $46.8 billion in 2014, and it is expected to escalate to $72.2 billion by 2020 (Marketandmarkets.com, 2015, p. 37). In 2010, the consumption of polyurethane was about 5%, but by 2012, the percentage had increased to 6% in all plastic industries. Figure 1.2 presents the percentage of global consumption of plastics in 2012.

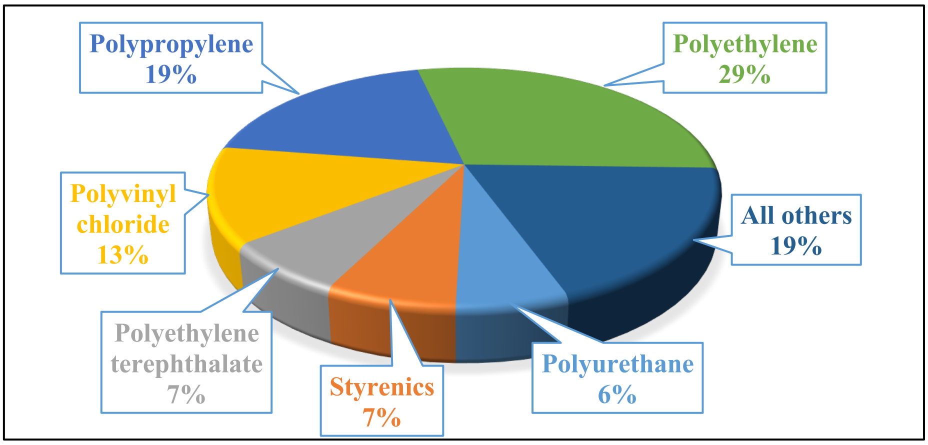


Figure 1.2. *Percentage global consumption of plastics in 2012 (Sonnenschein, 2014, p.2)*

1.3. Rigid Polyurethane Foam

RPUFs manufactured in large amounts are one of the most important thermoset polymers. PU is essentially a high molecular mass polymer that is produced as a result of polyaddition, polycondensation, or stepwise polymerization between polyisocyanates containing N=C=O groups and polyols containing O−H groups, as shown in Figure 1.3.

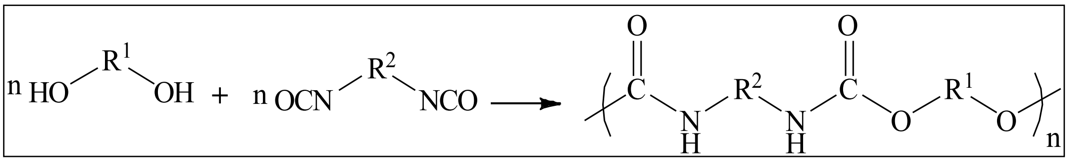


Figure 1.3. *Fundamental reaction of polyurethane*

RPUF is formed by the reaction of a polyisocyanate with a polyol in the presence of a selected catalyst, surfactant, and blowing agent. The basic steps involved in the preparation of foam are illustrated in Figure 1.4.

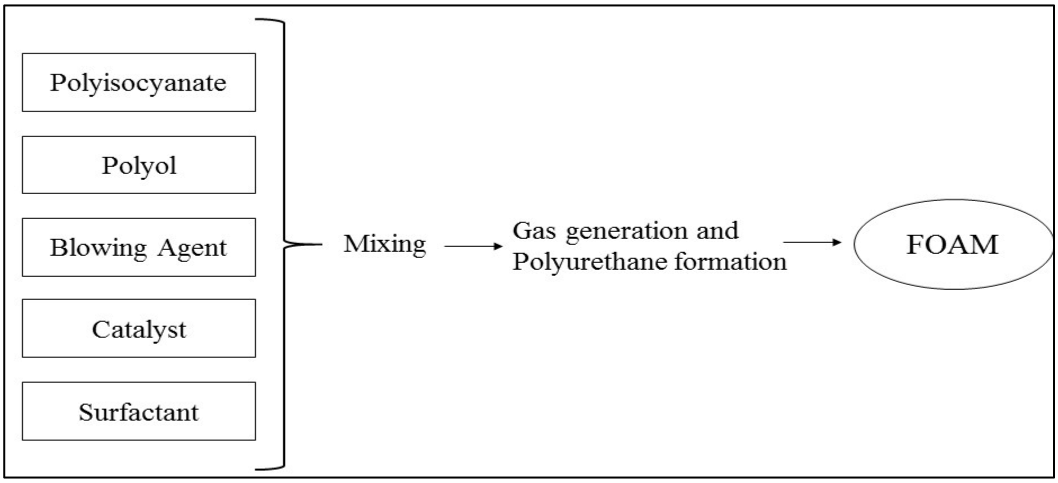


Figure 1.4. *Basic of preparation of foam (Landrock, 1995, p. 41)*

RPUFs are one of the versatile materials that have a wide range of applications, varying from domestic appliances to the automotive industry. They have several particular advantages as listed below:

- Excellent thermal insulation properties
- Produced in a wide range of densities
- Great adhesion to many type of materials, such as metal, wood, glass, and ceramics

- Ease of applications by spraying or pouring
- Display a broad range of physical properties (Szycher, 1999, p. 258)

1.3.1. Polyols

Polyols consisting of at least two hydroxyl groups are one of the main reaction partners with diisocyanates for the production of RPUFs. They react with N=C=O groups of polyisocyanate to form urethane linkages. There are two essential polyols for rigid foams—polyethers and polyesters. The physical properties of the final product are considerably affected by the choice of the polyol. The rigidity or the flexibility of the foam, its brittleness or sturdiness, and the degree of its permeability to gas and moisture are determined by the polyol used (Szycher, 1999, p. 267).

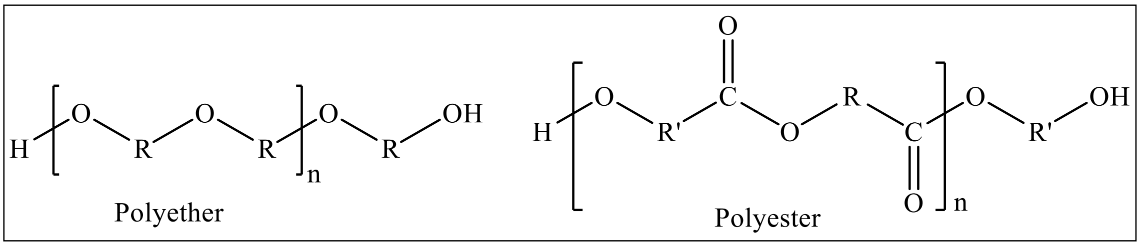


Figure 1.5. *Chemical structure of polyester and polyether (Sonnenschein, 2014, p.4)*

There are some points that can be used in the determination of the characteristics of polyols, such as equivalent weight, functionality, and rigidity or flexibility of the chain units. For example, if the equivalent weight of the polyol decreases, i.e., if the hydroxyl number increases, the compressive strength and dimensional stability will show a subsequent increase. The functionality of polyols also has considerable influence on the properties of the RPUFs. For instance, if a polyol having higher functionality is used, the RPUF will possess better heat resistance, dimensional stability, and compressive strength (Szycher, 1999, p. 268). In the recent years, foam industries have begun to use special polyols containing either halogen or phosphorous or both of them. These types of polyols are developed in an attempt to improve FR performances. The first halogenated polyester based polyol was discovered by Boulet and coworkers. (Boulet et al., 1979, U.S. Patent No. 4,173,710). For rigid foams, polyether-based polyols, which have ranging hydroxyl number from 350 to 600 mg KOH/g of polyol, are mostly preferred. In the year 2012, the production of polyether-based polyol was about 75% of the total polyol production (Sonnenschein, 2014, p. 28).

1.3.2. Isocyanates / Polyisocyanates

The importance of isocyanates, especially of polymeric isocyanates, is clearly seen in polyurethane chemistry. Toluene diisocyanate (TDI), diphenylmethane diisocyanete (MDI), and polymethylene polyphenyl diisocyanete (pMDI) are commonly used in rigid foam production. These isocyanates and their isomers are demonstrated in Figure 1.6. Isocyanates serve several purposes in RPUF, such as to react with water to form CO_2, which is a suitable gas for foaming, to join polyol molecules, and to obtain urea linkages, which provide rigidity and thermal resistance to the foam. Isocyanates are characterized by the NCO percentage content, their functionality, viscosity, and acidity, the acidity being a significant parameter that has the potential to affect the reactivity (Kapps and Buschkamp, 2004, p. 6).

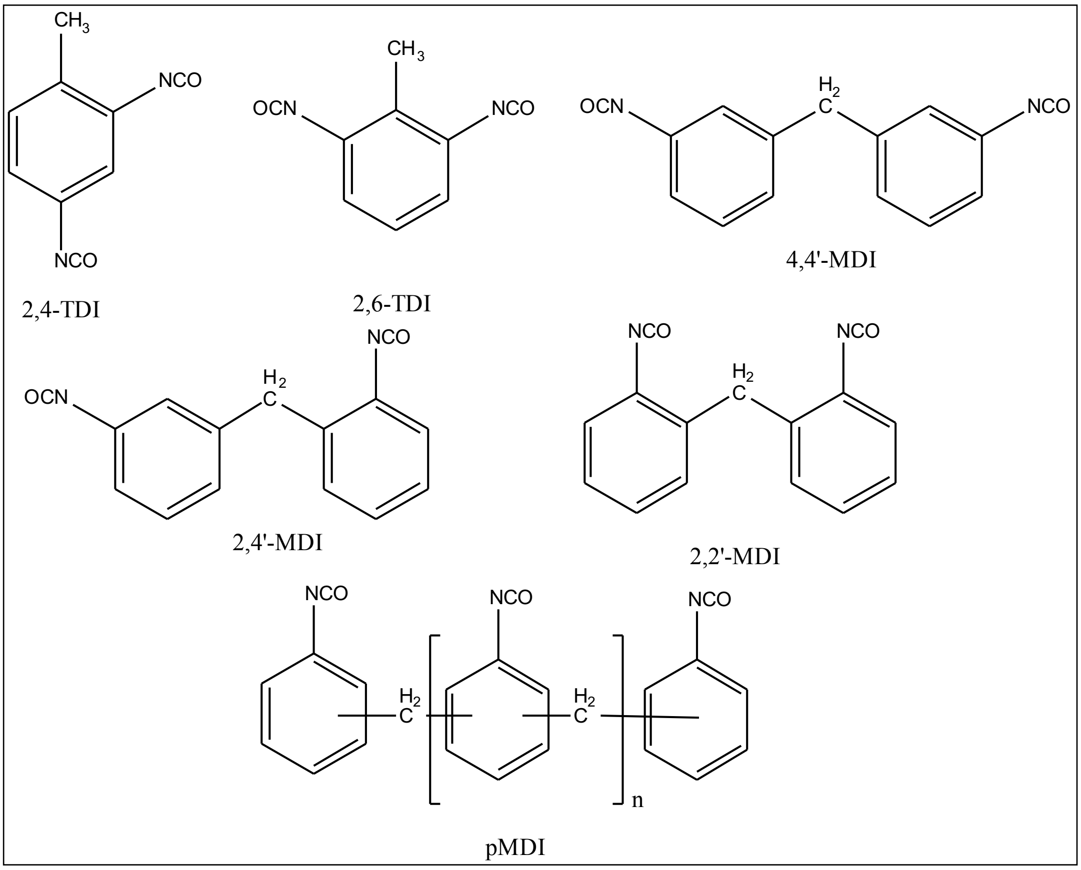
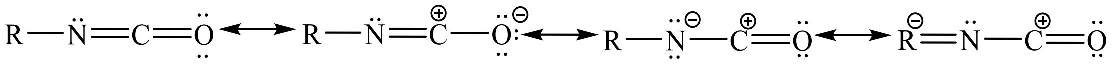


Figure 1.6. *Important isocyanates*

The PUs that are produced with the help of aromatic diisocyanates are known to be more rigid than those produced by aliphatic diisocyanates, the reason behind which is their reactivity. Polymeric isocyanates (such as pMDI) are extremely stable at the thermal level, but the oxidative stability of MDI and TDI is lower than that of aliphatic isocyanates (Chattopadhyay and Webster, 2009, p. 1084). The high reactivity of isocyanates has always been a matter of intrigue for researchers of organic chemistry. Its reactivity can be easily comprehended after an analyzation of the electronic structure of the isocyanates, as has been shown in Figure 1.7. The reactivity of isocyanates towards nucleophilic reagents is essential owing to the pronounced positive character of the C atom in the cumulative double bound sequence consisting of N, C, and O, more particularly in aromatic systems.



$$R-\ddot{N}=C=\ddot{O} \longleftrightarrow R-\ddot{N}=\overset{\oplus}{C}-\ddot{O}:^{\ominus} \longleftrightarrow R-\ddot{N}^{\ominus}-\overset{\oplus}{C}=\ddot{O} \longleftrightarrow \overset{\ominus}{R}=\ddot{N}-\overset{\oplus}{C}=\ddot{O}$$

Figure 1.7. *Resonance structures of the isocyanate group (Wang, 1998, p. 5.)*

The positive charge of the C atom is obvious from the resonance structures. Moreover, the negative charge can be delocalized onto the O atom, N atom, and the R group, if R is considered to be an aromatic group. It can be clearly understood why an aromatic isocyanate is more reactive than an aliphatic one. Another important reason why the substituents are located onto the aromatic ring is because they have the ability to easily influence the positive character of the NCO group. If there is an electron withdrawing group in the para or the ortho position of aromatic ring, the reactivity increases, while if there is an electron donating group, the reactivity reduces (Wang, 1998, p. 6).

1.3.3. Blowing agents

Cellular PUs are produced by means of blowing agents to form gas bubbles in the polymerizing reaction mixture. Two kinds of blowing agent processes are used in the preparation of PU foams—chemical and physical blowing agent processes. The oldest blowing agent is water, which reacts with isocyanates to form CO_2 for foaming, and this is referred to as a chemical agent process (Figure 1.8). The physical agent process is different from the chemical agent process. Physical blowing agents that have low boiling point vaporize because of the heat of the reaction, and the gas, which is constituted, is trapped by the cell of the foam.

There are some characteristics of blowing agents that should be paid close attention to during the choice of a blowing agent. These are its boiling point, molecular weight, vapor pressure in the temperature range of use, heat of vaporization, solubility in components and foam, compatibility with materials of construction, and reactivity (Singh, 2001, p. 7). The low thermal conductivity of blowing agents has an extensive effect on the thermal insulation of RPUFs for the thermal insulation applications (Modesti et al, 2007, p 1351).

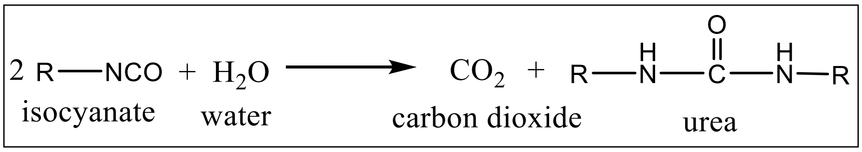


Figure 1.8. *Isocyanates/water reaction (Landrock, 1995, p. 24)*

After the use of chlorofluorocarbons (CFCs) in the late 1950s, specifically trichlorofluoromethane (CFC-11) as a blowing agent, some advantages were attributed to the closed cell rigid foams, such as low densities, good mechanical properties, and an extremely low thermal conductivity. Despite their superior attributes, it was decided by the Montreal protocol of 1987 that their utilization be discontinued because of the destruction of stratospheric ozone. In those days, hydrocarbons (n-, cyclo- and iso-pentanes), hydrogen chlorofluorocarbons (H-CFCs), and hydrogen fluorocarbons (H-FCs) had begun to be used as blowing agents instead of CFC-11. However, none of those blowing agents were equivalent to CFC-11.

Table 1.1. *Physical and environmental properties some important blowing agents (Singh, 2001, p. 10)*

	CO_2	**CFC-11**	**HCFC-141b**	**n-pentane**
Chemical formula	CO_2	CCl_3F	CH_3CCl_2F	C_5H_{12}
Molecular weight (g/mol)	44	137.4	116.9	72
Boiling point (°C)	-78.3	23.8	32.9	36.2
Gas phase thermal conductivity (mW/m.K) at 10 °C at 25 °C	15.3 16.4	7.4 7.9	8.8 10	13.7 15
Flammable limit in air (vol %)	None	None	7.6-17.7	1.3-8.0
Ozone depleting potential (ODP)	0	1	0.11	0
Global warming potential (GWP)	1	4600	700	11
Atmospheric lifetime (years)	120	45	9.2	Few days

1.3.4. Catalysts

Catalysts are also significant for the PU foams, because they accelerate the reaction rate and strike an appropriate balance between the chain extension and the foaming reaction. Isocyanate groups react quite slowly with alcohols, water, and themselves in the absence of the catalysts. If the urethane reaction is too slow, the gas will not be trapped, and the foam will not be obtained. However, if the urethane reaction takes place too fast, the PU foam will set up before the gas is formed, so that high densities polymers are obtained (Szycher, 1999, p. 278). The final properties of the PU foam depend on the amount of urethane, urea, allophanate, biuret, and isocyanurate bonds along the PU chain. On the other hand, these bonds depend on the type and the concentration of the catalyst and their mixtures, thus indicating that catalysts have a great influence on the PU structures and their final properties.

There are several types of catalysts mentioned in literature. In the case of RPUFs, the commonly used catalysts are tertiary amines, such as triethylamine and alkali metal salts such as stannous octoate and dibutyltin dilaurate. Especially when a physical blowing agent is used to form PU foam, the use of tertiary catalysts becomes necessary due to their reactivity higher than alkali metal salts. The catalysts are used in the range of 0.1–3% in diversified concentrations of the total reactants (Minogue, 2000, p. 15).

1.3.5. Surfactants

Surfactants play a great role in obtaining the required fine cell structures of RPUFs. If the surfactants are not used, the rigid foam may collapse or have a coarse cell structure. The surfactants also attribute different functions to RPUFs, such as emulsifying, foam stabilizing, and cell-size control. Surfactants for RPUF are generally silicone-surfactants. The most widely used surfactants are copolymers based on dimethyl polysiloxane and polysiloxane (Szycher, 1999, p. 281). The surfactants are used in the range of 0.1–2.01% of the total reactants.

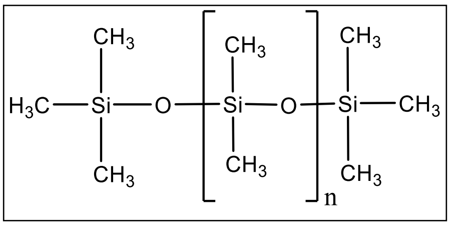


Figure 1.9. *Chemical structure of dimethyl polysiloxane*

1.4. Process of Rigid Polyurethane Foam Preparation

The main processes to prepare urethane foams are one-shot process, semi-prepolymer process, and prepolymer process. The most preferred process is the one-shot process (Figure 1.10). The semi-prepolymer process (Figure 1.11) is sometimes preferred due to the advantages it presents, such as easy processing, stabilized foam rise, and lower exotherm. In contrast, the prepolymer process (Figure 1.12) is used only for limited purposes.

The one-shot process can be used for both flexible and rigid foams. As shown in Figure 1.10, the ingredients are separately supplied to the mixing unit, but polyol, the blowing agent, the catalyst, and the surfactant are mixed in advance in order to adjust the viscosity and the mixing accuracy.

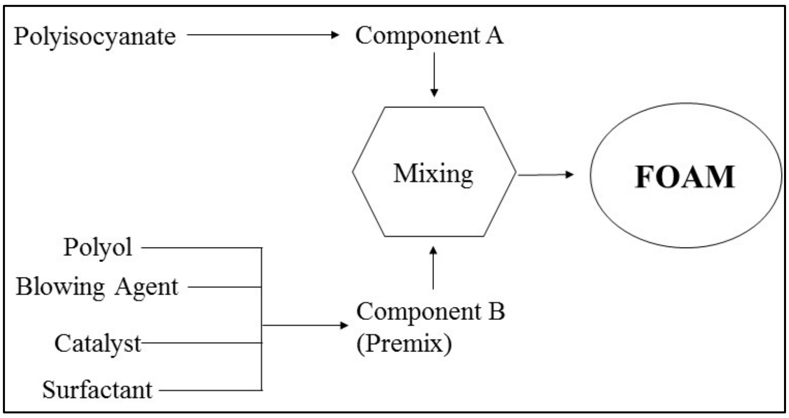


Figure 1.10. *One-shot process (Landrock, 1995, p. 44)*

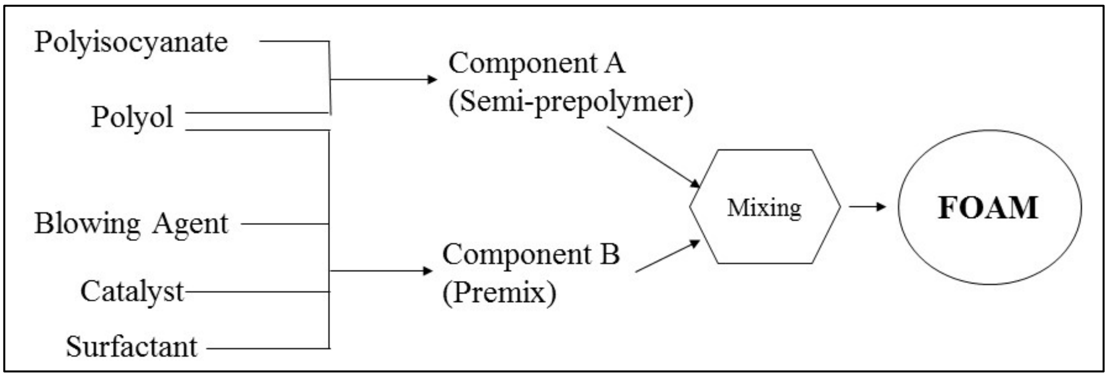


Figure 1.11. *Semi-prepolymer process (Landrock, 1995, p. 44)*

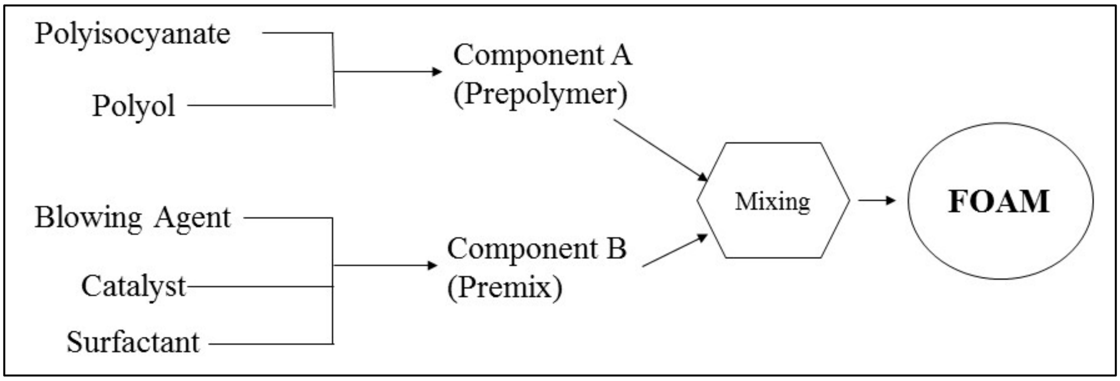


Figure 1.12. *Prepolymer process (Landrock, 1995, p. 44)*

1.5. Combustion

Combustion is a chemical reaction in which materials react quickly and uncontrollably with oxygen at a certain temperature. When the combustion process starts, it is highly difficult to control or stop, and as a result, unwanted fires take place. Unwanted fires bring about considerable loss of life and property every year. A big majority of unwanted fires are due to organic polymers which are easily combustible. Additives, called “flame retardant (FR)”, are incorporated into polymeric materials in an attempt to reduce bad consequences from the fires. The main purposes of these additives are as follows:

- To decelerate polymer combustion and degradation
- To lower smoke emission
- To prevent flame spread by dripping of hot or burning material

Fire safety regulations are arranged according to the factors which allows people the maximum amount of time possible to escape the fire. As seen in Figure 1.13, there are three required elements to continue combustion, and these elements are fuel, heat, and oxygen. When one of these elements are limited or removed from the fire, combustion may be prevented. FRs try to slow down combustion by restricting one or more of these elements (Xanthos, 2010, p. 310).

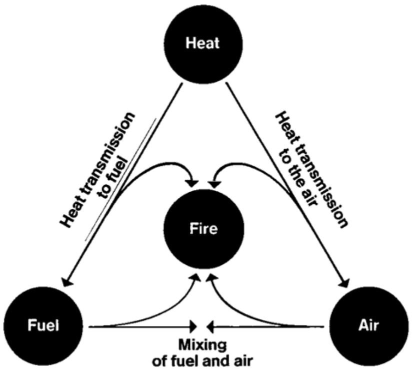


Figure 1.13. *Fire triangle (Prager and Rosteck, 2006, p. 5)*

In general, combustion is examined in terms of temperature development, and this development consists of the following four stages: ignition, growth, fully developed, and decay (Figure 1.14).

- Ignition is the first stage of combustion. In this stage, the heat that is present in the environment initiates the thermal deformation process of the material.
- Growth is completely related to how much oxygen is present in the environment. If there is enough oxygen in the environment, the flame-spread rate will be faster.

- Fully-developed is the stage in which the energy released is at the highest and the materials start to burn completely. In an addition to these, this stage is the most dangerous stage in which unburned gases are released into the environment.
- Decay is the last stage where the material is consumed by burning and the energy release rate is decreased. The heat released to the environment can go on for a while, but it diminishes later (http-2).

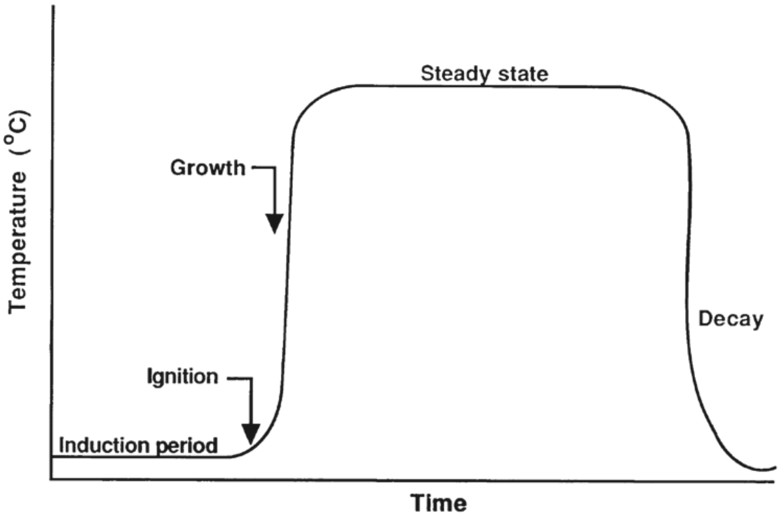


Figure 1.14. *Stages of fire (Hull and Baljinder, 2009, p. 3)*

The combustion stages of the RPUF should be well-known and FR additives should be incorporated into it such a way as to be the most effective at these stages. The upper stability temperatures for different urethane groups are bound with their activation energy. Thermal studies on RPUF and their composites are complicated by one or more of the following effects, which are specific intermolecular interactions via hydrogen bonding, crystallinity, and the presence of chemical crosslinking (Pielichowski, Kulesza and Pearce, 2003, p. 2319). With respect to thermogravimetric analysis (TGA) performed in air and nitrogen atmosphere, the thermal degradation process of RPUFs is a three-stage and a two-stage process respectively, and the oxygen in the air accelerates the process of thermal degradation. If a physical blowing agent is used for foaming, it is released at the initial stage. The temperature at which the urethane groups of RPUF (from the polyols segments of the isocyanates segments) begins to break apart from each other is about 200°C. With increasing temperature, the polyols segments split into some aliphatic ether alcohols, and the products become more complex after interacting with each other.

Between the range of 350–500°C, the dominant products of RPUF are primary amines, secondary amines, vinyl ethers and CO_2 gases (Jiao et al, 2013, p. 2695–2696).

1.5.1. Flame retardants

While selecting FRs, the most important thing is to know the structure of polymer and its fire stages. Despite the fact that FRs may vary from one another with regards to chemical structure, the mechanism of FRs can share similarities. They are mostly separated according to whether they are gas-phase-active and condensed-phase active. Gas-phase-active FRs can interrupt the radical reactions produced by the flame. The radical concentration drops below a critical value, and the flame can go out. The mechanisms of condensed-phase-active FRs greatly outnumber the mechanisms of gas-phase-active FRs. Charring is the most common known condensed-phase-active mechanism. FRs which are put out by the cooling effect of water, such as aluminum hydroxide and magnesium hydroxide, are almost physically active. On the other hand, there is no FR showing chemical activity alone. Chemical mechanisms are always accompanied by one or several physical mechanisms. FRs can be classified as explained below:

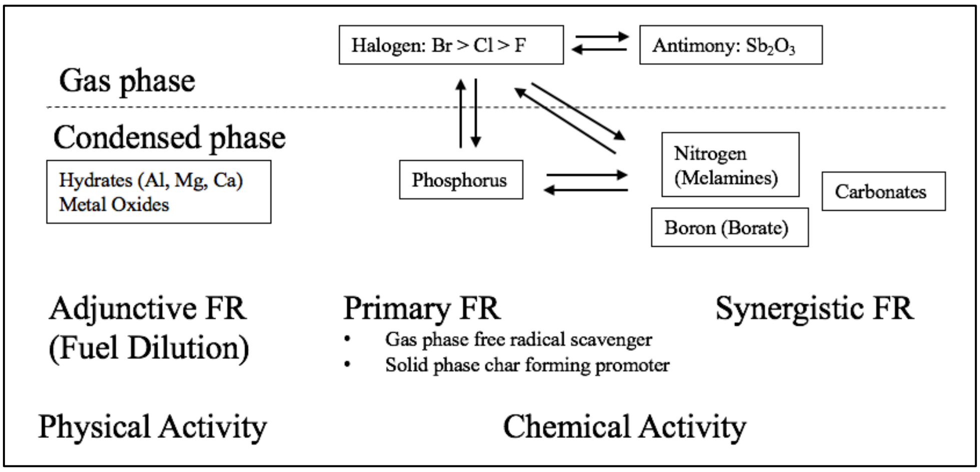


Figure 1.15. *Chemical mechanism of flame retardants (Xanthos, 2010, p. 318)*

Halogen-containing flame retardants: These groups represent the most diversified class of retardants. These needs to emit halogen in the form of radical or halogen halide at the same temperature range or below the temperature of decomposition of the polymer in an effort to be effective. Basically, fluorine, chlorine, bromine and iodine can use as halogenated FRs. Halogen-containing FRs, which are chemically active in the gas phase, prevent the formation of small molecules required for combustion, form a gas layer on the flame and thus the flame temperature decreases.

Phosphorus-based flame retardants: These are the second prevalently used class of FRs. Last research shows that FRs have shifted from halogen-containing FRs toward phosphorus-based and other halogen-free systems owing to their toxic effects. It is commonly said that FRs containing phosphorus are notably effective in the polymers bearing oxygen or nitrogen. Ammonium polyphosphate (APP), TPhP, phosphines, phosphonium compounds, elemental red phosphorus etc. are all used as phosphorus-based FRs. The mechanisms of these compounds generally take place in the condensed phase by enhancing char residue of polymer. But TPhP works only in the gas phase (Pawlowski and Schartel, 2007, p. 1404). This char residue on the surface of polymer provide a protective barrier blocking out oxygen entering into combustion zone.

Melamine flame retardants: Melamine is a peerless product with 67 wt% nitrogen in the molecule and pretty high thermal stability. It also makes up thermally stable salts with strong acids. It is widely used in flexible PU foams in combination with some phosphates. It is known that melamine does not melt, but sublimes at about 350°C. Upon sublimation, significant energy absorbed, which decreases the surface of the polymer.

Inorganic hydroxides flame retardants: These are inorganic compounds that contain water in their structure, such as ATH and magnesium hydroxide (MDH). These kind of FRs are usually chemicals that can release water upon heating above 200°C and this water which is released helps to slow down the combustion. Their biggest disadvantage of using ATH or MDH is that the mechanical properties of the polymers are adversely affected due to high loading level of the fillers to be incorporated into polymers in an attempt to obtain better flame retardancy.

Borate flame retardants: They are composed of two groups as water-soluble and water-insoluble, and the water-insoluble ones are more thermally stable. For instance, zinc borate $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$, known as Firebrake ZB, loses about 13.5 wt% water at 290 to 450°C. There are several zinc borates which release different amount of water. When the polymer doped with zinc borate is heated somehow, zinc borate loses water endothermically, and this water absorbs heat.

Intumescent flame retardants: Expandable graphite (EG) can be given as an example of an intumescent FR system. When the EG is heated it will expand up to 100 times its original thickness, constituting a worm-like structure that covers the whole burning surface of the material. The expanded graphite constitutes an insulating char layer over the burning material. This insulative char layer serves as a physical barrier preventing heat transfer from the flames into the material, also slowing the diffusion of oxygen into the underlying fuel (Adeosun, 2014, p.23).

Synergism: This concept is usually used in the optimization of flame retardant formulations; but synergism is sometimes misinterpreted. By definition, *synergism* means increased performance of the mixture of two or more components by comparison with the simple additive performance of the components at the same concentration. The two mostly used examples of synergism are halogens with antimony and phosphorus with nitrogen. Except for antimony, halogen-containing FRs are synergistic with other metal oxides, including Bi_2O_3, SnO_2, Fe_2O_3 and zinc borates (Morgan and Wilkie, 2007, p. 7–19).

1.6. Thermal Conductivity of Rigid Polyurethane Foams

Because of increasing energy needs throughout the world, thermal insulation has become one of the major concerns in the development of heat-transfer technology. Polymeric foams are more efficient thermal insulation systems than any other conventional products. The thermal insulation performance of RPUF compares with that of other materials in Figure 1.16. It is obviously seen in the figure that other materials need to be used at much higher thickness in order to match the insulation performance of 50 mm RPUF.

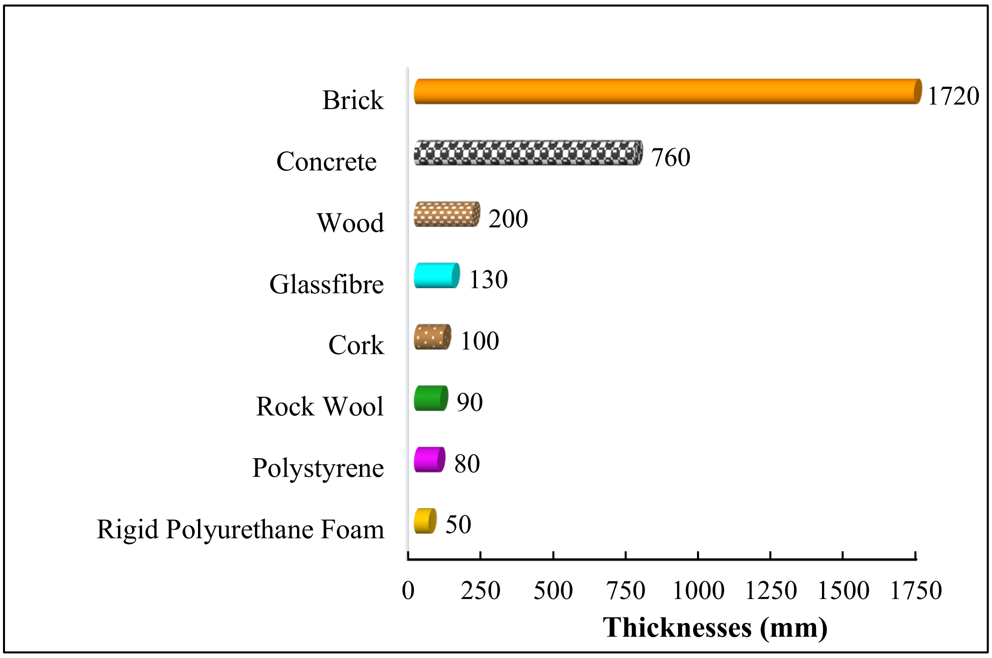


Figure 1.16. *Equivalent thicknesses for the same thermal insulation properties of different materials (Lee and Ramesh, 2004, p. 262)*

As seen above, one of the biggest advantage of RPUF is its low thermal conductivity, which is at 18-28 mW/(m.K). RPUFs predominantly contain closed-cell structures, and in the closed-cell structures of foams a blowing agent constituting the gas is trapped during production. The thermal conductivity of RPUF is strongly affected by this blowing agent. The lower thermal conductivity of the blowing agent, the lower thermal conductivity of RPUF. In addition to this, the mean cell size has also a great impact on the RPUFs thermal conductivity. In fact, the total thermal conductivity of RPUF can be explained as the heat transfer through foams, which includes three mechanisms: conduction through solid, conduction through cell gas representing at least 50% of heat transferred, and radiation representing about 30-40% of the total, as shown in Figure 1.17. One main problem about the use of RPUF is their thermal aging which means the getting worse of insulation properties in time. Conduction through cell gas changes in time due to outwards diffusion of gases inside the cells and inwards diffusion of air and radiation is mainly affected by the mean cell size: the lower the cell size, the lower the contribution. It has also been known that the contribution of gas convection is insignificant for the typical cell size of RPUF (Glicksman, 1994, p. 105, Modesti, Lorenzetti and Besco, 2007, p. 1351).

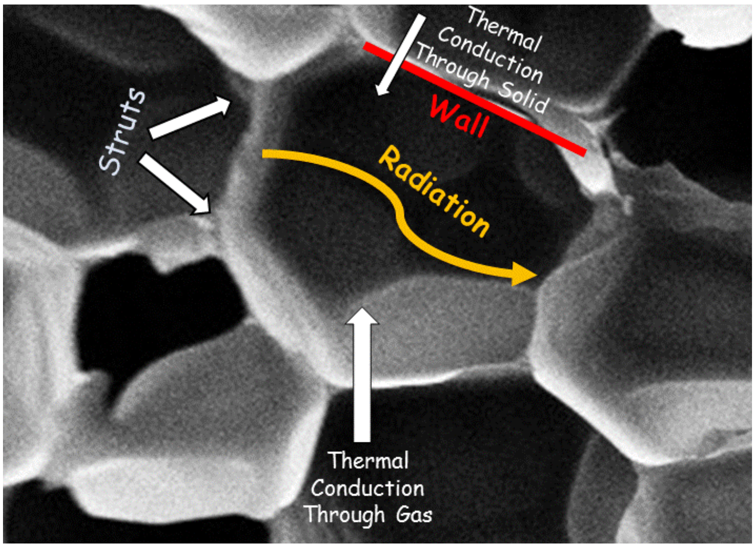


Figure 1.17. *Thermal heat transfer mechanism of RPUF*

1.7. Mechanical Properties of Rigid Polyurethane Foams

The widespread use of foams in engineering applications, especially in refrigerators, has forced researchers to improve their mechanical properties. RPUF is the most important structural element constituting the skeleton of the refrigerators besides providing high insulation for refrigerators. Thanks to this, refrigerators can stand for years. The mechanical properties of RPUF are basically influenced by various factors which are the mechanical properties of the solid material forming the cell edges (struts) and walls (membranes), cell structure, and gas inside the cells.

Mechanical properties of solid material: The mechanical properties of solid foams can be described as stiffness, strength, and viscoelasticity. These heavily depend on the mechanical properties of the solid material in the cell edges and walls. For instance, if the cell strut and wall material is stiff and strong, the solid foam is stiff and strong too.

Cell structure of foam: The mechanical properties of solid foam are not only dependent on the mechanical properties of the solid material in the cell edges and walls, but also cell structure. The deformation of the cell struts and walls influences the overall mechanical behavior of the foam. When solid foams are loaded by compression or tension, the struts at the cell edges deform, and they are exposed to bend and compression or tension. The bending is the primary deformation mechanism, and accordingly, the foam stiffness is influenced highly by the bending of the cell edges.

Gas inside the cells: Solid foams can be divided into two types according to whether their cells structure is open or closed. Because of the difference in their microstructure, these two types of foam behave disparately when loaded. Closed cell foams are filled with a gas. Owing to this, the mechanical properties of the foam are affected by the mechanical properties of the gas. For example, a gas with low compressibility can strengthen the foam (Ridha, 2007 p. 9–11).

2. LITERATURE REVIEW

The main objectives of the fillers that are incorporated into the production stages of RPUF are to reduce the production costs, enhance its mechanical and thermal insulation properties, and reduce combustion inclination. RPUFs are restricted in their application owing to their high flammability and the poisonous gases released during combustion. The most commonly used FRs are halogenated, phosphorus, and inorganic hydrates that are employed in an attempt to reduce combustibility. However, in the event of fire, halogenated FRs pollute the environment and, most importantly, pose a threat to human health as they release corrosive and toxic gases. On the grounds of this, there are severe concerns about their usage, and strict measures have been taken by the governments. Consequently, it is desirable that FR additives have an efficient flame protection and low pollution potential. In recent years, attention has largely shifted to the ability of the FRs to avoid the production of toxic gases and possess good flame protection. Such FRs include phosphorus, inorganic hydrates, and intumescent systems. At the same time, it is desirable that FR additives act as an agent for the decrease in the cell size of RPUF, thereby aiding in the enhancement of thermal insulation and the mechanical properties of foam structures.

According to Thirumal et al. (2010b, p. 2260), ATH, TPhP and their blends were incorporated into RPUF, and water was used as a blowing agent. In this study, the amount of ATH varied from 10 to 100 parts per hundred polyol by weight (php), and TPhP was used at 50, 75, and 100 php of ATH in a ratio of 1:5 for the development of the processing during RPUF preparation. The investigations of density, compressive strength, morphological and thermal conductivity, thermal stability, FR behavior, and smoke characteristics of RPUFs filled with different ATH concentrations were conducted. The density and compressive strength of the RPUFs filled with ATH diminished in beginning and then escalated in direct proportion to ATH content. It was claimed that this was due to an increase in the cell wall thickness. The thermal stability of the RPUFs did not manifest a significant change as a result of the increased ATH content. The addition of ATH with TPhP into RPUF led to a significant reduction in the flame-spread rate and an increase in the LOI. Thanks to the addition of TPhP, RPUF composites were easy to process and also led to the progress of FR characteristics of the foam.

As reported by Ye et al. (2009, p. 971), in order to develop not only the mechanical properties but also the FR performance, pulverized-EG (pEG) was encapsulated with a layer of poly(methylmethacrylate) (PMMA) and marked pEG-PMMA. It was specified that the average diameter of pEG was 39.8μm. The pEG-PMMA particles were added to RPUF to obtain uniform dispersion in the polymer matrix without destroying the cell structure of RPUF composites and, at the same time, preventing the outwards diffusion of blowing gases. As a result, the mechanical properties and FR performances of pEG-PMMA/RPUF composites were enhanced. When compared to RPUF composites filled with pEG-PMMA and solely pEG, pEG-PMMA/RPUF composites were observed to be superior to pEG/RPUF composites in all respects. It has been observed that this was possible due to the intense interaction of the PU matrix with the PMMA on the surface of pEG. As a result, the pEG-PMMA/RPUF composites depicted more advantages with respect to mechanical properties and FR performances as compared to pEG/RPUF.

In order to improve flame retardancy, Zheng, Wang and Xu (2014, p. 32) studied the two following systems: one, a phosphorus FR system of APP/TPhP blends, and the other, a montmorillonite system modified organically (OMMT) by adding into the first system and blending with increasing OMMT content. The first system, which was addition of APP/TPhP blends into RPUF, depicted a good thermal stability and the char yield of RPUF composites according to the thermogravimetric analysis (TGA). According to the cone calorimeter test, in the second system, one of the RPUF composites including 5% OMMT/8% APP-4% TPhP showed the longest combustion duration time, the slowest heat release rate, and the least total smoke production in comparison to the other RPUF composites. These results could be associated with the synergistic effect between OMMT and APP-TPhP during the combustion of RPUF composite. The blend also showed the best compression strength among the competitors.

According to Wang et al. (2017, p. 1), 2,2-diethyl-1,3-propanediol phosphoryl melamine (DPMM) as a phosphorous-nitrogen intumescent FR was synthesized and characterized. DPMM, with an increasing php from 5 till 25, was added into RPUFs, and distilled water was used as a blowing agent. The mechanical properties and the flame retardancy of DPMM on RPUF were studied. It was observed that DPMM/RPUF composites showed a small decline with regard to the mechanical properties of composite foams. In spite of that, the cell structure of the foam, including the 25 php DPMM, was not destroyed with regard to SEM images. The flame retardancy of DPMM/RPUFs was examined with the help of LOI, the vertical burning test, and the cone calorimeter. The LOI of RPUF composite containing 25 php was 29.5%, and UL-94 V-0 rating was obtained. The peak heat release rate of RPUF containing 25 php DPMM decreased from 75.2 kW/m^2 (RPUF without DPMM) to 37.3 kW/m^2. This led to a subsequent decrease of 50.4% in pHRR.

According to Wang and Li (2017, p. 1), the combination of SiO_2 nanospheres/GO hybrid (SNGO) and dimethyl methylphosphonate (DMMP) as a phosphorous-containing FR was incorporated into the RPUFs. The flame retardancy and the mechanical and thermal insulation properties of RPUF composites were studied. It was observed that the compressive strengths of RPUF composites containing DMMP declined with the increasing DMMP content. The reason behind this decline were some acidic substances, released by the liquid DMMP, that caused the RPUFs to plasticize. The compressive strengths of RPUF composites containing SNGO/DMMP blends increased with regard to the RPUF composites containing DMMP without SNGO, the cause of which was the rigidity of the SNGO. The thermal conductivity results showed that RPUF composites containing DMMP and SNGO/DMMP did not manifest considerable changes pertaining to thermal insulation properties. The LOI of pure RPUF was 18%. It was clear that the LOI of RPUF composites went up with the increasing DMMP. According to the cone calorimeter results, while the pHRR of RPUF was 344 kW/m^2, the foam composites containing 20 php DMMP and 2 php SNGO/18 php DMMP were decreased to 206 and 190 kW/m^2 respectively.

Thirumal et al. (2009, p. 704) reported that organically modified nanoclay (ONC) in varying quantities from 1 to 10 php was incorporated into the RPUFs, and the RPUFs were blown by means of distilled water. The mechanical and thermal insulation and the flame retardant properties of the RPUF nanocomposites were investigated. It was determined that the compressive strengths of RPUF nanocomposites went up to 3 php of ONC loading, before depicting a decline. This was associated with the structure of cells and the hydrogen bonding between ONC and urethane groups. The thermal conductivity of the RPUF nanocomposites declined to 5 php of ONC loading and then it increased, owing to the small cell size of RPUF nanocomposites. The LOI of pure RPUF was 22%, while that of the nanocomposites went up to 3 php of ONC loading before beginning its decline with increasing ONC content. This improvement of the LOI of the nanocomposites was due to the formation of a multi-layered carbonaceous silicate structure of the ONC in the condensed phase, whereas the drop in the LOI after loading 5 php ONC was due to the decrease in density of the nanocomposites.

According to Xu et al. (2015, p. 42842) EG, aluminum hypophosphite (AHP) and their blends were added to RPUFs, and HCFC-141b was used as a blowing agent. The fire behaviors and the mechanical properties of RPUF composites were studied. While the LOI of pure RPUF was 19.8%, that of RPUF composites containing 20 php EG, 20 php AHP, 10 php EG/10 php AHP, and 15 php EG/5 php AHP showed a sharp increase of 36.1%, 25.3%, 36.5%, and 37.8% respectively. This extraordinary increase in the LOI values of the composites was due to the synergistic effect between EG and AHP additives. According to the cone calorimeter results, while the pHRR of the pure RPUF was 108,8 kW/m^2, the pHRR of RPUF composites containing 20 php EG, 20 php AHP, 10 php EG/10 php AHP, and 15 php EG/5 php AHP declined to 55.1 kW/m^2, 76.4 kW/m^2, 51.0 kW/m^2, and 48.8 kW/m^2 respectively. The cone calorimeter results were parallel to the LOI results, and they can also be explained with the help of the synergistic effect in FRs. Due to the incompatibility of FRs with PU matrix, the compressive strengths of RPUFs filled with only EG or only AHP declined with increasing FRs. When the content of the total fillers was kept constant at 20%, the compressive strength of RPUF composite containing 15 php EG/5 php AHP was observed to be higher than that containing 20 php EG. This was possibly due to the effect of AHP on the mechanical properties of the RPUF composites.

Based on studies by Lorenzetti et al. (2012, p. 2364), inorganic and organic phosphinates were used to produce RPUF composites, and these phosphinates were included in PU foams for the first time in this study. All RPUF composites were filled with 10 wt% on the total foam mass of phosphinates. The fire behavior of the RPUF composites was also studied. According to the LOI results, the inorganic phosphinates were observed to be more effective than the organic phosphinates. When the cone calorimeter results were taken into account, while the pHRR of pure RPUF was 538 kW/m^2, the pHRR of the RPUF composite containing inorganic phosphinate declined dramatically to 200 kW/m^2. The pHRR of the RPUF composites containing organic phosphinates showed a decline in comparison with pure RPUF by approximately 30%. However, according to the pure RPUF, no big developments in their total smoke released (TSR) were observed.

3. EXPERIMENTAL STUDIES

3.1. Raw Materials

Polymeric 4,4'-diphenylmethane diisocyanate (pMDI), with NCO content 31%, and formulized polyether-based polyol, possessing a hydroxyl value of 386 mg KOH/g of polyol were obtained from Arçelik Refrigerator Plants. The polyether-based polyol consists of blowing agents, surfactants, and catalysts. Cyclopentane/isopentane blend was employed as physical blowing agent. Aluminum trihydrate (ATH, with a density of 2.44 g/cm^3 and average particle size of 20–25 μm) was provided from Entekno Materials. Zinc borate (ZnB, with average particle size of 9 μm and $4ZnO.6B_2O_3.7H_2O$ molecule formula) and triphenyl phosphate (TPhP) were supplied by Üçgen Pigments & Polymer Additives in Turkey.

3.2. Foam Preparation

Rigid polyurethane foam (RPUF) was prepared by using one-shot process with hand mixing. The formulized polyol was put into a 1.0 L polypropylene cup. After adding pMDI onto the polyol, the mixture was stirred for 8–10 seconds by means of a high-speed mechanical stirrer (at 2000 rpm). The mixture was immediately poured into a mold (with the inner dimensions 30 cm × 30 cm × 10 cm (length × width × thickness), preheated at 34±2°C, and allowed to cure for 5 minutes. Rigid polyurethane foam composite (RPUFC) was also produced in a similar way. An additive was added to polyol and obtained mixture was mixed with the high-speed mechanical stirrer (2000 rpm) throughout 2 min. pMDI was added to this dispersion. The mixture was poured into the preheated mold, and allowed to cure for 5 minutes. After removing the composite from the mold, it was cut into the desired shapes and sizes in accordance with the testing standards for the purpose of evaluation of different properties. The production of RPUFCs is schematized in Figure 3.1. The details of compositions for RPUFCs studied in this project are presented in Table 3.1.

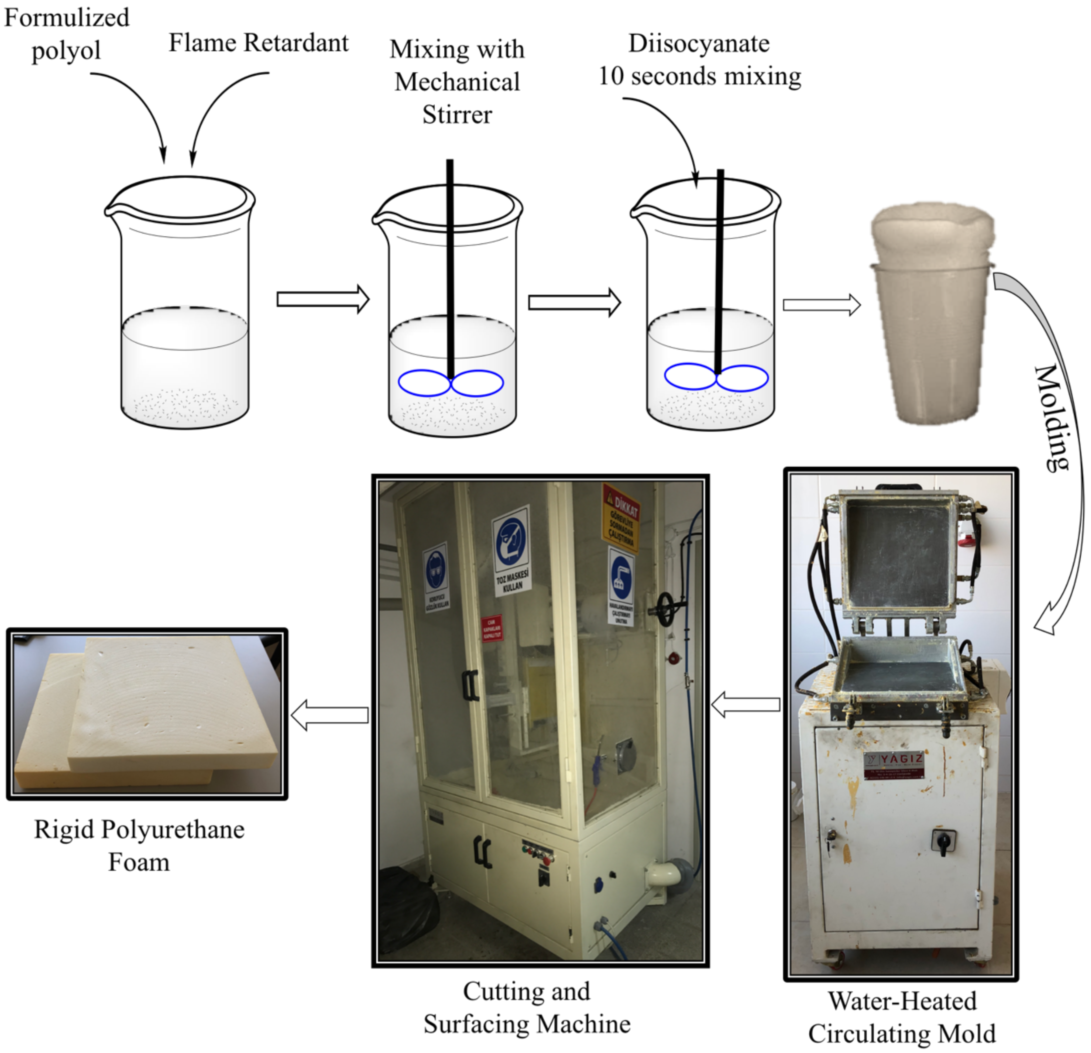


Figure 3.1. *Process of RPUFC production*

Table 3.1. *Compositions of RPUFCs'*

	Additive type and amount (by polyol weight %)		
Foam Code	ATH	TPhP	ZnB
RPUF	-	-	-
10A-50 A	10, 20, 30, 40, 50	-	-
10T-50 T	-	10, 20, 30, 40, 50	
10Z-50 Z	-	-	10, 20, 30, 40, 50
30A/10T	30	10	-
20A/20T	20	20	-
10A/30T	10	30	-
30A/10Z	30	-	10
20A/20Z	20	-	20
10A/30Z	10	-	30
10T/30Z	-	10	30
20T/20Z	-	20	20
30T/10Z	-	30	10

3.3. Characterization Methods

The measurement of the thermal conductivity of the foams, whose dimensions were 300 mm × 300 mm × 30 mm, was carried out deploying Linseis HFM 300 Heat Flow Meter (Figure 3.2) with respect to the standard procedure, which is known as ASTM C518. The temperatures of the upper and the lower plates were set at 38°C and 10°C, respectively, thus ensuring that the average temperature of foam was maintained at 24°C. Thermal conductivity measurements were done within 24 hours after demolding.

Figure 3.2. *Heat flow meter system*

After completing the conductivity measurement, the same foam was cut into three pieces, each with dimensions of 100 mm × 100 mm × 30 mm, from different parts of the foam to measure the compressive strength. Compressive strength measurements were done as per ASTM D-1621 by using universal test machine Zwick/Roell mode Proline instrument at room temperature. Compressive stress at 10% strain was performed to foams, and the strength values were obtained for this deformation. The compressive strengths of the three samples per foam were measured, and the average of these values was reported.

The foams were cut into three pieces with dimensions of 50 mm × 30 mm × 30 mm in order to determine their closed cell content and density. The final dimensions of each of the pieces were measured using a caliper without fail, and the pieces were later weighed for the calculation of the bulk density. Later, the closed cell content and density measurements of these pieces were carried out using a helium/nitrogen based gas displacement pycnometer (Micromeritics AccuPyc II 1340) (Figure 3.3) with regard to ASTM D-6226. The results were considered to be the average values.

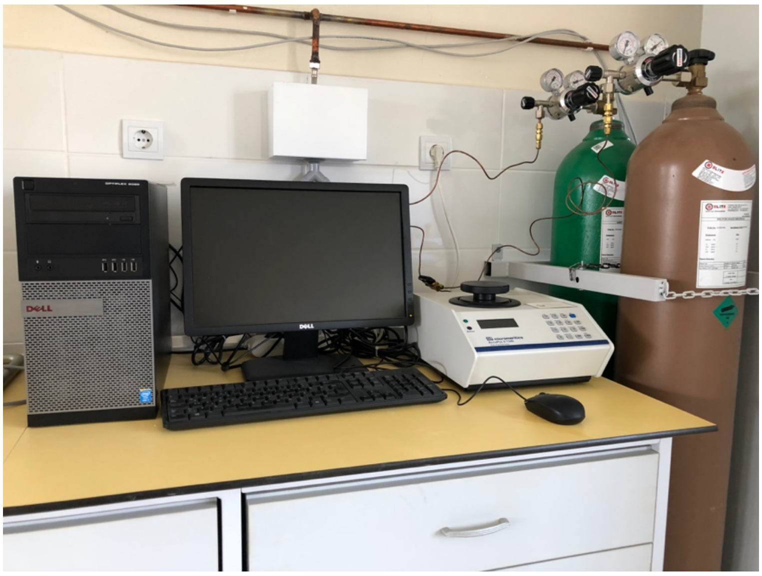


Figure 3.3. *Gas displacement pycnometer system*

After the determination of the closed cell content and density measurements, the same samples were used to examine the morphology of the foams. A sample was cut into thin slices and coated with gold to obtain an electrically conductive surface. The coated slices of the foams were studied under a Scanning Electron Microscope (Carl Zeiss Ultra Plus FESEM) at appropriate accelerating voltage and magnification. The mean cell size of a foam was determined from SEM images using ImageJ software. Approximately 100 cells were taken into consideration for calculating of the mean cell size.

Horizontal burning tests were performed by means of the UL 94 Horizontal Burning (UL-94 HB) test according to ASTM D635 (Figure 3.4). The foam was cut into five pieces with dimensions of 125 mm × 10 mm × 13 mm. A Bunsen burner was used with methane as a fuel as the ignition source. The gas flow was controlled and maintained at the rate of 105 mL/min with a proper regulator and meter in accordance with ASTM D5207. The 125 mm-long test samples were marked on the 25 mm and 100 mm positions, and the burning rate was measured between the 25 mm and 100 mm positions. The samples were then put onto a wire screen and flame was held to the free end of the samples for 30 seconds. The flame was immediately taken away from the samples if it reached the 25 mm position within 30 seconds. Burning rate (V, mm/min) was calculated using the equation $V = 60L/t$, where L is the burned length (mm) and t is the time (s), and their average values were reported.

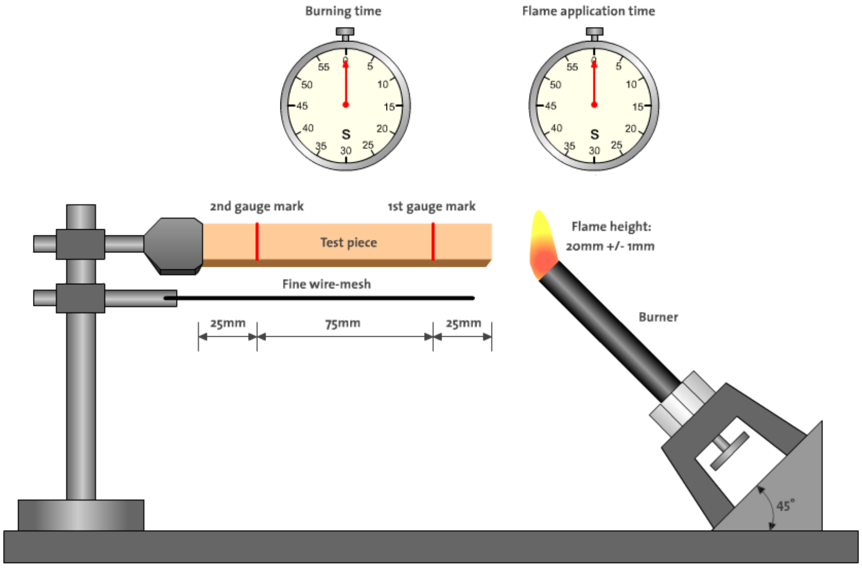


Figure 3.4. *Schematic representation of UL 94 HB test (http-3)*

Flammability tests were done by using LOI instrument according to ASTM D-2863-97. The foams were cut into five pieces whose dimensions were 100 mm × 10 mm × 10 mm, and the average LOI was determined.

The combustion coefficient of the foams was investigated using cone calorimeter (Figure 3.5) in accordance with ISO 5660-1 standard method. The samples employed in the strength measurements were also used for calorimetric tests. It was assumed that compressive stress was not the cause behind the structural deformation that affected the fire behavior test of the foams. Each sample was wrapped in an aluminum foil and exposed horizontally to an external heat flux of 35 kW/m^2. All computations in cone calorimeter were associated with the changes in the mass, temperature, smoke production, and gases (O_2, CO, CO_2, and NO), and these changes were recorded every second by means of a special software. The heat release rate (HRR), time to ignition (TTI), peak heat release rate (pHRR), total smoke release rate (TSR), and so on were calculated from the computations.

All of the characterization methods have been summarized in Figure 3.6.

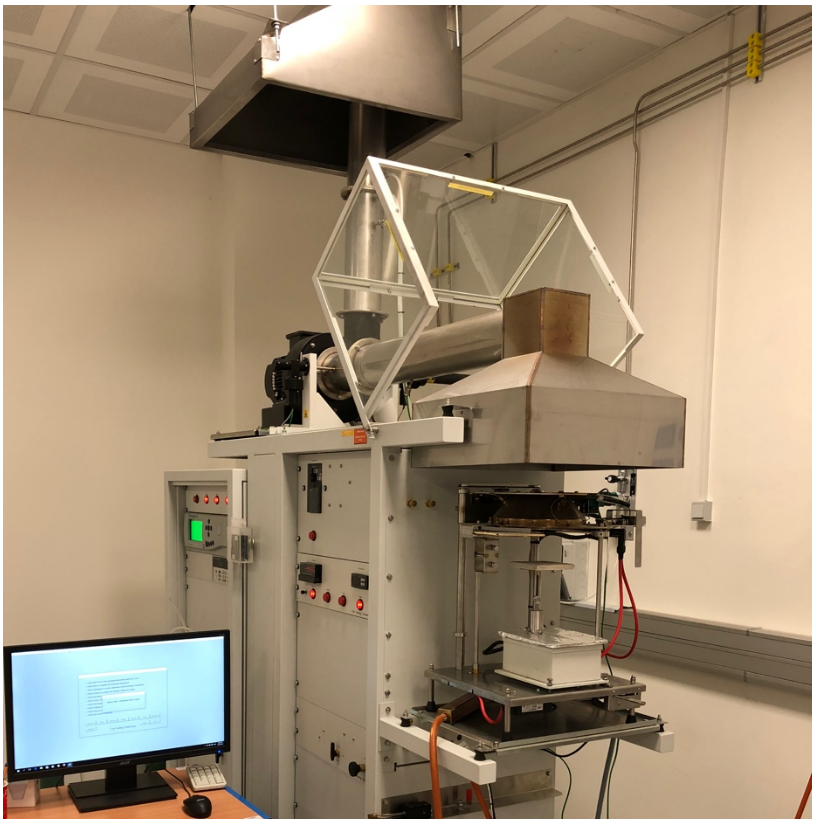


Figure 3.5. *Cone calorimeter*

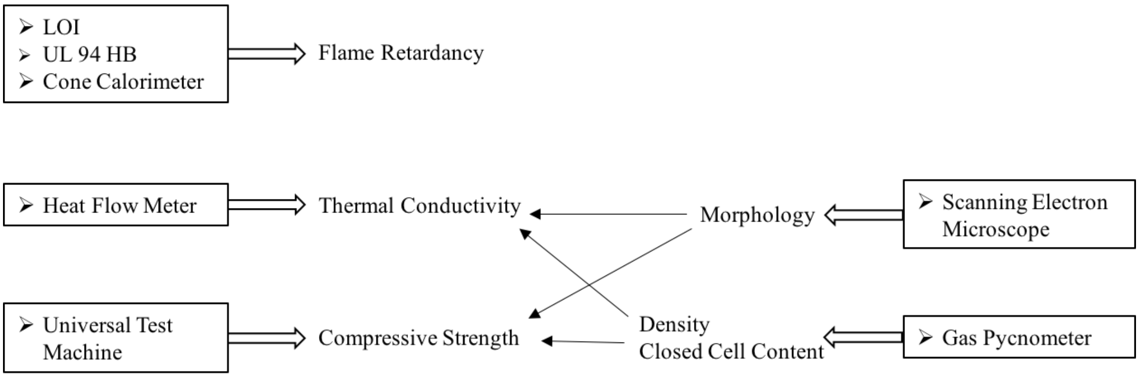


Figure 3.6. *Schematization of analysis process*

4. RESULTS and DISCUSSIONS

Improvement in the properties of RPUF is of significant importance for both the industry and the academia owing to the increasing interest in the properties of RPUF and its broad range of applications. In this study, a series of RPUFCs containing ATH, TPhP, ZnB, and their binary blends were prepared using one-shot method. The flame retardancy, thermal conductivity, and compressive strength of RPUFCs were investigated.

4.1. Changes in Flame Retardancy Properties

4.1.1. Effects of ATH, TPhP and ZnB

For the evaluation of the flame retardancy of the composites with different loading of ATH, TPhP, ZnB, and their blends, UL-94 HB, LOI, and cone calorimetric tests were performed. Figure 4.1 exhibits the effect of the FRs on the rate of flame spread of composites. The flame spread rate of RPUF is 303.4 mm/min. It is clear from the figure that the spread rate showed a sharp decrease with the increase in the amount of FRs. Self-extinguishing properties were observed in the case of composites at the higher loading level of ATH and TPhP. This phenomena could be attributed to water elimination from ATH by endothermically decomposing it and also the formation of aluminum oxide char on the surface of the foam. For TPhP, it may be due to the volatilization of TPhP and the condensed-phase mechanism of TPhP (Thirumal et al., 2010b, p. 2266–2967). The observed decrease of ZnB composites was due to the diluting effect of ZnB (Dike, Tayfun and Dogan, 2017, p. 895).

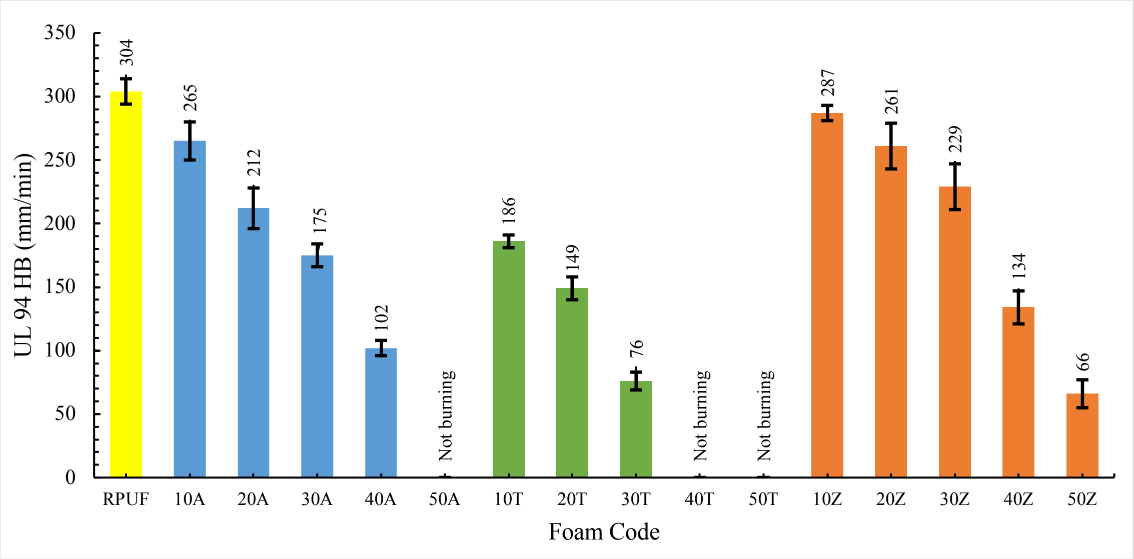


Figure 4.1. *Effect of FR type and amount on the rate of flame spread*

The LOI is a measure of the percentage of oxygen that is required to be present to support the combustion of plastic. Air contains approximately 21% oxygen, and therefore, any material with a LOI value of less than 21% will probably support burning in an open air. To summarize, the higher the LOI the lower the flammability. Figure 4.2 clarifies the effect of ATH, TPhP, and ZnB on the LOI of the composites. The LOI of RPUF was determined as 19.3% in this study. These values for composites containing 50% of ATH, TPhP, and ZnB increased to 21.9%, 22.2%, and 20.9%, respectively. The LOI showed a 15% increase for the foam of 50T. The increase of the LOI can be associated with the decrease of the flame spread rate since the cause for both remains the same.

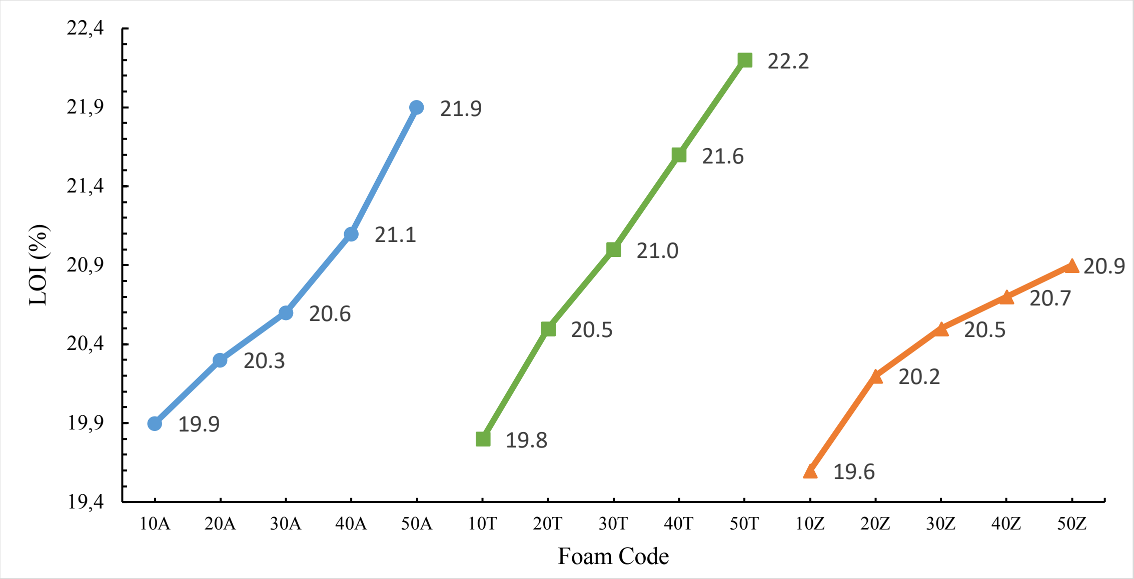


Figure 4.2. *Effect of FR type and amount on the LOI (LOI for RPUF: 19.3%)*

Cone calorimeter results are significant when it comes to the comparison of different materials and the expression of the intensity of a fire (Usta, 2012, p. 33). Parameters including time to ignition (TTI), heat release rate (HRR), peak heat release rate (pHRR), time to peak heat release rate (t pHRR), total heat release (THR), the mean CO and mean CO_2 yields, total smoke release (TSR), total smoke production (TSP), and maximum average rate of heat emission (MARHE) were employed to evaluate the flammability of composites. The curves of HRR are presented in Figure 4.4 and the corresponding data is compiled in Table 4.1.

Polyurethane foams are materials with short TTI due to their closed cellular structures and high radiant heat flux (30 kw/m^2) (Modesti et al., 2008, p. 2169, Zhang et al., 2015, p. 432). The obtained results show that while the TTI value of RPUF was 1 s, TTI values of composites were between 2–4 s. As a result of the addition of 40% ATH, the TTI increased from 1s to 4s compared to the RPUF.

HRR is known to be one of the important parameters in the evaluation of combustion tendency. It is associated with fire spread and flashover phenomena in a real fire situation. (Chung, Kim and Kim, 2009, p. 892, Yang et al., 2015, p. 107). As seen in Figure 4.4, HRR curves of RPUF indicate that foam manifests a two-step process. RPUF was observed to burn very quickly after ignition and reached first peak HRR in 10 s which is lower than almost all foam composites. There is a possibility that this observation is associated with the release of polyol decomposition products (Gaan et al., 2015, p. 188).

An increase in HRR is observed until the formation of a protective char layer. Additionally, a second peak in the HRR curve may originate from the cracks of the char layer (Modesti et al., 2008, p 2170). However, with the exception of RPUF, HRR curves of all composites depicted more than two peaks. This has been, in all likelihood, originated the effects of simultaneous activated FRs as a result of high radiant heat flux.

It can be seen from Figure 4.4 and Table 4.1 that all FRs could reduce the pHRR and HRR values of composites, suggesting that FRs (especially ATH and ZnB) promote to form a protective charred layer during the process of degradation. The pHRR thus showed a gradual reduction especially for the composites of T series. The pHRR value of RPUF is 272.9 kW/m^2. For 40A, 40T, and 40Z foams, these values are 205.5, 243.6, and 231.6 kW/m^2, respectively, showing a respective decrease of 24.7%, 10.7%, and 15.1% in comparison with RPUF. While peak 2-HRR of composites are relatively higher in comparison with the peak 2 of RPUF. As compared to RPUF, these peaks of composites appear much later, thus suggesting the formation of good charred layer. From Figure 4.4(b), it can be observed that the HRR values of RPUFCs containing TPhP decreased sharply to 0 in about 100s, and the burning stopped. However, other composites and RPUF were still kept their HRR and continued to burn. The THR value of RPUF was about 22.9 MJ/m^2. As can be seen from Table 4.1, in the case of low level of FR loading, this value for composites was observed to be lower than that of RPUF. However, with the increase in the FR loading level, the THR value of composite also increased. The mass of samples may play a role in the manifestation of the said observations (Xu and Wang, 2015, p. 8).

MARHE is a beneficial parameter for the estimation of the scale of a fire. While the MARHE value of RPUF was determined to be 233.4 kW/m^2, the MARHE value declined to 174.5 kW/m^2 in the case of composites containing 40% of ATH.

Toxic gases and smoke are known to pose as much danger as fire. Therefore, TSR, TSP, mean CO, and mean CO_2 yields are significant parameters in the evaluation of secondary fire hazards of materials (Li et al, 2018, p.3). Composites doped with ATH were observed to reduce the TSR and TSP values at all levels of loading. Owing to the organic structure of TPhP, the TSP and TSR values of the composites with TPhP increased in direct proportion to the contents of TPhP. Interestingly for the composites containing TPhP, while the mean CO yield depicted a significant increase, the mean CO_2 yield decreased as the content of TPhP increased. This in turn meant that the smoke was more toxic, because the mean CO yield was high for the composites with TPhP. The mean CO and mean CO_2 yields of composites filled with ATH and ZnB were showed a slight decrease in comparison to the RPUF.

Figure 4.3. *RPUF sample for cone calorimeter test (before and after burning)*

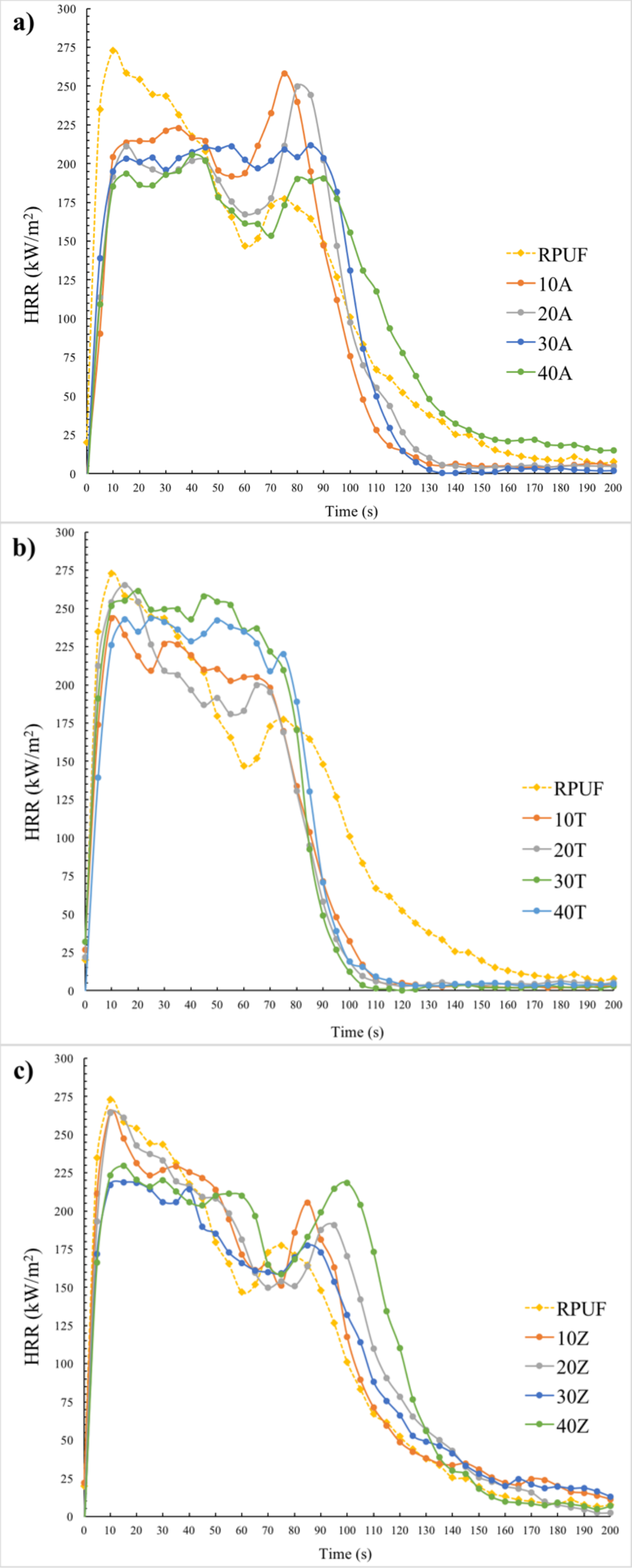


Figure 4.4. *Effect of FR type and amount on the HRR: a) ATH, b) TPhP, c) ZnB*

Table 4.1. *Results of cone calorimeter tests*

Parameter	RPUF	10A	20A	30A	40A	10T	20T	30T	40T	10Z	20Z	30Z	40Z
TTI (s)	1	4	4	3	4	3	2	2	3	2	4	3	2
t pHRR (s)	10	75	80	85	40	10	15	20	25	10	10	15	15
pHRR (kW/m^2)	272.9	258.1	249.8	211.7	205.5	245.8	265.3	261.5	243.5	264.6	264.2	218.7	231.6
THR (MJ/m^2)	22.9	20.9	20.8	21.0	23.8	19.0	18.4	20.5	20.4	20.4	24.5	23.2	24.5
Mean COY (kg/kg)	0.068	0.058	0.076	0.065	0.060	0.079	0.086	0.112	0.128	0.065	0.054	0.056	0.060
Mean CO_2Y (kg/kg)	1.84	1.60	1.66	1.62	1.75	1.50	1.28	1.18	1.10	1.75	1.85	1.75	1.73
TSR (m^2/m^2)	786.8	774.5	721.5	743.7	751.5	845.1	991.6	1378.3	1673.1	849.7	917.7	874.6	955.6
TSP (m^2)	7.0	6.8	6.4	6.6	6.6	7.5	8.8	12.2	14.8	7.5	8.1	7.7	8.4
MARHE (kW/m^2)	233.4	202.0	188.4	194.9	174.5	212.7	222.1	237.4	219.5	220.2	220.2	195.6	204.6

4.1.2. Effect of blends

Figure 4.5 shows the effect of FR blends on the flame spread rate of RPUF composites. The rate of flame spread of all composites containing the blend of FRs decreased in comparison to the composites having the same amount of corresponding FR only. For example, the rate of 20Z and 20T was 261 and 149.1 mm/min, respectively. Due to the addition of 20% ZnB and 20% TPPh by polyol weight percentage into RPUF matrix, the rate of flame spread decreased to 32.9 mm/min. Moreover, the foams of 30A/10T and 20A/20T could not be burned according to the UL94 HB test procedure. These results were likely due to the synergistic effect among FRs.

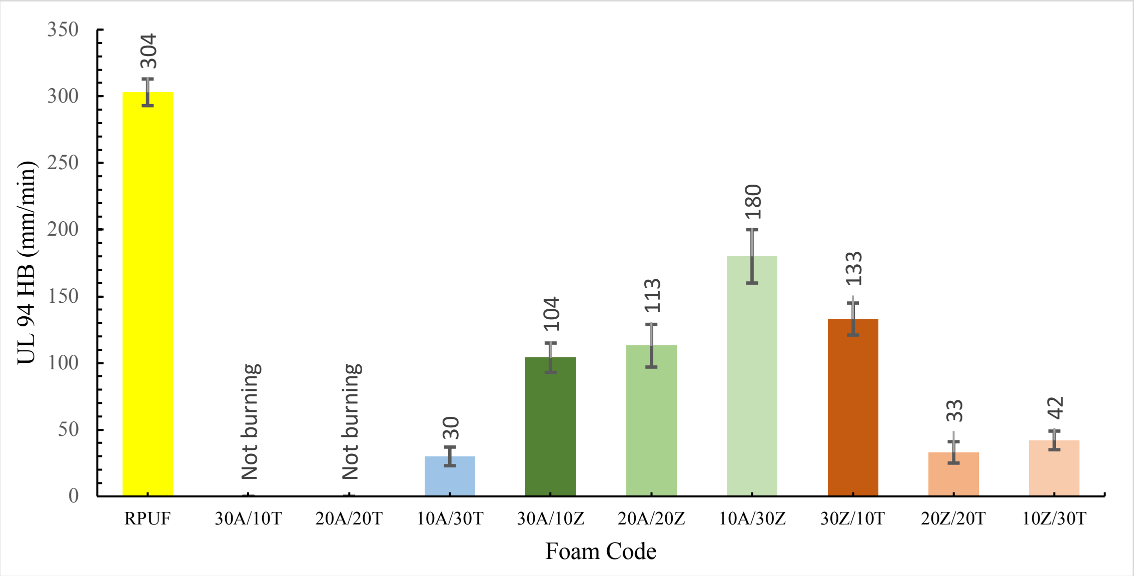


Figure 4.5. *Effect of blend type and composition on the rate of flame spread (UL 94 HB)*

Figure 4.6 shows the effect of blends on the LOI of RPUFCs. The presence of TPhP to ATH further lowered the LOI according to the composites filled with the same amount of ATH. While the LOI of 20A and 20T composites were 20.3% and 20.5% respectively, this value of 20A/20T sample was increased 21.7%. Besides, while the LOI of 30T sample was 21%, the LOI of 10Z/30T sample was 21.8%.

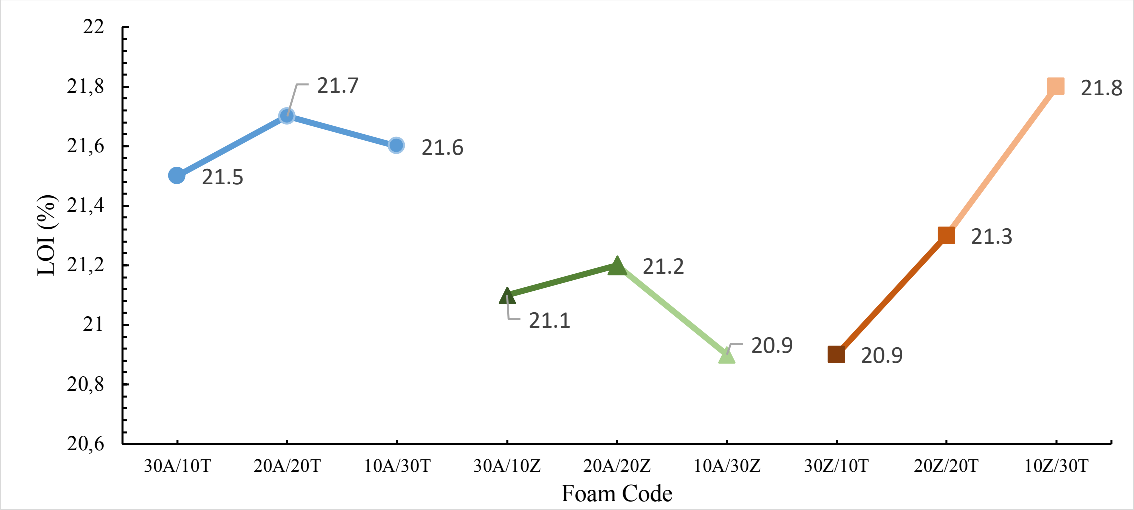


Figure 4.6. *Effect of blend type and composition on the LOI (LOI for RPUF 19.3%)*

For binary or ternary combination systems, the numerical values of LOI may be shifted from those the theoretically calculated ones. While the upward shift is known as synergism, the downward shift is known as antagonism. The theoretical LOI values of RPUFC with binary blends have been calculated from a knowledge of their experimental values under identical loadings conditions with the individual additives and without additive. For example, the LOI values of a polymer filled with binary combinations (LOI_{ab}) could be calculated as (4.1):

$$LOI_{ab} = LOI_a + LOI_b - LOI_{RPUF} \tag{4.1}$$

where LOI_{RPUF} is the LOI value without additive, and LOI_a, LOI_b are LOI values with the additives a and b, respectively (Varughese, De and De, 1989, p. 120). As shown in Table 4.2, while in some cases the upward shift in LOI values was determined, the downward shift was observed in some cases. According to the LOI test, the experimental LOI of the 30A/10T, 20A/20T, 30A/10Z and 10Z/30T foams were greater than their theoretical values of LOI. Therefore, the RPUFCs containing these binary FRs combinations showed synergistic effect. This could be associated with the combinations of phase mechanism of FRs.

Table 4.2. *Theoretical and experimental LOI values of RPUFC*

	30A/10T	**20A/20T**	**10A/30T**	**30A/10Z**	**20A/20Z**	**10A/30Z**	**30Z/10T**	**20Z/20T**	**10Z/30T**
Experimental	21.5	21.7	21.6	21.1	21.2	20.9	20.9	21.3	21.8
Theoretical	21.1	21.5	21.6	20.9	21.2	21.1	21.0	21.4	21.3

The curves of HRR are depicted in Figure 4.7, and the corresponding data is listed in Table 4.2. When the composites containing blends are compared with ones containing the same amount of corresponding FRs, generally, the efficient synergistic effect was not observed with respect to pHRR and THR values. It is most likely that this was due to the presence of an extremely combustible blowing agent mixture (pentane/cyclopentane) in the cells of the foam structure. As mentioned above, HRR curves of composites containing binary blends also depicted more than two peaks. This can be associated with the effects of simultaneous activated FRs as a result of high radiant heat flux.

While the MARHE values of RPUF and 30Z foam were 233.4 and 195.6 kW/m^2 respectively, the value of 30Z/10T composite foam was 153.5 kW/m^2. The MARHE value of 30Z/10T foam was improved by 35% and 21.5%, respectively, according to the RPUF and 30Z foams.

The TSR and TSP increased with the presence of the blends in the RPUF, the reason for which could be ascribed to the char promotion effect of the FRs used. These additives may disturb the sufficient burning of the foam (Xu et al., 2015, p. 8). However, the CO yield of the composites containing ATH/ZnB blends decreased effectively according to the other composites, indicating that their toxicity was lesser than the others. The CO_2 yields of all composites containing binary blends were lower than that of RPUF. While the CO yield of 30A sample was 0.065 kg/kg, the CO yield of 30A/10Z sample was 0.046 kg/kg. Almost all composites with ATH/ZnB blends had not higher value of CO yield than those of composites containing solely ATH or ZnB. This was possibly due to the smoke suppression feature of ZnB. On the other hand, as expected, the CO emission of composite increased with the increasing TPhP content of the FR blend.

4.1.3. Flame retardancy mechanism

The flammability of polymeric materials is heavily bound up with the thermal degradation process which occurs on exposed to heat. For this reason, the thermal degradation mechanism of polymers is rather significant in understanding the combustion process and flame retardancy. Generally, the effective FR should possess the degradation temperature close to that of polymer matrix without FR additives (Thirumal et al, 2010a, p. 1144). The flame retardancy mechanism of RPUFC containing ATH/TPhP is illustrated in Figure 4.7. It has been thought that the liquid of TPhP and the particle of ATH are dispersed on the cell wall and struts. When RPUF heats, it first starts releasing flammable blowing agent gases from the closed cells, and ATH particles absorb heat until the temperature of RPUF reaches 220°C. After ignition, the release of flammable gases from the RPUF is started due to its thermal decomposition. For one thing, ATH particles eliminate the water bonding chemically and this water helps to cool hot polymer matrix, and form aluminum oxide char on the surface of RPUF then acts as physical barrier for inhibiting the heat and mass transfer. For another, the thermal decomposition of TPhP produces phosphoric acid. Phosphoric acid helps the degradation of PU to form the compact char layer on the surface of RPUF and further decomposes to PO and PO_2 with quenching effect in the gas phase. Therefore, because of the combined physical and diluting effects of ATH and the catalysis of charring formation and volatilization effects of TPhP, a good flame retardant effect between ATH and TPhP has been observed in RPUF (Xi et al, 2015, p. 41, Yang et al, 2014, p. 1042, Thirumal et al, 2010b, p. 2267).

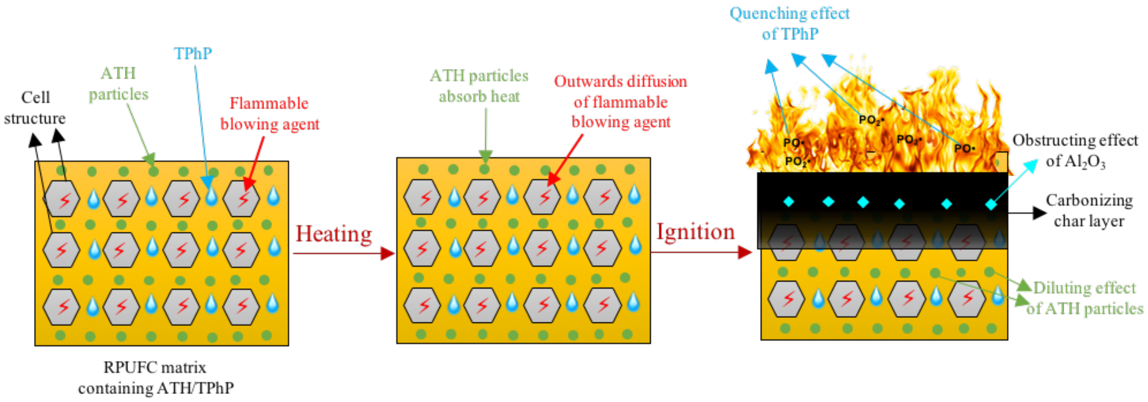


Figure 4.7. *Illustration of flame retardancy mechanism of RPUFC containing ATH/TPhP*

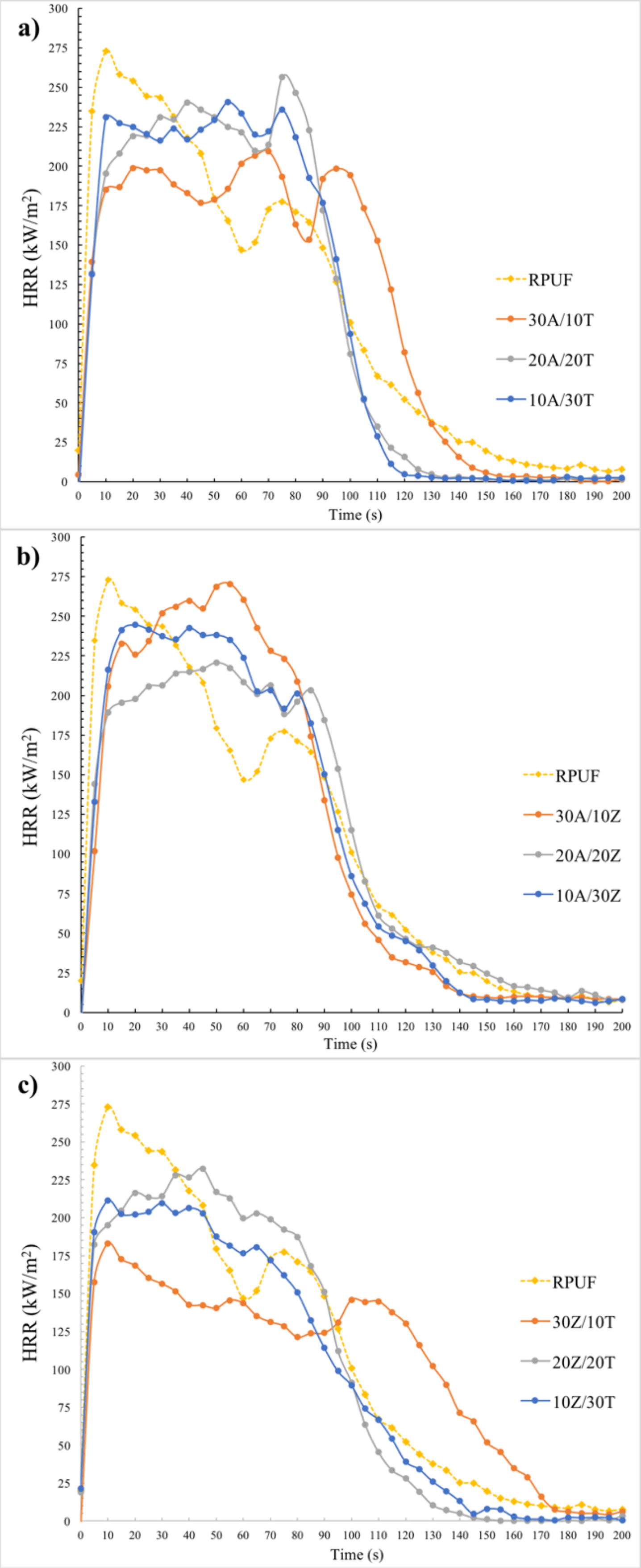


Figure 4.8. *Effect of blend type and composition on the HRR: a) ATH-TPhP, b) ATH-ZnB, c) ZnB-TPhP*

Table 4.3. *Results of cone calorimeter tests for blends*

Parameter	RPUF	30A/10T	20A/20T	10A/30T	30A/10Z	20A/20Z	10A/30Z	30Z/10T	20Z/20T	10Z/30T
TTI (s)	1	3	4	4	4	3	3	2	2	2
t pHRR (s)	10	70	75	55	55	50	20	10	45	10
pHRR (kW/m^2)	272.9	209.4	256.3	240.6	270.2	220.6	244.5	183.1	232.2	211.4
THR (MJ/m^2)	22.9	22.4	21.7	21.6	23.4	22.6	23.0	21.0	14.6	14.2
Mean COY (kg/kg)	0.068	0.082	0.112	0.140	0.046	0.048	0.055	0.085	0.102	0.117
Mean CO_2Y (kg/kg)	1.84	1.60	1.43	1.42	1.61	1.74	1.66	1.71	1.35	1.24
TSR (m^2/m^2)	786.8	1010.4	1317.1	1551.8	826.9	836.5	833.1	966.6	1246.9	1404.9
TSP (m^2)	7.0	8.9	11.6	13.7	7.3	7.4	7.4	8.5	11.0	12.4
MARHE (kW/m^2)	233.4	182.2	213.3	212.9	227.0	195.5	217.9	153.5	204.3	193.7

4.2. Changes in Thermal Conductivity of the Composites

4.2.1. Effects of ATH, TPhP and ZnB

Thermal conductivity of RPUF depends on several parameters, such as mean cell size, thermal conductivity of blowing agent gas in the cells, cell orientation, density of foam, closed cell content, and thermal conductivity of additives (Marrucho, Santos and Dohrn, 2005, p. 208, Thirumal et al., 2007, p. 255, Zhao et al., 2015. p. 312, Lim, Kim and Kim, 2010, p. 368, Modesti, Lorenzetti and Besco, 2007, p. 1354, Nikje, 2009, p. 149).

The changes in the cell morphology with the addition of the FRs were demonstrated with the help of SEM images (Figure 4.8). It is clear from the images that the cell size of RPUF composites reduced than that of RPUF. Figure 4.9 depicts the changes in the mean cell size varying with the amount of FRs of composites. Both the thermal insulation capacity and the mechanical performance of rigid foams are positively affected by the reduction in the cell size and the protection or enhancement of the close cell content (Kabakci et al., 2017, p. 8, Danowska et al., 2013 p. 2275, Zhu et al., 2012, p. 4704, Thirumal et al., 2009, p. 708).

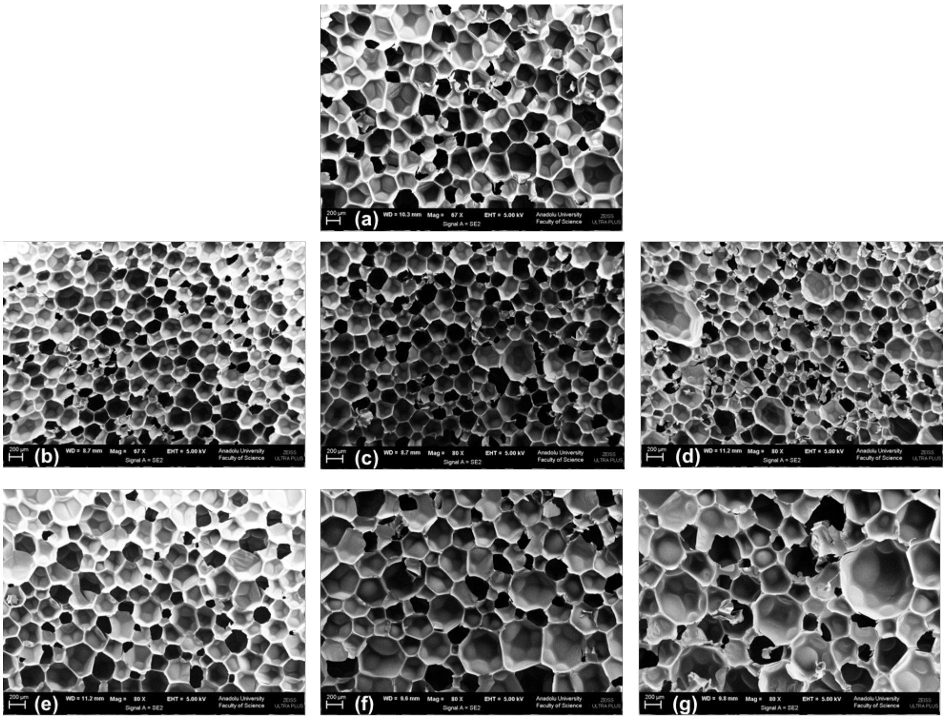


Figure 4.9. *SEM images of the foams a) RPUF, b) 10A, c) 30A, d)50A, e) 10T, f) 30T, g) 50T*

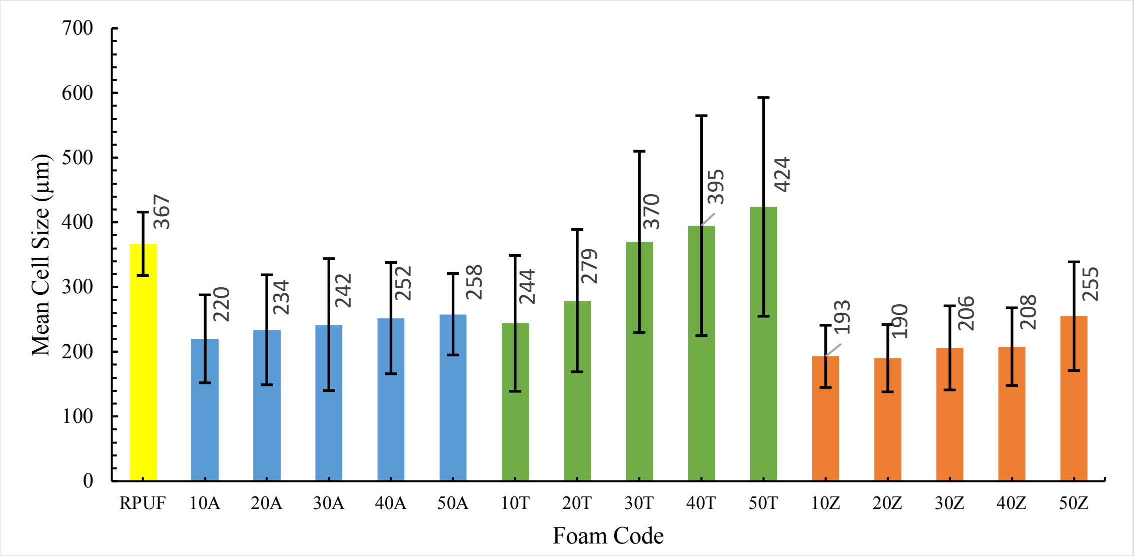


Figure 4.10. *Effect of FR type and amount on the mean cell size*

The mean cell size of RPUF was observed to be 367 µm. In most cases, composites had lower mean cell size than RPUF. While the mean cell size of the RPUFCs containing all FR additives was increased as the content of FRs increased, the mean cell size of the composites of solely 30T, 40T and 50T was higher than that of RPUF. The RPUFCs filled with ATH and ZnB, which are solid additives, showed the least mean cell size. However, the mean cell size of RPUFCs containing TPhP, which is liquid additive, became bigger than that of RPUF. While the addition of 50% ATH and ZnB caused a reduction of around 30 % both, the addition of 50% of TPhP caused an increase of around 13.5%. The reason why the mean cell size increased with the increasing FR additives could be the coalescence of cells during nucleation (Harikrishnan, Patro and Khakhar, 2006, p.7132). Table 4.3 shows the effects of closed cell content of RPUF composites filled with FRs. The closed cell content of the RPUF was determined to be 87.1%. In general, by the addition of FRs, the closed cell content manifested a slight increase. Although the closed cell content increased also after the addition of TPhP, it depicted a decrease with higher loadings. It has been speculated that small changes in the closed cell content similar to those in this study did not have a significant influence on thermal conductivity.

Table 4.4. *Closed cell content of the composites (Closed cell content of RPUF: 87.1%±2)*

Foam Code	**Closed Cell Content (%)**	**Foam Code**	**Closed Cell Content (%)**	**Foam Code**	**Closed Cell Content (%)**
10A	91.6	10T	91.8	10Z	93.2
20A	91.3	20T	91.7	20Z	91.4
30A	92.2	30T	91	30Z	91.4
40A	92.3	40T	87.5	40Z	90.8
50A	91.9	50T	87.1	50Z	90.0

Thermal conductivity of rigid foams is a fundamental parameter as an indicator of thermal insulation properties. The effect of composites with FR additives is illustrated in Figure 4.10. The thermal conductivity value of RPUF was determined as 22.53 mW/m.K. It was observed that the thermal conductivities of composites filled with ATH and ZnB were lower than those of RPUF, even in the case of 50A and 50Z foams. The thermal conductivity values of 50A and 50Z were 21.99 and 21.76 mW/m.K respectively, indicating that the thermal conductivity was decreased at the level of 2.4% for 50A and 3.4% for 50Z. This can be primarily attributed to the small mean cell size of RPUF composites compared with the RPUF (Thirumal et al., 2010b, p. 2264). Although the thermal conductivity of composites containing TPhP was lower than that of RPUF at lower loadings, the conductivity values depicted a subsequent increase as the content of TPhP increased. It is suggested that this can be associated with the increasing mean cell size.

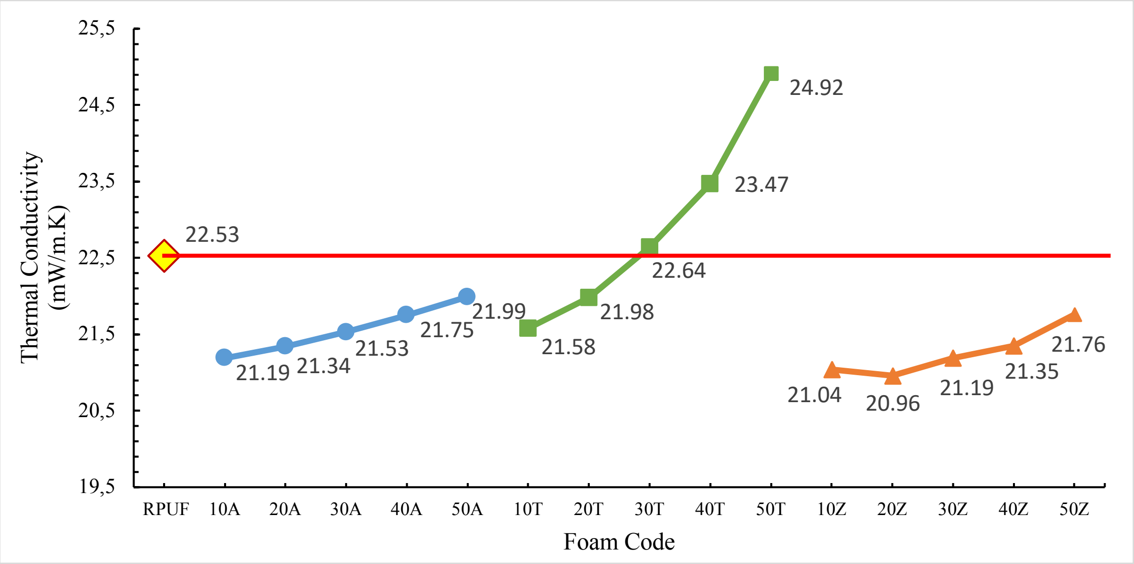


Figure 4.11. *Effect of FR type and amount on the thermal conductivity*

4.2.2. Effects of blends

Depending on the loading of FR blends composites filled with the blends of FRs, the mean cell size was demonstrated in Figure 4.11. It was pointed out in the same figure that the incorporation of the FR blends into foam matrix reduces the mean cell size according to the RPUF. In the composites containing ATH/TPhP, ATH/ZnB, and ZnB/TPhP, the mean cell size increased with the increasing content of TPhP, ZnB, and TPhP respectively, except for 30A/10Z foam. As also seen from Figure 4.12, when the TPhP content increased, the uniform structure of the cells began to disintegrate. It may be due to the effect of the immiscibility of TPhP with polyol at the high level of TPhP content. The SEM images also revealed that cells increased in size with the subsequent increase of TPhP in the blend. Compared to RPUF, 30A/10Z, 30A/10T, and 30Z/10T composites displayed 20%, 23%, and 26% reduction in the mean cell size respectively.

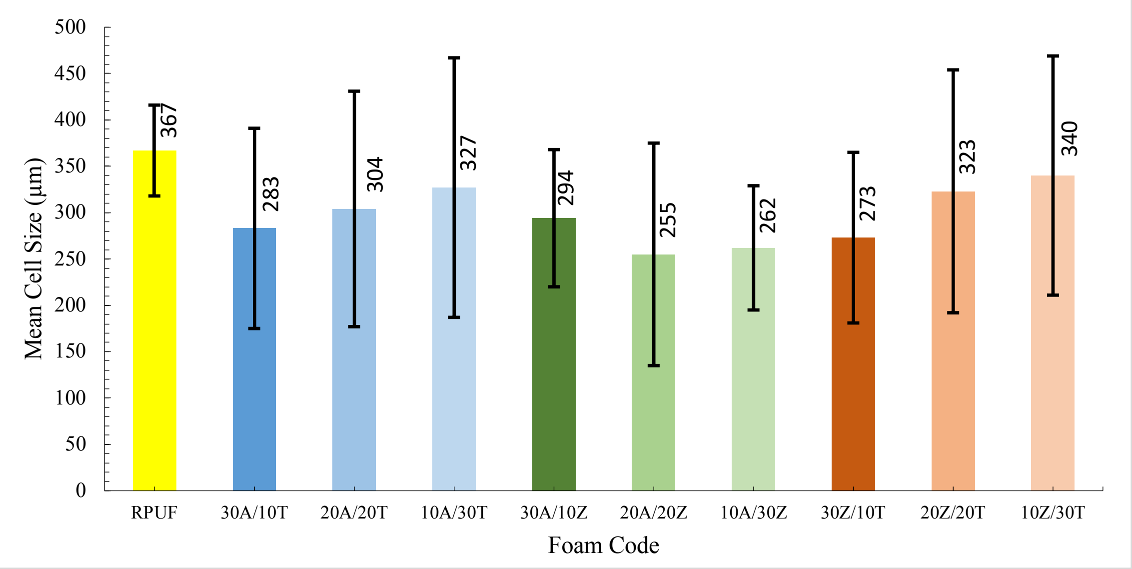


Figure 4.12. *Effect of blend type and composition on the mean cell size*

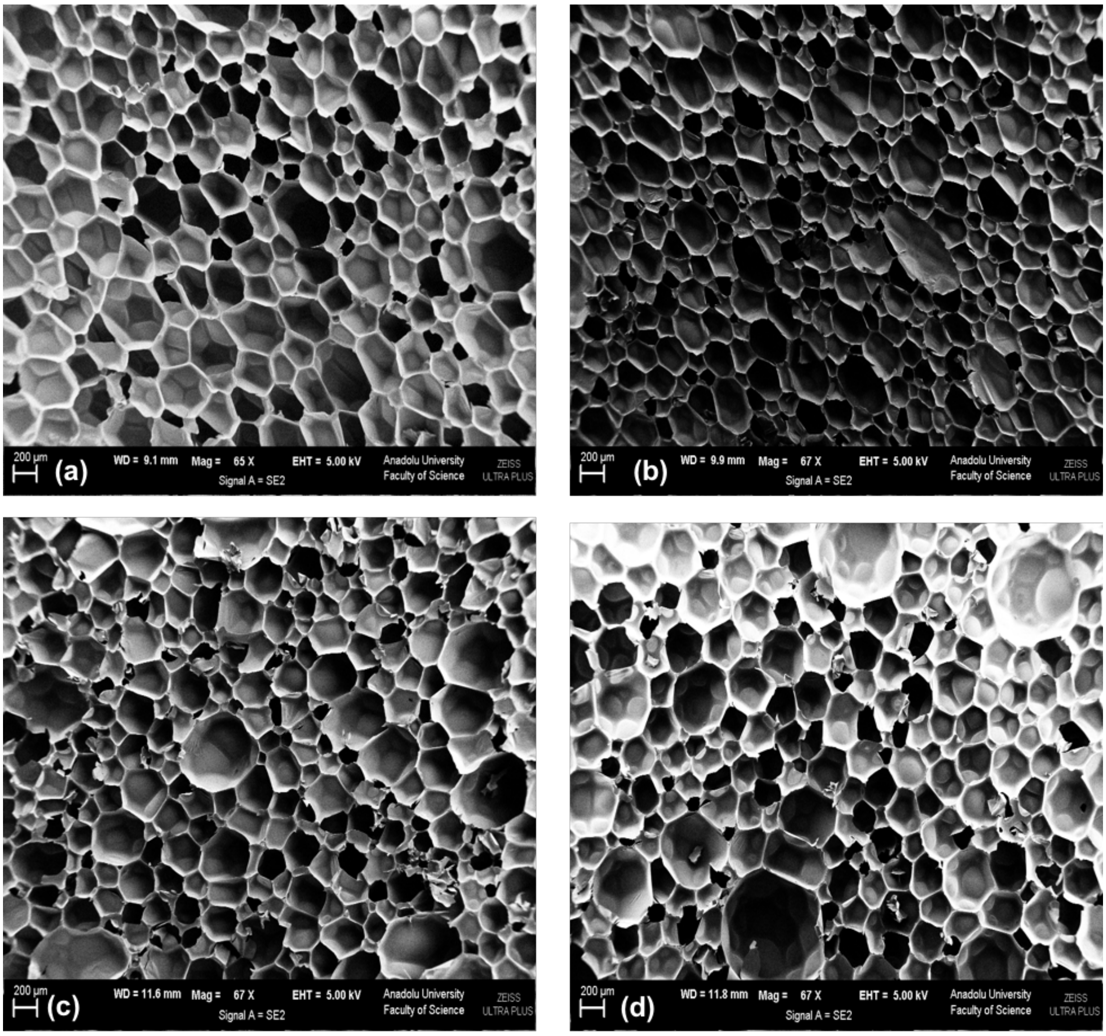


Figure 4.13. *SEM images of the foams a) RPUF, b) 30A/10T, c) 20A/20T, d) 10A/30T*

Table 4.4 depicts the effects of blend type and composition on the closed cell content of foam composites. The closed cell contents of composites containing blends were observed to be higher than that of RPUF. However, it can be recommended that these changes in closed cell content could not affect the thermal conductivity and compressive strength of the foams.

Table 4.5. *Closed cell content of the composites containing blends (RPUF: 87.1%±2)*

Foam Code	Closed Cell Content (%)	Foam Code	Closed Cell Content (%)	Foam Code	Closed Cell Content (%)
30A/10T	91.7	30A/10Z	91.2	30Z/10T	92.7
20A/20T	92.6	20A/20Z	91.5	20Z/20T	93.4
10A/30T	91.8	10A/30Z	92.0	10Z/30T	92.8

The variation of thermal conductivity of composites with blend type and composition is shown in Figure 4.13. In accordance with mean cell size, thermal conductivity values of foam composites also increased with increasing TPhP content of blends, and interestingly, conductivity values of A/Z combinations were observed to be lower than that of RPUF for all compositions. The foams of 20A/20Z showed the lowest thermal conductivity value of 20.78 mw/m.K among the composites. The decrease in its cell size was a factor that contributed to the mentioned results (Thirumal et al., 2010b, p. 2264).

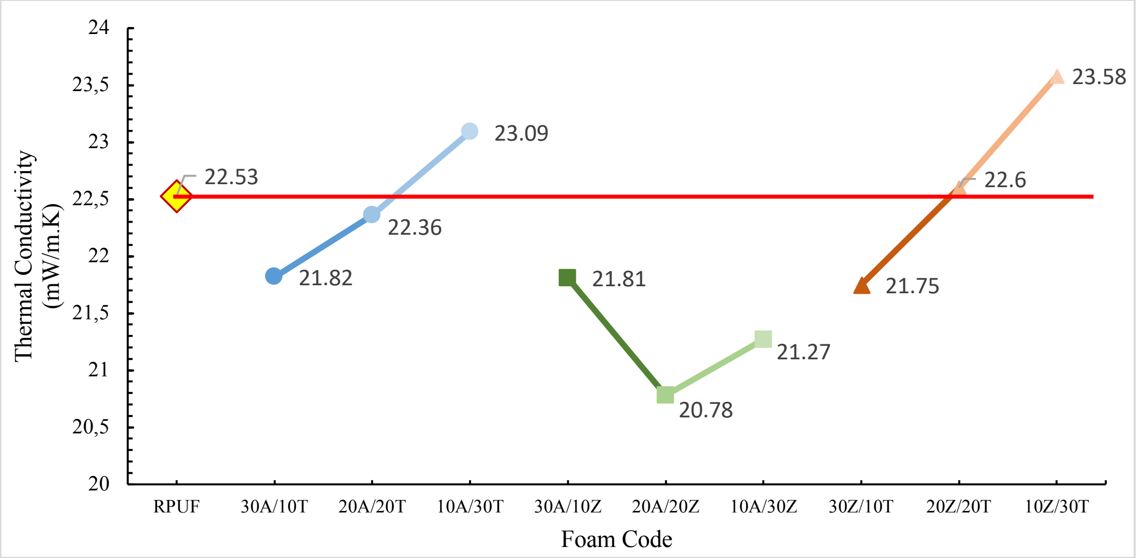


Figure 4.14. *Effect of blend type and composition on the thermal conductivity*

4.3. Changes in Compressive Strength

4.3.1. Effects of ATH, TPhP and ZnB

Foam density is one of the most significant parameters that affect the mechanical properties of RPUFs. The density of foams can vary with the changes in the type and amount of blowing agents and the additives used (Thirumal et al., 2007, p. 249). In this study, the blowing agent content was fixed and the content of FR additives varied from 10% to 50% by polyol weight percentage. The effect of type and loading level on the density of the composites is shown in Figure 4.14. The density of RPUF was observed to be 36.2 kg/m^3. The figure indicates that the density marked a linear increase with the increasing amount of FR additives. The reasons for the increase in density of foam composites can be evaluated as the higher density of FRs (ρ_{ATH}: 2443.9 kg/m^3, ρ_{TPhP}: 1205.5 kg/m^3, ρ_{ZnB}: 469.34 kg/m^3) than that of RPUF and increasing viscosity that results into hindering the foaming process in the presence of FRs (Piszczyk et al., 2012, p. 1729, Thirumal et al., 2010b, p. 2263).

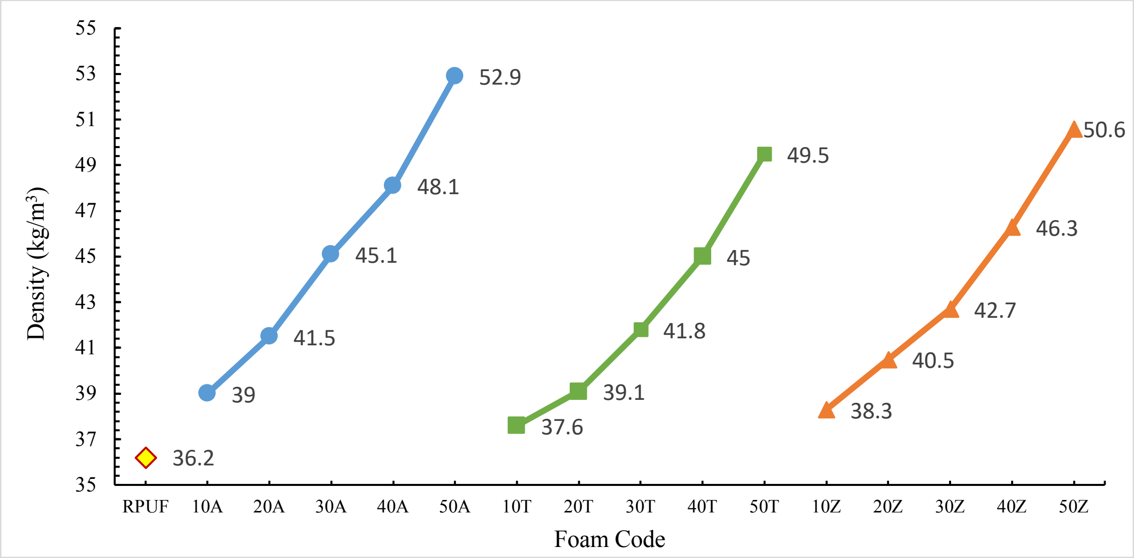


Figure 4.15. *Effect of FR type and amount on the density*

As known from literature, the presence of additives has a great impact on the mechanical properties of the RPUF. The compressive strength of the foams is one of the most important parameters to determine their applications (Kabakci et al, 2017 , p. 11). Figure 4.15 shows the effect of the increasing loading of ATH, TPhP, and ZnB on the compressive strength. The red line on the 120 kPa shows an acceptable compressive strength value for most of the applications. The compressive strength of RPUF was determined to be 140 kPa. By the addition of ATH until 40%, the compressive strength first increased and then decreased with the further addition of ATH. Moreover, the compressive strength at 50% ATH content was even higher than that of RPUF. Similar results were obtained from the other composites filled with TPhP and ZnB. Almost all foam composites were in acceptable values of the strength. One of the other important parameters that affects the compressive strength is the interaction among additive particles and polymer chains (Lorenzetti et al., 2010, p. 3674, Xu et al., 2007, p. 445, Cao et al., 2005, p. 781). The contribution of H-bond formation among urethane groups to the compressive strength is well known. The FRs may interfere with the H-bond formation in polyurethane foams, which in turn has a negative effect on the mechanical properties. As a result, the increase in density competes with the hindering of H-bond formation among urethane groups in order to determine the compressive strength. The reason behind the decrease in the compressive strength after 40% ATH loadings could be the dominant effect of interference with the H-bond formation. This explanation is applicable to the other composites containing TPhP and ZnB.

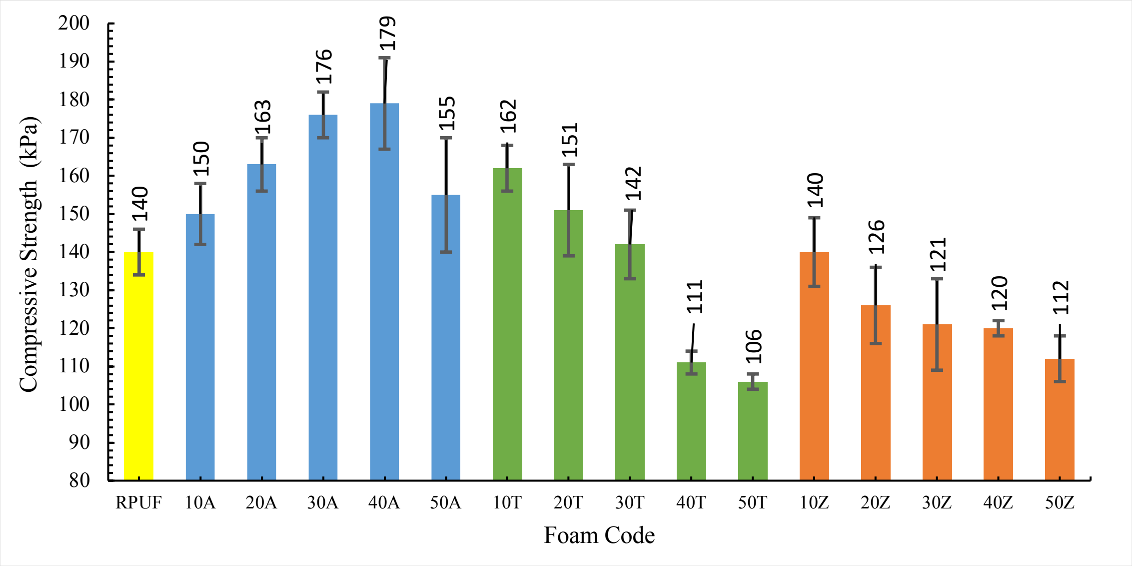


Figure 4.16. *Effect of FR type and amount on the compressive strength*

4.3.2. Effects of blends

Figure 4.16 depicts the effect of the blend type and composition on the density of foams. It is indicated that the addition of blends causes an increase in density as compared to the foam without additive. This was mainly associated with the higher densities of FR additives than that of RPUF. The highest density among the foams was specified in the case of the 30A/10T foam. This was probably due to the higher density of ATH as compared to that of TPhP and ZnB. Also, the density of 30A/10T foam was higher than that of 30A foam. While the density of 30A/10T foam was 49.6 kg/m^3, the density of 30A foam was 45.1 kg/m^3.

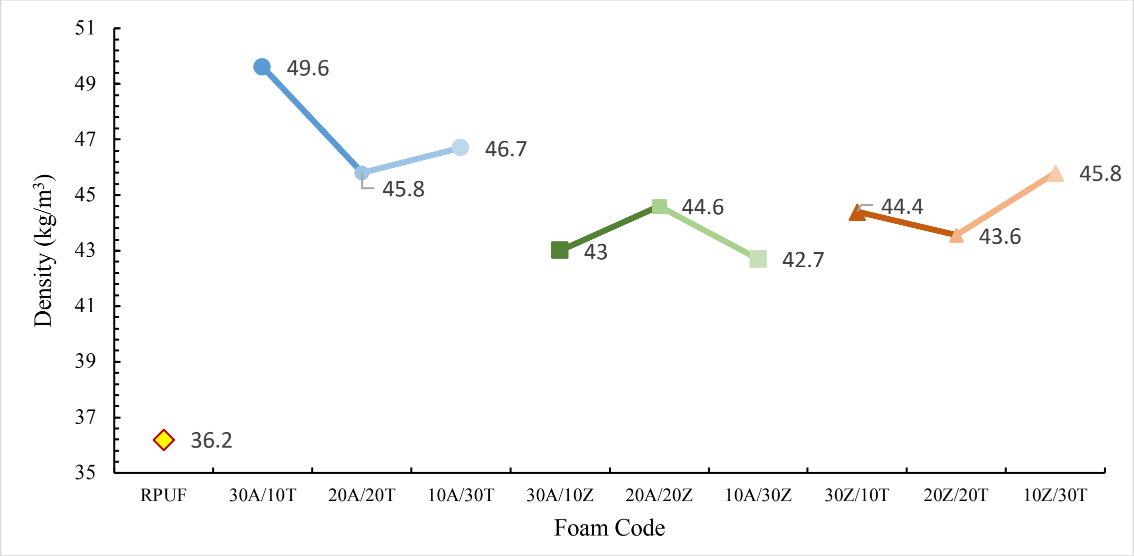


Figure 4.17. *Effect of blend type and composition on the density*

Figure 4.17 illustrates the effect of the blend type and composition on the compressive strength of foams. As seen in the figure, all composites were above the 120 kPa, and all RPUF composites containing blends have been observed to contribute to the rigidity of the composites. While the compressive strength value of 30A, 30T and 30Z was determined as 176, 142 and 121 kPa, respectively, these values increased for the composites with blends containing the same amount of corresponding FR (except for 30A/10Z), 149 kPa for 30T/10Z, 195 kPa for 30T/10A, 141 kPa for 30Z/10A, 170 kPa for 30Z10T, 144 kPa for 30A/10Z and 181 kPa for 30A/10T. The compressive strength of 20A/20T was lower with respect to that of 20A, the reason behind which was probably the plasticizing effect of TPhP with ATH, which matched up with the change in density (Thirumal et al.,2010b, p. 2263).

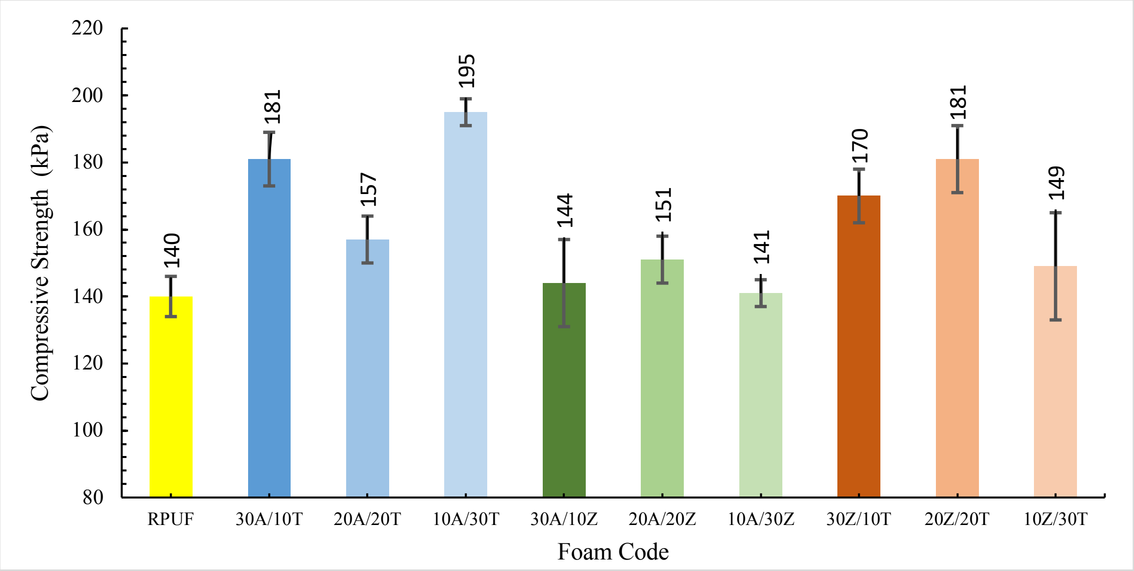


Figure 4.18. *Effect of blend type and composition on the compressive strength*

5. CONCLUSIONS AND SUGGESTIONS

The objective of this research was to produce rigid polyurethane foam composites possessing improved flame retardant properties besides both thermal insulation (with low thermal conductivity) and mechanical (with high compression strength) properties. For that purpose, ATH, ZnB, and TPhP and their binary blends were incorporated into RPUF at different loadings. Some thermal, microscopic, calorimetric, and physical techniques/machines were applied/used for the characterization of the foams. LOI, UL 94 HB, and cone calorimeter tests were conducted for flame retardancy, heat flow measurements for thermal conductivity, and mechanical tests for compressive strength. The results are summarized below:

- Almost all FRs or blends could improve the FR properties of composites. The flame spread rates for composites depicted a significant reduction in comparison to the RPUF. Moreover, self-extinguishing was observed for 50A, 40T, 50T, 30A/10T and 20A/20T.
- The LOI values depicted a linear increase with the addition of FRs to the foam. The most efficient additive was TPhP, where the LOI of the 50T foam increased by 15% with respect to the RPUF. This increment ratios for 50A and 50Z were 13.5% and 8.3%, respectively.
- From the cone calorimeter results, two peaks were observed in the HRR curves. The first peak was seen because the HRR value increased greatly until the formation of a char layer, following which it started to decrease. A second peak was observed as soon as the char layer cracked.
- The TTI, t pHRR, and pHRR values marked an improvement with the addition of FRs for almost all composites. The TTI values for the composites were higher than the TTI value of RPUF. TTI increased from 1 s to 4 s for in the presence of some FRs of blends. Morever, due to the presence of good charred layer the peak of 2-HRR of composites appear much later. HRR values of T series composites decreased to 0 in about 100s, while the other composites and RPUF continued heat release. The pHRR value of 30Z/10T was 183.06 kW/m^2, and this value improved by 20% and 33% in comparison with the 30Z composite and the RPUF, respectively. In addition to this, the MARHE value of the 30Z/10T sample, which was 153.5 kW/m^2, depicted an improvement of 35% and 21.5% according to the RPUF and 30Z sample respectively.

- TSR, TSP, mean CO and mean CO_2 yields decreased with the addition of ATH. Due to the increment mean CO yield, toxicity of released gas increased for the T series composites. Moreover, the higher loading level of TPhP, the toxicity was much. Similarly, with increasing the ratio of TPhP in the blend, realeased gas became more dangerous. However, the mean CO and mean CO_2 yields increased significantly increased with the increase in the content of TPhP.
- In many cases, the presence of FRs had effects of reducing the mean cell size. The addition of 50% ATH and ZnB caused the reduction of around 30% for both, and the addition of 50% TPhP caused an increase of 13.5% when compared to that of RPUF.
- The closed cell content of RPUF was about 87%. With the addition of FRs, this content of composites rose up to the level of 90–91%. It is acceptable that considerable changes were not observed in the closed cell content in the presence FRs/with increasing loading of FRs.
- The thermal conductivities of composites doped with ATH and ZnB were lower than that of RPUF, even at the foams of 50A and 50Z. The thermal conductivity values decreased at the level of 2.4% for the 50A sample and 3.4% for the 50Z sample. The lowest thermal conductivity value was obtained as 20.78 mW/m.K in the foam of 20A/20Z, corresponding to the reduction of 7.8%.
- The densities of all composites depicted a linear increase with an increasing amount of FRs. While the density of RPUF was measured to be 36.2 kg/m^3, the densities of the 50A, 50T, and 50Z samples were 52.9, 49.5, and 50.6 kg/m^3 respectively. For composites containing blend, this value changed between 42.7 and 49.6 kg/m^3.
- Almost all the obtained composites were within the acceptable value. The compressive strength marked an increase till the addition of ATH till 40%, after which it decreased. The compressive strength at 50% ATH content was higher than that of RPUF. Compressive strength gradually decreased for the composites incorporated TPhP or ZnB with increasing doping amounts. However, composites possessing low amount of TPhP or ZnB had still better mechanical properties in comparison to RPUF.

It was proven by means of this study that incorporating ATH, ZnB, TPhP, and their binary blends into foam enhances the flame retardancy performance. In addition to this, composites that have better thermal insulation properties and mechanical properties were produced.

The challenges encountered during the analysis of the experimental and numerical results form the basis for the following recommendations for future works.

- All experiments that have been carried out could be conducted again by using Reaction Injection Molding (RIM) instead of hand molding.
- The FR additives and their proportions could be varied.
- The effect of FRs on the products that RPUFs released during combustion can be studied.
- The char residue after burning RPUFC with cone calorimeter can be examined with SEM, and an attempt could be made to relate between FR and its char residue.

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- Irmak, C., Suvacı, E., Erdem, M., Uysal, O., Sayer, G., Kaya, M. and *Akdoğan, E.* "Effect of Phyllosilicate Type Organoclay Addition on The Properties of Rigid Polyurethane Foam" Polyurethane Technical Conference, Baltimore, Maryland USA, September 2016
- *Akdoğan, E.*, Erdem, M., Üreyen, M., E., Uysal, O., Irmak, C., Suvacı, E., Sayer, G. and Kaya, M. "Effects Of Halogen-Free Flame Retardant Additives on The Flame Retardancy, Thermal İnsulation And Mechanical Properties Of Rigid

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