

**DEVELOPMENT OF FIRE-RESISTANT  
POLYSTYRENE COMPOSITES FOR THERMAL  
INSULATION OF BUILDINGS**

BY

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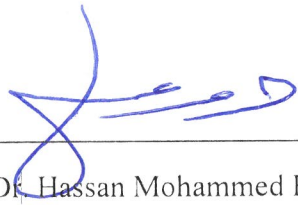
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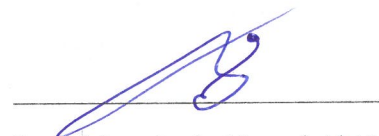
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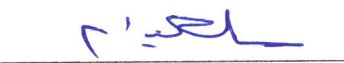
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**Dedicated to**

My lovely parents [Khadijah Isma'il] and [Isah Abdullahi], siblings, and friends

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## LIST OF ABBREVIATIONS

|      |   |                                       |
|------|---|---------------------------------------|
| LOI  | : | Limiting Oxygen Index                 |
| TGA  | : | Thermogravimetric Analysis            |
| DTG  | : | Differential Thermogravimetry         |
| PS   | : | Polystyrene                           |
| FR   | : | Flame Retardant                       |
| APP  | : | Ammonium Polyphosphate                |
| PA   | : | Phytic Acid                           |
| MEL  | : | Melamine                              |
| PER  | : | Pentaerythritol                       |
| UF   | : | Urea Formaldehyde                     |
| ASA  | : | Acrylonitrile Styrene Acrylate        |
| LDH  | : | Layered Double Hydroxide              |
| PCL  | : | Triheyltetradecylphosphonium Chloride |
| CNT  | : | Carbon Nano Tube                      |
| HBCD | : | Hexabromocyclododecane                |
| TPP  | : | Triphenyl Phosphate                   |

|       |   |                                                         |
|-------|---|---------------------------------------------------------|
| PHRR  | : | Peak Heat Release Rate                                  |
| TPU   | : | Polyurethane Elastomer                                  |
| THR   | : | Total Heat Release                                      |
| CC    | : | Cone Calorimeter                                        |
| EP    | : | Epoxy                                                   |
| MDH   | : | Magnesium Dihydroxide                                   |
| ATH   | : | Aluminium Trihydroxide                                  |
| MH    | : | Metal Hydroxide                                         |
| RD    | : | Red Phosphorous                                         |
| TDCPP | : | Tris(1,2-dichloro-2-propyl) Phosphate                   |
| PVC   | : | Polyvinyl Chloride                                      |
| ZB    | : | Zinc Borate                                             |
| EPS   | : | Expanded Polystyrene                                    |
| PSPR  | : | Peak Smoke Production Rate                              |
| PHTD  | : | Phosphorylated Histidine-amino Triazine-diamino Propane |
| XRD   | : | X-ray Diffraction                                       |
| FTIR  | : | Fourier Transform Infrared                              |

|     |   |                                      |
|-----|---|--------------------------------------|
| SEM | : | Scanning Electron Microscope:        |
| EDX | : | Energy dispersive x-ray spectroscopy |
| BET | : | Brunauer-Emmett-Teller               |
| DMA | : | Dynamic Mechanical Analysis          |

|

## **ABSTRACT**

Full Name : [MUTAWAKKIL ISAH]

Thesis Title : [Development of Fire-Resistance Polystyrene Composites for Thermal Insulation of Buildings]

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The development of zero-energy buildings has become increasingly essential to preserve energy resources and to reduce the energy demand. In addition, buildings should be healthy and economically viable places to live and work. Recently, polystyrene has been widely used in nonstructural elements, insulation material, partitioning, and fillings due to its low cost, availability, lightweight, and the good thermal insulation properties. However, due to the poor flame-retardant properties of polystyrene, its applications as insulation material are limited. Although it has excellent thermal insulation properties. Therefore, its thermal stability needs to be improved. There are well-established additives used as flame retardants in the polymer industry to improve fire resistance. However, these materials are hazardous to our environment despite their higher thermal stability such as halogen containing compounds. Recently, considerable efforts have been dedicated to the use of various halogen-free flame retardants to overcome such failures such as intumescent and nanomaterials, etc. In this study, two environmentally friendly flame retardants based on intumescent and layered double hydroxides were synthesized for polystyrene. The thermal stability and flammability of the composites were analyzed using thermogravimetric analysis (TGA) and limiting oxygen index (LOI), respectively. The results have shown that these materials are nontoxic and improved thermal stability of polystyrene.

## ملخص الرسالة

الاسم الكامل: متوكل عيسى

عنوان الرسالة: تطوير مركبات البوليسترين المقاومة للحريق من أجل العزل الحراري للمباني

التخصص الهندسة الكيميائية

تاريخ الدرجة العلمية: ديسمبر 2023

أصبح تطوير المباني الخالية من الطاقة أمرًا ضروريًا بشكل متزايد للحفاظ على موارد الطاقة وتقليل الطلب على الطاقة. كما يشترط أن تكون المباني ذات طابع صحي ومجدية اقتصاديًا للعيش والعمل. في الآونة الأخيرة، يتم استخدام البوليسترين على نطاق واسع في العناصر الغير هيكلية، والمواد العازلة، والتقطيع والحشوات لما يتميز به من انخفاض تكلفته، وتوفره، وخفة وزنه بالإضافة إلى خصائص العزل الحراري الجيدة. بالرغم من ذلك فإن خصائص البوليسترين تعاني ضعفًا في مقاومة اللهب، مما يحد تطبيقه كمادة عازلة على الرغم من أنها تتمتع بخاصية عزل حراري ممتازة. ولذلك نحتاج إلى تحسين الثبات الحراري. هناك إضافات راسخة تستخدم كمثبطات للهب في صناعة البوليمر لتعزيز مقاومة الحريق؛ إلا أن هذه المواد تشكل خطورة على بيئتنا على الرغم من ثباتها الحراري العالي مثل المركبات التي تحتوي على الهالوجين. مؤخرًا، هنالك مؤثرات معتبرة و متنوعة تم تخصيصها للاستخدام كمثبطات للهب كما أنها خالية من الهالوجين للتغلب على مثل هذه الأضرار؛ كالمواد المنتفخة والمواد النانوية وما إلى ذلك. في هذه الدراسة تم تصنيع اثنين من مثبطات اللهب الصديقة للبيئة والتي تعتمد على هيدروكسيدات مزدوجة، و منتفخة، و ذات طبقات من أجل البوليسترين. تم تحليل الثبات الحراري، والقابلية للاشتعال للمركبات باستخدام تحليل قياس الوزن الحراري (TGA) و مؤشر الأكسجين المحدد (LOI) على التوالي. وقد أظهرت النتائج أن هذه المواد غير سامة كما أنها ساهمت في تحسين الثبات الحراري للبوليسترين.



# CHAPTER 1

## INTRODUCTION

### 1.1 Background

Recently, energy consumption in buildings has made up a significant amount of global energy consumption, which has attracted a lot of attention [1]. Building materials with exceptional insulation properties have been widely used to solve the issue of energy waste, as the reduction of emission in buildings is highly dependent on these materials [2]. Zero-energy buildings are increasingly becoming important due to limited energy resources and an increasing demand for energy. Polymers have been widely used as energy-saving materials with excellent properties, including corrosion resistant, low electrical and thermal conductivity, lightweight, strong, and easy to work with [3]. One of the thermoplastic polymers that has drawn much attention is polystyrene (PS), whose unique properties are desired in building applications [4], [5]. In 2021, 15.61 million metric tons of polystyrene were produced globally. It is expected to grow slightly by 2026, and the production capacity is anticipated to reach 16.75 million metric tons [6]. Due to its excellent thermal and electric insulation, higher specific modulus, and flexibility, polystyrene continues to be used in current zero-energy construction [7]. However, this material is well known to be flammable or/and combustible materials due to the carbon-hydrogen bonds. Consequently, it is easy to start a fire, and other serious hazards while using, it may jeopardize people's lives. Much attention has been paid to this safety issue

[8], [9]. Due to the poor flame retardant properties of polystyrene, its application as an insulation material was limited. Although it has excellent thermal insulation properties. Therefore, its thermal stability needs to be improved and the emissions of harmful gases and smoke need to be suppressed. To ensure its dependability and safety in a variety of applications [10].

In order to make PS compounds more flammable and thermally stable, numerous flame retardant compounds have been used to address this technical challenge by dispersion in the PS matrix [11], [12]. Currently, there are numerous flame retardants, including halogen-based substances, organic and inorganic, nanofillers, renewable biomass, and intumescent flame retardants [13]. However, some flame retardants, such as halogenated-based compounds, despite their effectiveness as flame retardants, have been restricted due to their substantial risks to the environment and health [14]. Therefore, Halogen-free flame retardants are recommended. When it comes to halogen-free materials [15]–[17], intumescent flame retardants (IFRs) have gained substantial attention as due their excellent flame retardant effectiveness and environmental friendliness [18]–[20]. Acid, carbon, and gas sources are the required number of components that must be included in an intumescent flame retardant [21]–[23]. Melamine, ammonium polyphosphate (APP), and pentaerythritol (PER) are typical IFRs compounds that are frequently used to give polymers flame retardancy [24]. Qin et al. developed an IFR system to treat polystyrene for flame retardancy by using melamine (MEL), Phytic acid (PA) and acrylonitrile-styrene-acrylate (ASA). When the flame retardant content reached 20 wt% by weight, the composite has passed the vertical burning test (UL-94) level V-0. The limiting oxygen index (LOI) has enhanced to 37% [25]. Cao et al. modified urea formaldehyde resin (UF)

by incorporating melamine to increase the solid content. When the IFR load reached 35wt%, the LOI of the PS compound improved by 36.3% and has the level V-0 [26]. The intumescent flame-retardant polymer system's "three sources in one" is an important area for further research. By combining the gas, carbon, and acid sources into a single material, a phosphorus-nitrogen synergistic flame retardant with enhanced properties is developed, which enhances the effectiveness of the flame retardant. By developing a synergistic P-N flame retardant called PDMPD, Tai et al. were able to improve the char formation of a PS material [27]. Furthermore, Yan et al. were able to synthesize a new IFR in which carbonization agent and ammonium polyphosphate were used to produce flame resistant PS. with LOI value of 32.5% and UL-94V-0 classification with an IFR, loading of 28 wt% [28]. The loading of flame retardants is typically substantial to obtain great flame resistance; however, this high concentration will significantly compromise mechanical quality and restrict the use of PS products [29].

In this research, a cost-effective approach for the synthesis of two novel and environmentally friendly materials were successfully synthesized. Firstly, a novel intumescent flame retardant was synthesized via a hydrothermal method. Here, a novel unified nanosheet was formed and exfoliated on graphene sheets. Melamine (gas source), ammonium dihydrogen phosphate (acid source), and graphene (carbon source). Lastly, ZnAl-LDH (layered double hydroxide) was modified by graphene and phosphonium-based ionic liquid trihexyltetradecylphosphonium chloride (PCL) as flame retardants aiming to improve the flame retardancy, thermal stability, and mechanical properties of the polystyrene matrix.

## **1.2 Aim and Objectives**

The purpose of this study is to synthesize an environmentally friendly flame retardant which will be used to develop a fire-resistant polystyrene for thermal insulation of buildings.

The specific objectives of the study are:

- i Synthesis of a highly dispersed flame retardant.
- ii Chemical functionalization of the synthesized filler for improved dispersion
- iii Prepare polystyrene composites with varying composition
- iv Study the effect of various materials on the flame resistance of PS
- v Study the effect of nanomaterials on the thermal stability, thermal conductivity, and mechanical properties of PS |

## CHAPTER 2

### LITERATURE REVIEW

Foamed polystyrene (PS) is commonly used in building and construction as insulating, partitioning, and filling material due to its low cost and availability. However, there is a need to lower the flammability of the PS material. One of the approaches to improve the flame retardancy of PS is to blend it with nanomaterials and produce a well-dispersed nanocomposite. Nanomaterials such as graphene, CNT, graphene oxide,  $\text{Sb}_2\text{O}_3$ , etc. have been reported to impart flame resistance to PS or other polymers. Generally, the mechanism of flame retardancy can be classified into two pathways [30]–[32].

1. Gas-phase active flame retardants: Such flame retardants work on the principle of inhibition chemistry. For example, these materials are likely to produce a radical scavenger upon heating. This radical scavenger captures the free radicals produced during decomposition, which decrease the rate of degradation. Examples of such flame retardants are hexabromocyclododecane (HBCD), triphenyl phosphate (TPP), and triphenyl phosphine sulfide (TPPS).
2. Condensed-phase active flame retardants: This type of flame retardants slows down the degradation process by forming a solid or char layer, which insulates the remaining bulk of the polymer from heat and further degradation. Examples include phosphorus-derived flame retardants such as triphenyl phosphate. Similarly, clay-based PS nanocomposites are also reported to improve the flame retardancy by barrier formation [32].

The PS matrix does not possess carbonyl functional groups. Therefore, the catalytic effect on the degradation due to nanoparticles or metals/metal oxides resulting from the decomposition of the flame-retardants can be neglected. The degradation of PS proceeds through the hydrogen elimination of the main polymer chain resulting in the formation of a weak PS radical followed by further degradation via  $\beta$  scission [33]. A Molecular dynamics study by Beach et al. [34] showed that the most favorable cleavage site is the hydrogen on the 3° carbon of PS.

Yang and Nelson [35] studied the thermal stability and flame retardancy of attapulgite clay/PS and silica/PS nanocomposites. The authors reported a significant 66 °C increase in 10% weight loss temperature for 10% silica/PS nanocomposites against a nominal increase of 5 °C for attapulgite clay/PS nanocomposite. The oxygen index (OI) of both silica/PS and attapulgite/silica nanocomposites also improved. Moreover, the addition of silica or attapulgite to sink-filled PS also resulted in reduced dripping during vertical burning. Improved thermal stability was attributed to the synergistic effect of free radical scavenging and restriction of chain movements due to the interaction between PS chains and the nanomaterials. Lu and Wilkie [32] studied the combined effect of MWCNTs, clay (Cloisite 15A), and brominated flame-retardant (bromine-antimony oxide ( $\text{Sb}_2\text{O}_3$ )) on the flame retardancy of PS. It was reported that the addition of 2 wt.% MWCNTs and clay resulted in a 67% and 61% reduction in peak heat release rate (PHRR), respectively, as compared to a mere 24% reduction due to the addition of brominated-antimony oxide. The authors also reported a higher synergy between MCWNTs and Br- $\text{Sb}_2\text{O}_3$  as compared to clay and Br- $\text{Sb}_2\text{O}_3$ . Xue et al. [36] studied the flame retardancy of PS/heterionic of organic montmorillonite (OMt) nanocomposites, i.e., NaOMt/PS, CaOMt/PS, and FeOMt/PS. It

was reported that all these varieties of OMt improved the flame retardancy of PS, evidenced by the delay in reaching the peaks of heat release rate (HRR), CO-release rate, smoke production rate, and mass loss rate. Moreover, the heat release rate was reported to be minimum in the case of PS/NaOMt nanocomposites, and it increased in the order PS/NaOMt < PS/CaOMt < PS/FeOMt. Moreover, Si et al. [30] reported enhanced flame retardancy of PS-reinforced modified MXene ( $\text{Ti}_3\text{C}_2$ ) nanocomposites. MXene was functionalized long-chain cationic functionalities, i.e., OTAB, DDAB, and DTAB. The modified MXene/PS nanocomposites showed enhanced flame retardancy evidenced by a 20 °C or more increase in 5% weight loss temperature, 20% or more reduction in PHRR, and a notable reduction in the formation of CO and  $\text{CO}_2$  gases. Sabet et al. [37] discovered that adding graphene oxide filler to polystyrene and polypropylene polymers lowered the heat release rate, making it a good alternative for fire safety. Sulong et al. [38] reviewed the numerous applications of expanded polystyrene, highlighting its excellent thermal insulation, impact resistance, and load-bearing capabilities. Wang et al. [39] developed a flame retardant material by combining brominated polymeric flame retardant, polystyrene, and a combination of hydrotalcite,  $\text{Sb}_2\text{O}_3$ , OMMT, and graphite. They observed that the presence of hydrotalcite improved its thermal stability and flame retardancy.

Recently, Wen-Juan et al. [40] improved the thermal stability of thermoplastic polyurethane elastomer (TPU). TPU is a highly combustible material with hazardous droplets and smoke, which severely limits its practical use. In their work, a halogen-free flame retardant was created to increase TPU's flame resistance. The TPU/AL-APP5 composites, which contain phosphorus and nitrogen elements, were created by modifying

ammonium polyphosphate (APP) with sodium alendronate (Al). The LOI of these composites was found to increase from 20.7% to 26.5%, surpassing the V-0 rating in the UL-94 vertical measurement without any droplets. Additionally, the peak heat release rate (PHRR) and total heat release (THR) of the TPU/AL-APP5 system were decreased from 1021 to 255 kW/m<sup>2</sup> and 87.5–61.2 MJ/m<sup>2</sup> respectively in the cone calorimeter (CC) measurement, compared to the purchased TPU. The results of thermogravimetric-infrared and Raman spectroscopy show a positive correlation between the creation of inert gas and the development of a continuous carbon layer of AL-APP in improving the fire resistance of TPU composites. Additionally, the elongation at break of TPU/AL-APP5 experienced a significant increase by 19.9 % compared to neat TPU, showing a better softness and elasticity than neat TPU. According to the findings, it was determined that this work is advanced by a straightforward technique that provides high flame-retarding efficiency and good mechanical performance for TPU composites.

While, Jiang et al. [41] have reported a very effective flame retardant for epoxy by constructing polyphosphazene functionalized titanium carbide (Ti<sub>3</sub>C<sub>2</sub>Tx). Polyphosphazene-functionalized Ti<sub>3</sub>C<sub>2</sub>Tx (MXene-PZN) nanosheets were prepared and added to epoxy resin (EP) to prepare EP/MXene-PZN nanocomposites. It was observed that EP/MXene-PZN follows both vapor and condensed phase mechanisms during burning. Due to the complexity of the processes that take place during combustion, the mechanism of Ti<sub>3</sub>C<sub>2</sub>Tx and the modifying agent is unclear. The thermal stability test has shown that the peak heat release rate and total heat release of EP/MXene-PZN were reduced by 44.8% and 54.8%, respectively. While CO and CO<sub>2</sub> production rates also decreased to 49.4% and 41.9%, respectively, compared to pure EP. The findings indicated an enhanced interfacial

interaction and commendable compatibility of MXene-PZN nanosheets within the EP matrix. This led to a 46.5% elevation in the storage modulus and a 68.4% increase in the tensile strength of EP/MXene-PZN-2.0 when 2 wt.% MXene-PZN was incorporated into the EP matrix.

## **2.1 Flame retardant**

A flame retardant is a substance or chemical compound that is applied to materials, such as polymers, textiles, or other flammable substances, to reduce their flammability and decreases the spread of flames when exposed to fire. Flame retardants work by interfering with the combustion process through various mechanisms, such as dilution of flammable gases, heat absorption, or the formation of a protective char layer. Flame Retardants are substances that are used with polymers to stop the fire from starting or spreading., which can either be Additive FR (physical mixing) or Reactive FR (Chemical reaction). The most used FR are additives, FR has the following use;

- i. Slows down polymer combustion and degradation
- ii. Reduces smoke emission
- iii. Avoid dripping
- iv. inhibits the spread or growth of a fire
- v. increases escape time

The use of flame retardants in this research aims to enhance the fire resistance of polystyrene materials, thereby improving their safety in construction applications.

## 2.2 Combustion mechanism

An exothermic chemical reaction called combustion occurs when an oxidant and fuel combine to produce an oxidized product. Combustion requires three constituents for the initiation and continuation of the fire which are; heat, oxygen, and fuel as shown in Figure

1. polymer serves as a source of fuel upon combustion.

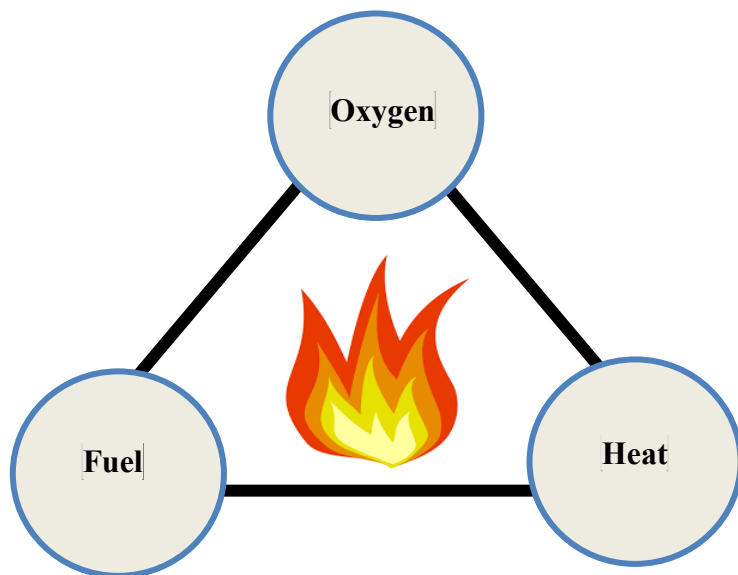


Figure 1 Combustion triangle

Generally, polymer combustion comprises four steps such as pyrolysis, ignition, combustion, and feedback. Polymers decomposed evolving flammable volatiles in the presence of enough source of heat [42]. Once polymeric materials are heated by an external source they will start degrading and reach a characteristics temperature. The polymer combustion process involves instantaneous combinations of mass transfer, polymer degradation, heat transfer, and fluid dynamics [43]. The availability of oxygen on the surface of the polymer depends on the types of polymers used, which plays a vital role in its surface decompositions (i.e., Thermo-oxidative degradation of polymer). Depending on the rate of polymer decomposition, flammable gases will be produced and diffused to the

flame front which fuels the fire. There is an increase in the number of combustible and flammable volatiles produced and released into the vapor phase when a polymer is exposed to external heat. The volatiles produced serves as a source of fuel by mixing with oxygen in the atmosphere [44]. Condensed (solid), vapor (gas), and mesophase phases are all possible during polymer burning. If enough heat is produced and enough heat is absorbed by the polymer, combustion may become self-propagating [45]. To maintain the combustion process going, the heat generated through this process is returned to the polymer's condensed phase. Additionally, polymeric materials are capable of melting and flowing, creating pools of combustible elements that could cause a secondary fire hazard since this typically causes a larger fire [46]. When the temperature reaches a certain level, the polymer material automatically produces flammable compounds with volatile characteristics. When the combustible compounds build up in the air to a specific concentration, combustion will then occur [47]. Degradation and combustion in thermal oxygen are two different types of polymeric material combustion. In this process, components in the condensed phase are degraded and decomposed, and the end products are diffused into the solid and gaseous phases. When the decomposed materials are combined with air, a chain reaction occurs [48].

### **2.3 Flame retardant mechanism**

The development of novel, efficient flame retardants requires a thorough understanding of fire retardancy mechanisms. The main aim of flame retardants is to improve the thermal stability of polymers and keep the flames from spreading. The fire triangle of oxygen, fuel, and heat must be broken in order to stop combustion. Consequently, one or more components, such as oxygen, fuel, and heat, must be eliminated or reduced in order to

accomplish flame retardancy. Flame resistance mechanisms are either physical, chemical, or both. Figure 2 illustrates flame retardant additives mechanisms.

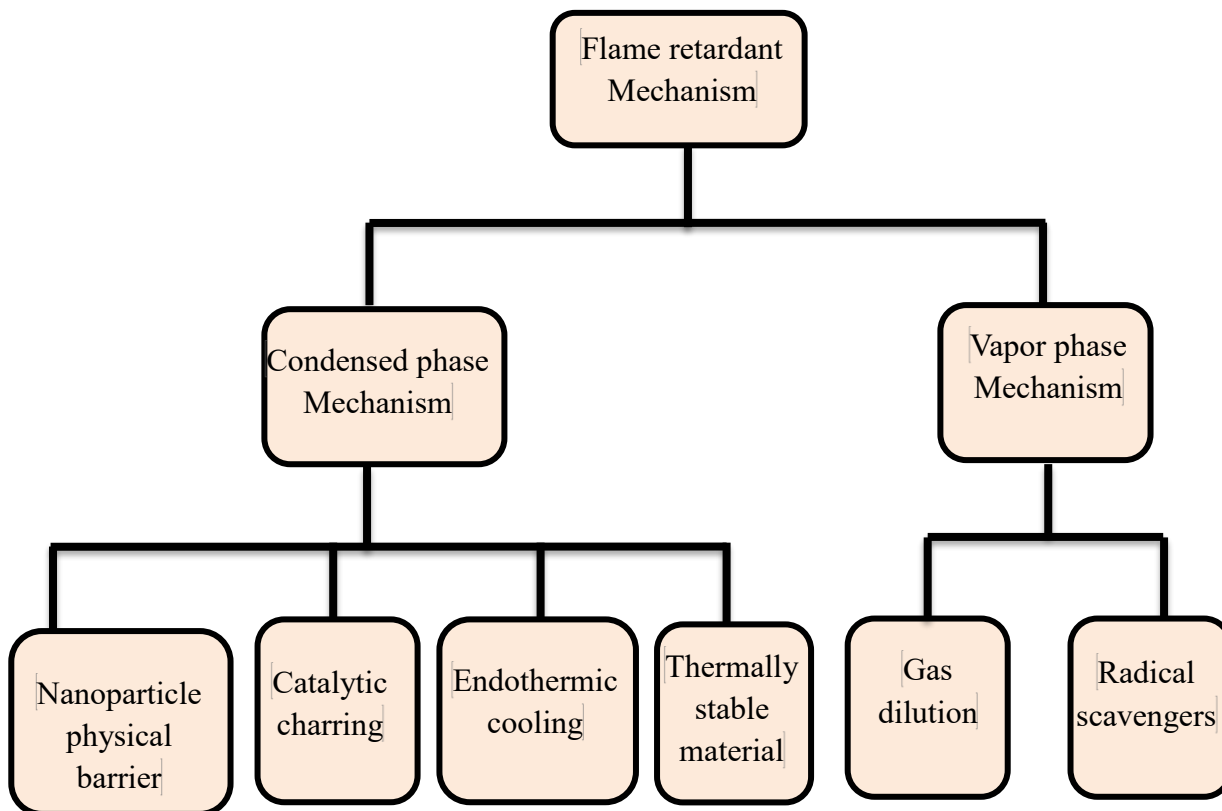


Figure 2 Flame retardant mechanism

### 2.3.1 Vapor phase mechanism

Vapor phase reaction can be inhibited by either gas dilution or radical scavengers. This instance of premixed methane, as well as oxygen flame combustion, has been well examined. A free-radical chain reaction, that is primarily made up of chain branching, propagation, and termination processes, is what makes methane burn. As a result, the methane-oxygen model can be used to analyze an extremely complex polymer flame [49]. Any flame retardant that either accelerates the rate of termination or lowers the rate of

propagation by reducing the concentration of these radicals is considered a vapor phase flame inhibitor [50].

#### **2.3.1.1 Gas dilution**

This is a non-flammable gas that is generated by the decomposition of particular flame-retardant substances at elevated temperatures. As the rate of production of this gas increases the flammable gas concentration will gradually drop. This leads to the suffocating effect of the fire and prevents the continuation of the burning process [51].

#### **2.3.1.2 Radical scavengers**

These are free radical inhibitors that stop the flame front from experiencing the effects of free radical propagation. By stabilizing radicals after being pyrolyzed by polymers (fuel). These flame-retardants include substances like phosphorous compounds, organochlorine and organobromine, which lowers the rate of heat release by scavenging free radicals. According to the combustion reaction theory, free radicals are necessary for combustion to continue. once free radicals are stabilized, the flame density will be decreased in the burning area which lowers the rate of burning until it is completely quenched. Thus, after sufficient heat and free radicals have been eliminated from the process, the combustion will stop [47], [48].

### **2.3.2 Condensed phase mechanism**

Solid phase flame inhibition will be achieved with the use of substances that disintegrate endothermically in the pyrolysis zone of the burned material. Condensed phase inhibition can also be attained by cooling or char barrier formation [52]. The addition of thermally

conductive fillers enhances cooling because they have higher thermal conductivities compared to polymers.

#### **2.3.2.1 Endothermic cooling mechanism**

Such flame retardants can work in vapor or condensed phases. This filler breaks down endothermically when the composites are heated, which cools the polymer, by releasing water vapor and non-combustible gases like carbon dioxide which will dilute the source of fuel (polymer). Simultaneously, the residue that these chemicals leave behind essentially shields the polymer. Such additives include metal oxides (Aluminum hydroxide), mineral fillers, and carbonates [53]. Polyvinyl alcohol is less combustible than polyethylene oxide due to its ability to endothermically form water molecules [54].

#### **2.3.2.2 Nanoparticle physical barrier mechanism**

Nanocomposites conduct heat away from hot regions due to their excellent thermal conductivities compared to polymers. Therefore, it's difficult to burn during the combustion process. But for the cooling effect higher loadings are required which leads to polymer mechanical properties [55]. Polymeric nanocomposites decrease flammability and increase thermal stability in polymers. Two mechanisms are involved which are; catalytic charring and physical barrier. A physical barrier occurs on the surface during combustion when the fillers form a net of floccules that combine with carbonaceous char. This char acts as a thermal shield on the surface/layer, It is thermally stable and serves as a shield between the flame and the material [56].

### 2.3.2.3 Catalytic charring mechanism

These types of flame retardants mostly operate in a solid phase by consolidating the polymer into strongly cross-linked char. such as intumescent, phosphorous compounds, etc. while burning these flame retardants creates stable bonds while breaking the old ones by reacting with thermally decomposed polymer. Therefore, higher fire retardancy can be achieved when flame retardant can form char upon heating because it limits the production of flammable products [57]. As shown in Figure 3 upon heating at certain temperature polymers tends to generate solid residues and volatile products. These residues may either be inorganic or carbonaceous char or both [58].

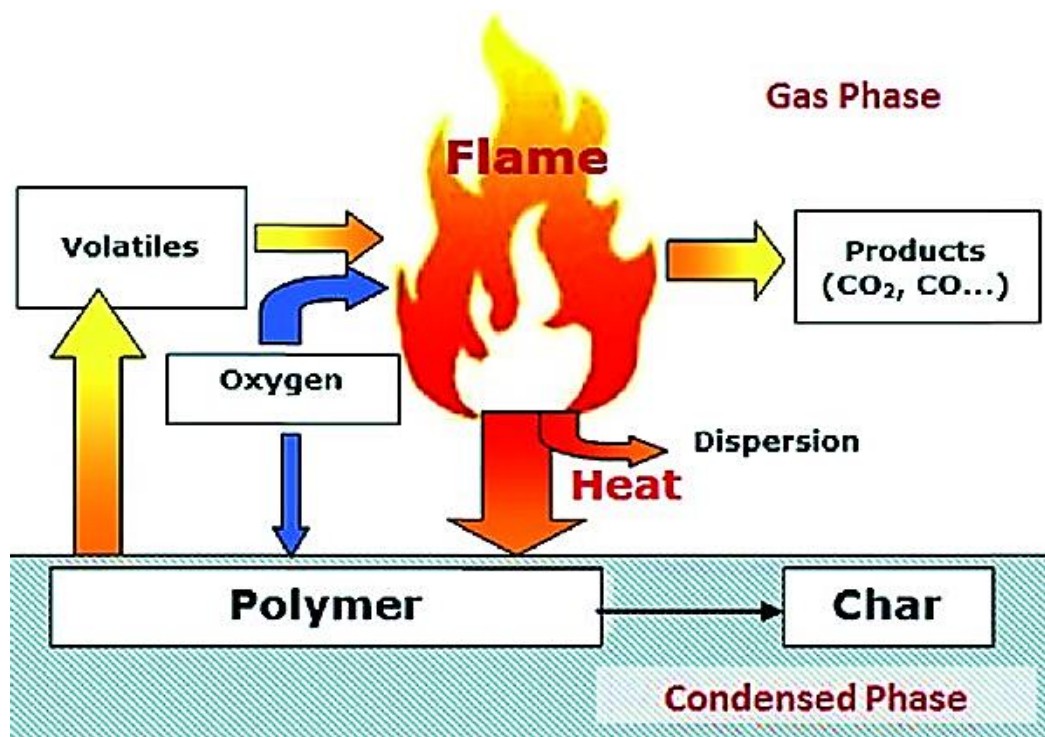


Figure 3 Char formation [59].

## **2.4 Recent Flame Retardants**

Currently, there are numerous types of flame retardants which includes; halogen-based agents, organic compounds, inorganic compounds, nano-filler materials, renewable biomass, and intumescent flame retardants. The organic flame retardants include silicon-based compounds, organophosphorus, etc. While An inorganic flame retardants are made up of metal hydroxides, nitrogen-based compounds, boron-based compounds, inorganic phosphorus flame retardants, etc. [56], [57], [59].

### **2.4.1 Halogen-based groups**

These are class of flame retardants that comprises of halogen for example; fluorine, chlorine, bromine, etc. Chlorine and bromine are the most used as halogenated flame retardant additives for plastics. These groups can be Aliphatic fluorinated compounds, polybrominated, biphenyl ethers, Tetrabromobisphenol, etc. Halogen compounds have better thermal stability compared to many polymers. In temperatures comparable to or lower than the temperature at which polymers decompose, they do not emit halogen free radicals. Their radicals serve as radical scavengers, with the following mechanisms:

- i. The flame retardants produce a huge quantity of hydrogen halide gas covering the materials' surfaces and isolate oxygen from the combustion cycle due to its higher density compared to air.
- ii. In the area of the material where gas phase combustion occurs, it releases active free radicals. These radicals later react with hydrogen halide and produce a stable inert radical, thus suffocating the fire.

- iii. It reduces material's temperature when it is decomposed, by absorbing heat as the material

Halogen-based flame retardants have the following benefits; Thermally stable, efficient radical quencher, low cost, stable in processing, easy dispersion, and high efficiency [60], [61]. However, it has drawbacks due to its ability to release toxic/corrosive smoke during the combustion process e.g., hydrogen halide gas. Therefore, it is under environmental scrutiny. Also, it is classified as persistent, bio-accumulative, and difficult to recycle. The bio-accumulation effect remains in the food chain which affects humans' health [62]–[64]. European countries have banned the use of halogenated agents such as brominated compound, this leads to the synthesis of highly efficient and environmentally friendly flame retardants [65]. Recently, polybrominated diphenyl ether alternatives have been established. Brominated trimethylphenyl compounds are in use due to their thermal stability. pentabromobenzyl acrylate as introduced by Dvir et al., [66], showed there is a decrease in the burning rate of magnesium dihydroxide (MDH) as loading increases. Halogenated groups are widely used in polymers. And have a better flame retardancy compared to metal dihydroxide and Aluminium trihydroxide (ATH). Tai and others MDH to produce a highly thermal composites by combining it with phosphate bromide and antimony [67]. The composites' performance was analyzed using the LOI testing, the result showed that just a 30% by weight mixture of antimony and bromide acid can attain the flame retardancy of 60w t% of MDH.

**Table 1 Some Halogenated flame retardant with their advantages and disadvantages**

| <b>Halogenated Flame Retardant</b>     | <b>Advantages</b>                                                                                                                                            | <b>Disadvantages</b>                                                                                         | <b>References</b> |
|----------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------|-------------------|
| Polybrominated diphenyl ethers (PBDEs) | Good compatibility with electronic materials, low cost, easy blending, excellent electric insulation.                                                        | Toxic, persistent, bioaccumulative, endocrine disruptors, neurodevelopmental impairments                     | [68]              |
| Polybrominated biphenyls (PBBs)        | Excellent fire resistance, easy mixing, well-matched with electronic materials, good electric insulation, cheap                                              | Toxic, persistent, bioaccumulative, endocrine disruptors, carcinogenic, immunotoxic <sup>2</sup>             | [69]              |
| Polychlorinated biphenyls (PCBs)       | Easy to mix, good electric insulation, well-suited for electronic materials, cheap, excellent flame retardance                                               | Toxic, persistent, bioaccumulative, endocrine disruptors, carcinogenic, immunotoxic                          | [70]              |
| Tetrabromobisphenol A (TBBPA)          | Cheap, good fire resistance, easy to blend, well-matched with electronic materials, good electric insulation                                                 | Toxic, bioaccumulative, endocrine disruptors, neurodevelopmental impairments, thyroid disruption             | [71]              |
| Hexabromocyclododecane (HBCD)          | Well-suited for electronic materials, excellent fire resistance, easy mixing, low cost, good electric insulation                                             | Persistent, bioaccumulative, endocrine disruptors, neurodevelopmental impairments, thyroid disruption        | [72]              |
| Decabromodiphenyl ether (decaBDE)      | Elevated flame retardant properties, facile integration, favorable compatibility with electronic materials, effective electrical insulation, and economical. | Toxic, persistent, bioaccumulative, endocrine disruptors, neurodevelopmental impairments, thyroid disruption | [73]              |

## **2.4.2 Organic flame retardants**

### **2.4.2.1 Silicone flame retardant**

Organosilicon flame retardant follows a condensed phase mechanism, due to its ability to produce a cracked carbon layer. It also makes this layer more oxidation-resistant. Silicone flame retardant improves the polymer surface layer. Because it normally moves to the polymer surface when it is added to a material. When heated an inorganic oxygen and insulation layer, comprising Silicone and/or silicone-carbon bonds of polysiloxane characteristic will be formed. Therefore, it inhibits polymer thermal degradation, and volatile combustion products and leads to low toxic smoke production. Its excellent mechanical properties, environmental adaptability and friendliness, and other properties make silicone flame retardant unique. It may be inserted into the molecular chain of the polymer by grafting, polymerization, and cross-linking. Even though silicon-containing flame retardants have higher oxidation resistance, heat resistance, and burn resistance, they are expensive. Currently, silicone flame retardants mainly include silicates, polysiloxane, and silicone resin flame retardants [74], [75]. Huihui Liu et al., [76] incorporated 50 % metal hydroxide (MH) with 45 wt% silicone resin (CCSI@MH) and 5 wt% red phosphorus (RD). they achieved a V-0 rating in the UL 94 test with a limit oxygen index (LOI) of 31%. Also, dripping behavior of the polymer (ethylene–vinyl acetate) was inhibited. Also, the mechanical properties were improved, and the tensile strength and the elongation at break were improved by 48% and 41 respectively.

#### **2.4.2.2 Organophosphorus flame retardant**

Organophosphorus-based retardants includes Tris(1,3-Dichloro-2-propyl) phosphate (TDCPP) is extensively employed to many materials which include; plastics, furniture, paints, foams, electronics, etc. They have a good performance and double functions of flame retardancy and plasticization. TDCPP has been shown to have toxicological effects in both in vitro and in vivo test models, although it is yet unknown whether it has genotoxic or carcinogenic effects on human cells [77]. The flame retardant has both condensed and vapor phase mechanisms. Firstly, these compounds upon heating they decomposes and releases volatile radicals e.g.,  $\text{PO}_2$ ,  $\text{PO}$ , etc. which can capture free radicals such as  $\text{H}$ , and  $\text{OH}$  in the vapor phase, and inhibit chain reaction during the burning process. Furthermore, the degradation of organophosphorus generates non-combustible gas which decreases the oxygen concentration by diluting the surrounding air. Decomposition of organophosphorus flame retardants during the condensed phase results in phosphoric acid compounds. By enhancing the dehydration and carbonization of the polymer matrix, phosphoric acid compounds create a glass-like molten layer. Lately, researchers have found that flammability and thermal stability of polymeric materials can be enhanced through synergizing organophosphorus and sulfur elements [78].

#### **2.4.3 Inorganic flame retardants**

These flame retardants consist of an inorganic element with high heat resistance ultrafine inorganic metal oxide in form of substances or compounds. due to their versatility, They exhibit a broad spectrum of applications. They are low cost, outstanding heat stability, long-lasting non-volatility, and other properties. Inorganic flame retardants can follow

either condensed or vapor phase mechanisms. Such retardants can be inorganic phosphorus, nitrogen, metal hydroxide, boron compounds, silicone series, etc. [79].

#### **2.4.3.1 Inorganic phosphorus flame retardants**

Inorganic phosphorus-based flame retardants can be red phosphorus, ammonium polyphosphates (APP), etc. Red phosphorus has considered to be among the most vital flame retardants, due to its low toxicity, non-halogenated, strong flame resistance, and a synergistic combination of several flame retardants [80]. Nevertheless, it has several drawbacks, because it absorbs water easily from the atmosphere and produces phosphoric acid, phosphate, and other compounds. Additionally, it is difficult to spread and has poor resin compatibility, which makes it difficult to operate due to increase in the density of resins. Red phosphorus releases a hazardous  $\text{PH}_3$  gas after long contact with air. The aforementioned shortcomings can be overcome by coating red phosphorus with organic, inorganic, or both (organic-inorganic) materials, which is called coated red phosphorus. The physical and chemical properties of the products are partially affected by the coating of red phosphorus, though it enhances its resin compatibility, synergistic effectiveness, and impact resistance. Polyphosphoric acid contains high nitrogen and phosphorus with excellent thermal stability, low toxicity, and good dispersibility [81]. Additionally, it serves as the foundation of an intumescent flame retardant compound. It has numerous applications in the flame retardation of textile, polymers, fiber, etc. [79], [82]–[84]. Li et al., [85] have demonstrated the impact of novel functionalized magnesium phosphate monomers on the mechanical and flame retardant characteristics of polyethylene terephthalate copolymers. Three separate new functionalized monomers were produced by individually modifying three phosphoric acids with inorganic magnesium hydroxide (MH).

The thermal stability of the composite was improved. While LOI of 32.5% and UL-94 test reached V-0 grade was achieved.

#### **2.4.4 Metal oxide flame retardants**

Typical representatives of metal oxides are; Aluminum trihydroxide (ATH), Magnesium dihydroxide (MDH), Antimony (III) oxide, etc. They have strong thermal stability. They are cost-effective and environmentally friendly. Also, they reduce smoke emissions upon the combustion of plastics. They have good flame retardant properties and are widely available. However, they require a high dosage with decreases mechanical properties and fluidity of the materials, this make them difficult to process. Metal hydroxides act on condensed phase mechanisms [86]. During combustion, when metal hydroxides compound decomposes, they release water, which reduces the polymer matrix's temperature and concentration of oxygen in the surrounding atmosphere. The metal oxides produced during combustion stick to the matrix's surface, which forms a shielding layer to hinder heat and mass transfer. ATH effectively improves the thermal stability of material when 40 wt% of ATH is added. It reduces the thermal decomposition of Polyethylene, polyvinyl chloride (PVC), polypropene etc. While 60 wt% is utilized in construction materials. While 50 wt% MDH compound requires to enhance the thermal stability of a polymer. MDH has a decomposition temperature of 340-490°C, which has better temperature inhibition than ATH. By combining ATH and MDH strong synergistic effect will be achieved, and it could lower the price of flame retardants [87].

#### **2.4.5 Nitrogen-containing flame retardants**

These flame retardants include melamine, melamine cyanurate, guanidine salts, dicyandiamide compounds, etc. Nitrogen-based flame retardants have numerous advantages such as; high flame retardancy, low impact on density, cost-effective, environmentally friendly, less smoke produced during combustion, less corrosive, excellent thermal stability, and decomposition temperature [88]. However, these flame retardants have poor polymer compatibility [89]. Thus, most of the research focuses on improving material compatibility through modification and lowering the thermal conductivity of nitrogen-based flame retardants. While burning these materials generate non-combustible gases, which inhibit gas phase combustion.  $\text{NH}_3$  and  $\text{N}_2$  are generated from melamine and its derivatives, which diffuse to the burning region, consequently decreasing the concentration of the gaseous fuel. Simultaneously carbon and nitrogen in the triazine structure could contribute to the carbon formation reaction and strengthen the carbon layer [90], [91].

#### **2.4.6 Boron-containing flame retardants**

Boronated flame retardants include zinc borate (ZB), where water crystal and  $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3$  are combined to produce  $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$ , which is the most frequently used. Water is released when huge external heat is absorbed at a temperature above  $260^\circ\text{C}$ . The released water reduces the polymer's endothermic degradation process, which generates steam and absorbs a huge amount of heat [92]. It was measured that every gram of  $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$  decomposition, generates vapor, water, and other compounds. The heat absorbed reaches 924 J, which decreases temperature during combustion. while the

nontoxic water vapor dilutes the inflammable gas and isolates the surrounding air to some extent [93]. The polymer surface will then be coated by a non-volatile  $B_2O_3$  glassy material produced by  $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$  at the burning temperature. The shielding layer serves as an isolation film. ZB has a good synergistic effect with antimony oxide, where it effectively decreases smoke generation. Thus,  $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$  is a flame retardant that is non-toxic and smokeless. It enhances the generation of a porous carbon layer upon combustion, wherein boron trioxide can stabilize [94]. During the combustion process, ZB generates a porous residue similar to glass. Therefore, isolation of surrounding air prevents secondary fire by inhibiting the formation of droplets [95].

#### **2.4.7 Nanofillers flame retardants**

Nanofillers such as nano-metal oxides and hydroxides, Nano-clay, carbon nanotubes, multi-walled nanotubes, siloxanes, etc. reportedly show better thermal stability, low cost, chemical resistance, light-weight and less permeability to gases, water, and hydrocarbons [96]. Previously microscale fillers were used in the polymer matrix. Even though they offer significant thermal stability, micro-fillers require high dosage filler to achieve good flame retardancy. Due to the higher density of these fillers compared to the polymers, high fillers load affects the mechanical properties of the materials. However, a small dosage of nano-fillers increases the surface/volume ratio and interaction between fillers and polymers [97]. The distribution of nano-fillers in a polymer matrix has significant effects on the surface area of the nano-fillers, which determines how well they interact with the polymer. Nano-filler strictly works in condensed phase (i.e., physical barrier effect and catalytic charring effect). They improve the formation of carbon, increase ignition time, and decrease the emission of flammable volatile during the combustion process. Nano-fillers'

retardancy depends on their chemical structure and geometrical shape. Nano-fillers have better polymer-flame retardant interactions, which reduces fillers dosage and preserves the original properties of the material [98].

**Table 2 Some advantages and drawbacks of nanomaterials flame retardants**

| <b>Nanomaterial Flame Retardants</b> | <b>Advantages</b>                                                                                                                                                                                                                                           | <b>Disadvantages</b>                                                                                                                                                                  | <b>References</b> |
|--------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------|
| Metal–Organic Frameworks (MOFs)      | MOFs are novel fire retardants that have been broadly used for a variety of polymers. They comprise plenty of transition metal species, elements that prevent fire, and possible carbon source.                                                             | The recent literature of MOFs are suggestive of developmental neurotoxicity.                                                                                                          | [99]              |
| Two-Dimensional Nanomaterials        | Various two-dimensional nanomaterials exhibit properties such as potential conductivity, high thermal conductivity, catalytic activity, and resistance to ultraviolet radiation, making them suitable for fulfilling the flame retardant needs of polymers. | The primary challenge in utilizing two-dimensional nanomaterials as flame retardant additives lies in their high cost and the low production yield of the exfoliated sheet structures | [100]             |
| Metal-Family Flame Retardants        | These are eco-friendly flame retardants that can provide polymers with excellent smoke suppression and flame resistance, while also minimizing the generation of toxic gases.                                                                               | Most of these substances readily burn in the air, and the combustion process results in the production of a significant amount of hazardous smoke and toxic gases.                    | [34]              |
| Nanocarbon-Based Flame Retardants    | Nanocarbon-based flame retardants can be produced with outstanding magnetic, electrical, optical, mechanical, and catalytic properties.                                                                                                                     | Require high loading, poor compatibility, high cost, limited availability, need for surface modification                                                                              | [97]              |

|                                          |                                                                                                                                                                                                                                                       |                                                                                                                                                                                                           |       |
|------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------|
| Layered double hydroxides (LDHs)         | High thermal stability, high char yield, good dispersion, low smoke emission, low toxicity, synergistic effect with other flame retardants                                                                                                            | Require high loading, poor compatibility, high cost, limited availability                                                                                                                                 | [100] |
| Graphene                                 | These substances exhibit high thermal stability, produce a large amount of char, and provide an effective barrier. They also emit low levels of smoke and have low toxicity. Additionally, they can work synergistically with other flame retardants. | Require high loading, poor compatibility, high cost, limited availability, potential environmental and health risks                                                                                       |       |
| Montmorillonite (MMT)                    | High thermal stability, high char yield, good barrier effect, low smoke emission, low toxicity, synergistic effect with other flame retardants                                                                                                        | MMT tends to cluster together within polymer matrices, a process which not only diminishes its flame retardant capabilities, but also adversely affects the mechanical properties of the matrix material. | [97]  |
| Expandable graphite (EG)                 | These substances demonstrate excellent thermal stability, produce a high yield of char, and offer an effective barrier. They also emit minimal smoke and are low in toxicity. Furthermore, they can work in synergy with other flame retardants.      | These substances necessitate high loading, exhibit poor compatibility, and are costly. Their availability is limited and they require surface modification.                                               | [96]  |
| Molybdenum disulfide (MoS <sub>2</sub> ) | High thermal stability, high char yield, good barrier effect, low smoke emission, low toxicity, synergistic effect with other flame retardants                                                                                                        | Require high loading, poor compatibility, high cost, limited availability, need for surface modification                                                                                                  | [99]  |

#### **2.4.8 Intumescent Flame Retardant**

These flame retardants are environmentally friendly and highly efficient which does not contain halogenated compounds. These compounds produce carbonaceous char during combustion on the surface of polymer [101]. Thus, when exposed to heat they decompose and produce a dense carbonized layer. Which breaks a combustion cycle by isolating heat, oxygen and smoke suppression [102]. Intumescent flame retardants comprise of three main elements which are; gas source, carbon source, and acid source. Acid source is the most important element and occupies major proportion of the elements [103]. This makes it a true flame retardant, it is generally inorganic acid or substances that can generate inorganic acid when heated to a specific temperature [104]. Some of these compounds are; phosphoric acid, ammonium polyphosphate (APP), phosphorus oxychloride, etc. While gas and carbon sources serve as a synergistic agent. While the carbon source also referred to as carbonization accelerator or dehydrating agent, serves as a basis of producing the carbonized foam layer. Mostly it contains higher carbon content such as polyhydroxyl compounds, for instance starch, pentaerythritol and triazine derivatives. The gas source also known as foaming source [105]. Normally foaming sources include melamine, piperazine, dicyandiamide, ethylenediamine, etc. in order to achieve good flame retardancy when it is blended with a polymer it improves its thermal stability, processing performance and compatibility [106]. The polymer processing temperature should be lower than thermal degradation temperature. When exposed to fire dense carbonization layer is produced on the surface of the polymer to stop the fire [107]. An intumescent flame retardant is an environment friendly. Because it does not produce toxic, corrosive or harmful gases when subjected to thermal decomposition [108]. Recently Wang et al. [1]

were able to design an efficient intumescent by preparing thermoplastic RR (TOP) sheets. These compounds do not degrade mechanical properties and processability of polymer caused by high dosage loading. Because of the decreased loading and enhanced flexibility, makes it an effective flame retardant. The TPO sheet, which contains just 13.06% expanded flame retardant, can be aided to achieve V-0 grade in the UL-94 test by a coating (thickness: 120  $\mu$ m) with expanded flame retardant and TPO (film-forming resin). Also 30.5% LOI was achieved and rate of heat release, as measured by cone calorimetry, was significantly decreased. Also, Chen et al. [109] were able to synthesize a novel triazine-based intumescent flame retardant phosphorylated histidine-amino triazine-diaminopropane (PHTD). They achieved a good thermal stability of expanded polystyrene (EPS) foams. EPS-PHTD foams composites showed UL-94 V-0 rating and LOI up to 28%. While peak heat release rate (PHRR) and peak smoke production rate (PSPR) were reduced to 74.9% and 77.3% respectively. Moreover, the mechanical properties were not affected by incorporation of PHTD, compressive strength was improved by 20.0%. Yuan et al. [110] were able to synthesize a Nitrogen-phosphorus base intumescent where they used biphenyl-4,4'-diphosphonic acid and melamine (BA-MA) as a Phosphorus-Nitrogen-Carbon synergistic nanolayered flame retardant for polystyrene. 68% peak heat release rate reduction was accomplished by incorporating 1 wt% loading of BA-MA. Due to its ability of reducing the amount of combustible gases upon combustion by producing incombustible gas. It also isolates oxygen and heat transfer by producing aromatic carbon layers.

## CHAPTER 3

### MATERIALS AND METHOD

#### 3.1 Materials Acquisition

Polystyrene (general purpose) PS-155 was supplied by SABIC Saudi Arabia. Ionic liquid (trihexyltetradecylphosphonium chloride), Aluminum nitrate nonahydrate, sodium hydroxide, Zinc nitrate hexahydrate, and sodium carbonate were purchased from Sigma Aldrich. Melamine ( $C_3H_6N_6$ ) (99%), Ammonium dihydrogen phosphates  $[NH_4]H_2PO_4$  (98%), and ethanol (99%) was obtained from Honeywell, Germany. Graphene nanoplate 50-100nm (99%) was purchased from Grafen Chemical industries, Turkey. All the chemicals were used as received

The following materials were acquired to produce various filler systems.

#### *Material Required to Prepare Intumescent (MAG)*

- a. Graphite powder
- b. Melamine (99%)
- c. Ammonium dihydrogen phosphates (98%)
- d. Ethanol (99%)
- e. Deionized water

#### *Materials Required to Prepare ZnAl, Layered Double Hydroxide and Its Composites*

- a. NaOH
- b.  $\text{Na}_2\text{CO}_3$
- c. Zinc nitrate hexahydrate,
- d. Aluminum nitrate nonahydrate
- e. Graphene
- f. Hydrazine
- g. Phosphonium ionic liquid
- a. Deionized water

## **3.2 Preparation of PS Composites**

### **3.2.1 Blending Procedure**

The series of PS composites was formed through blending it with variable loads of fillers were prepared as demonstrated in Table 1. In the processing, different mass fractions of PS resin and fillers were introduced into the internal torque rheometer Brabender Mixer (Brabender Technologie GmbH & Co. KG, Duisburg , Germany) at 175 °C with a rotational speed of 75 rpm for 10 min until the torque was stable [111]. The compound was taken out from the mixer while hot and compressed in a carver press at 175 °C for 5 minutes to get a sheet with a thickness of 3mm. The amount of filler in its blend with PS was 1% w/w, and 3% w/w. The samples are labeled as PS-Filler-% for example PS-MAG-1, PS-GO-1, etc. All the composites are listed in Table 3.

**Table 3 Polystyrene and its composites codes**

| S/N | Sample Code      | PS/weight% | MAG/weight% | Graphene % | Phosphonium Ionic liquid % |
|-----|------------------|------------|-------------|------------|----------------------------|
| 1   | PS               | 100        | 0           | 0          | 0                          |
| 2   | PS-MAG1          | 99         | 1           | 0          | 0                          |
| 3   | PS-MAG5          | 95         | 5           | 0          | 0                          |
| 4   | PS-MAG10         | 90         | 10          | 0          | 0                          |
| 5   | PS-MAG15         | 85         | 15          | 0          | 0                          |
| 6   | PS-MAG20         | 80         | 20          | 0          | 0                          |
| 7   | PS+5%ZnAl        | 95         | 0           | 5          | 0                          |
| 8   | PS+5%ZnAl-G      | 95         | 0           | 5          | 0                          |
| 9   | PS+5%ZnAl-G-PCL  | 95         | 0           | 2.5        | 2.5                        |
| 10  | PS+10%ZnAl-G-PCL | 90         | 0           | 5          | 5                          |
| 11  | PS+5%ZnAl-G-PCL  | 85         | 0           | 7.5        | 7.5                        |

### 3.3 Preparation of Materials

#### 3.3.1 Synthesis of Intumescent nanosheet (MAG)

The MAG was synthesized by hydrothermal method using a Soxhlet reflux. The synthesis comprised of two stages. Firstly, melamine was mixed with ammonium dihydrogen phosphate to form a melamine-ammonium dihydrogen phosphate complex, and then latter mixed with graphene. Finally, the nanofiller was dispersed in the PS matrix. The three experimental sections were described below;

1. Pure melamine (M) and ammonium dihydrogen phosphate (A) were used as received from the manufacturers. The M powder was perfectly mixed with the A powder for dispersion in deionized water (DI) at ambient temperature to avoid

formation of a hard (about 5 mm) particle. M reacted with a A in 150ml of DI with molar ratio 0.0159:0.0348 and the solution was mixed by ultrasonic for 30 min at 26 °C and a speed of 250 rpm. The solution was then transferred to the round bottom flask.

2. The graphene powder (G) was subsequently incorporated to the M-A solution with mass ratio 1:2:0.25 (M:A:G) and then vigorously stirred with 100 ml of DI for 20 min at 26 °C and a speed of 350 rpm. Subsequently, It was transferred into a round-bottom flask equipped with a reflux apparatus, the reaction was set for 72 h at 110 °C and 350 rpm. The final product was filtered by centrifugation, washed with ethanol and dried in a vacuum oven at 80 °C for 24 h to a constant weight. Then, nano-layered MAG was obtained.

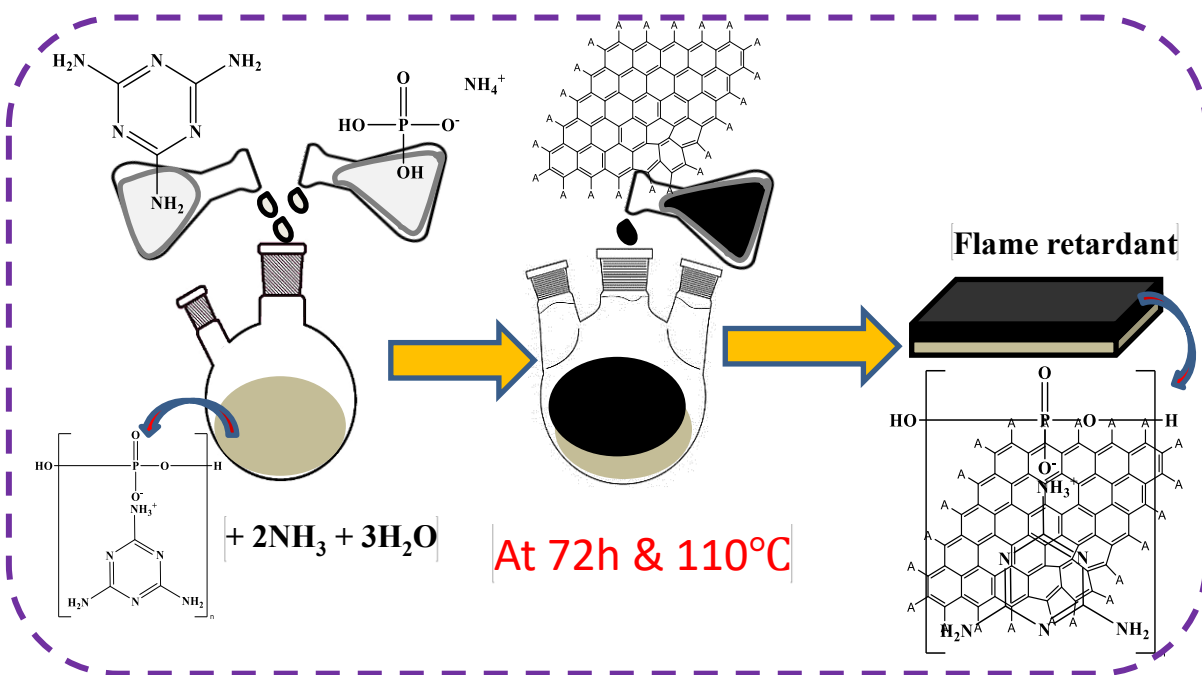


Figure 4 Synthesis of MAG

### 3.3.2 Preparation of ZnAl-LDH pristine and its composites

ZnAl tertiary layered double hydroxide (ZnAl-LDH) was prepared as follows. First solution A (0.3348 M NaOH + 0.0279 M Na<sub>2</sub>CO<sub>3</sub>) was prepared by dissolving 0.7106 g Na<sub>2</sub>CO<sub>3</sub> and 3.2182 g NaOH into 240 mL distilled water. Then, solution B (0.06 M zinc nitrate hexahydrate + 0.02 M aluminum nitrate nonahydrate) was prepared by dissolving 17.859 g zinc nitrate hexahydrate and 7.5 g aluminum nitrate nonahydrate into 150 mL deionized water. After that, about 100 mL of deionized water was placed in a beaker. The pH of the distilled water was adjusted to pH ~9.5 using solution A. Then, solutions A and B were added simultaneously in a drop-wise manner to the pH-adjusted distilled water while stirring the reaction mixture. The pH of the mixture was maintained at around 9.5 throughout the process. After the complete addition of solutions A and B, the mixture was further stirred at room temperature for 30 min. Then, it was refluxed for 24 h at 90 °C. After 24 h, the produced ZnAl-LDH was purified by washing with deionized water at least 7 times (centrifuge at 8000 rpm for 10 min in each wash) the last one with ethanol. Then, the purified ZnAl-LDH was dried in an oven for 20 h at 80 °C.

While the ZnAl-LDH modifications was carried out using the following techniques:

1. Graphene modification; graphene was intercalated into the LDH layers, by dispersing the graphene into 150 ml of 0.1MNaOH solution and sonicated for 30 min. Few drops of hydrazine was added to the mixture. Lastly the solution was added into the ZnAl-LDH solution. And the above procedure was followed.
2. Phosphonium ionic liquid and graphene modification; the ionic liquid was firstly dissolved in to 90 ml of ethanol and then mixed with graphene solution.

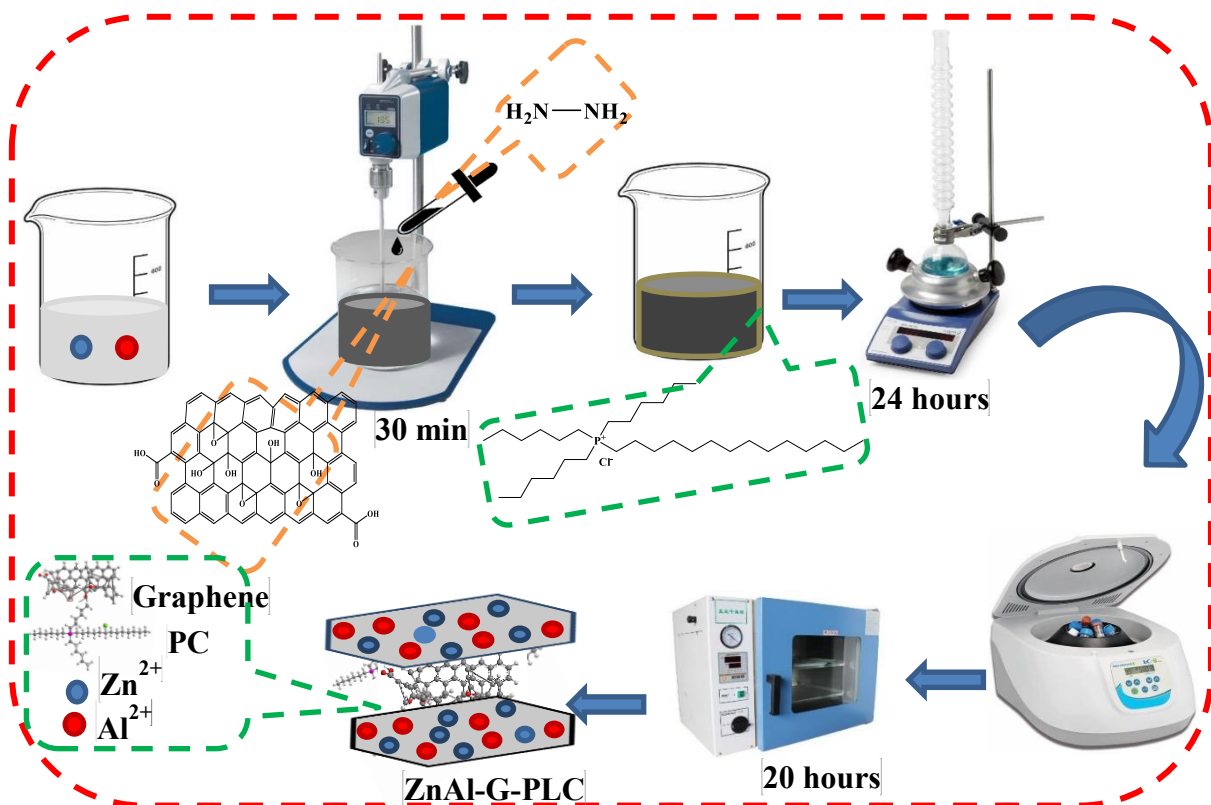


Figure 5 Graphical diagram of the ZnAl-LDH hybrids preparation.

### 3.3.3 Synthesis of ZnAl-G nanocomposite

ZnAl-G nanocomposite was synthesized according to our previous study [112] using co-precipitation method. Firstly, 300 mg graphene was probe-sonicated in a 50 mL DI and 50 mL of 0.1M NaOH in a beaker for 30 minutes using amplitude of 50 Hz. The sonicated graphene sheets and NaOH (1.0M) are added to the three necked flask dropwise having 0.06 M solution of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 0.02 M of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O under vigorous stirring. The pH of the mixture was adjusted at  $9.5 \pm 0.1$  followed by 24 hr. refluxing at 90 °C. The resulting slurry is centrifuge and washed several times with DI and ethanol followed by drying for 24 hr. in vacuum oven. Approximately, 9g of ZnAl-G composite is obtained from this step.

### **2.3.4 Fabrication of phosphonium IL modified LDH (ZnAl-G-PCL)**

The graphical representation for the synthesis of ZnAl-G-PCL is shown in Fig. 5. The precursors salts of Zn and Al were taken as 0.06M and 0.02M respectively in a three necked flask. Initially 300mg of graphene was probe-sonicated in 100ml of DI and 0.1M NaOH mixture for 30 minutes. Approximately twice the anionic exchange capacity (2 AEC) of PCL was added to 50mL of ethanol solvent and stir it for 30 minutes. The PCL mixture was then added to graphene solution and introduced to the salt solution dropwise. The pH was adjusted at  $9.5 \pm 0.1$  using 1.0M NaOH, followed by overnight reflux [113]. The resultant slurry was centrifuge, washed and kept for drying overnight in vacuum oven. Approximately, 12g of ZnAl-G-PCL nanocomposite was synthesized from the yield.

### **3.4 Material Characterization**

First, X-ray diffraction (XRD) analysis of the synthesized flame retardant was carried out by utilizing copper (Cu) as the X-ray generation source at 40 kV, 15 mA and 5°/min with a  $K\alpha_1$  Cu wavelength of 1.54059. The nanolayer's diameter and porosity properties were examined by  $N_2$  sorption measurements at pressures up to 71 kPa and -195.747°C (Micromeritics ASAP 2020, USA). Prior to the test, MAG underwent a degassing process at a temperature of 120 °C for 12 hours. The total volume was determined from nitrogen adsorbed at  $P/P_0 = 0.99$ . Furthermore, using the Barrett-Joyner-Halenda (BJH) approach, the pore size distribution was determined from the nitrogen isotherm's desorption branch [114]. Fourier transform infrared (FT-IR) spectroscopy analysis of the samples was done using a Nicolet 6700 spectrometer (Thermo-Nicolet, Japan) with a scanning range of 4000-400  $cm^{-1}$ . The Zeiss laser crossbeam (Laser-FIB 550 SEM) was used to analyzed the shape, sizes, surface morphology, and dispersion of the material in the PS's matrix. Also, field

emission electron microscope (JEM-2100F, Japan) was used to further analyzed the surface morphology of MAG. Elemental analyses were conducted using the Oxford ultimax (170 EDX) detector mounted on the SEM. The LOI was obtained using fire testing technology limited (West Sussex, United Kingdom) oxygen index apparatus with an air flow of 17l/min at  $23 \pm 2$  °C using PS specimen dimensions of  $90 \times 6 \times 3$  mm<sup>3</sup> according to method 141 and ISO 4589. Thermal analysis was carried out using SDT Q600 (DSC-TGA) at a temperature range from ambient temperature to 700 °C under nitrogen flow at heating rate of 100ml/min at heating rate of 10 °C/*min*. Dynamic mechanical analysis (DMA) was conducted using DMA, Discovery (DMA 850 New Castle, DE, USA), it was carried out at constant frequency of 1 Hz, amplitude of 15µm and temperature range from room temperature to 150 °C at a heating rate of 10 °C/*min*. The thermal conductivity analysis was examined using FOX50 110 °C (Massachusetts, USA) at an average temperature of 60 °C .

## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 Nanosheet Intumescent Flame retardant

##### 4.1.1 Material Characterization

A novel flame retardant (MAG) was initially developed, and it has a hyperbranched nanolayered structure. Which contain ammonium dihydrogen phosphates, melamine, and graphene. Subsequently, the MAG was mixed with the pure PS to achieve a composite of PS. It is noteworthy to mention that ammonium dihydrogen phosphate contains ammonium and phosphonic groups, which can effectively serve as acid source. However, melamine serves as a gas source, while graphene serves as a carbon source. Moreover, the synthesized material is nanolayered, which improves its dispersion in the PS matrix. It is well known that the crystal structure changed as a result of changes in the chemical structure. Therefore, X-ray diffraction was used to examine the crystal structure of MAG. Figure 7 shows the MAG XRD patterns. Figure 6 indicates the comparison of XRD patterns of M, A, G and MAG respectively. Compared to the peaks of M before and after the reaction, the characteristic peak pattern of M has disappeared in the MAG pattern that might be related to the significant hybridization between M and A, leading to a high degree of hybridization, which destroys the original crystal structure of M and generating a new form of aggregation. However, the characteristic peaks of the A pattern changed after reacting with M because of  $\pi$ - $\pi$  stacking interactions between M and A, which resulted in a change in

the interlayer spacing [115]. On the contrary, the characteristic peak of G remained unchanged because there was no chemical reaction between M-A and G. Using the Bragg equation ( $2d\sin\theta = n\lambda$ ), the interlayer spacing of M ( $2\theta = 26.54^\circ$ ) is 0.336 nm, that of A ( $2\theta = 24.14^\circ$ ) is 0.370 nm, and also that of G ( $2\theta = 26.85^\circ$ ) 0.332 nm [116]. While after reaction between M and A and physical interaction with G, the interlayer spacing of MAG ( $2\theta = 26.78^\circ$ ) is 0.333 nm.

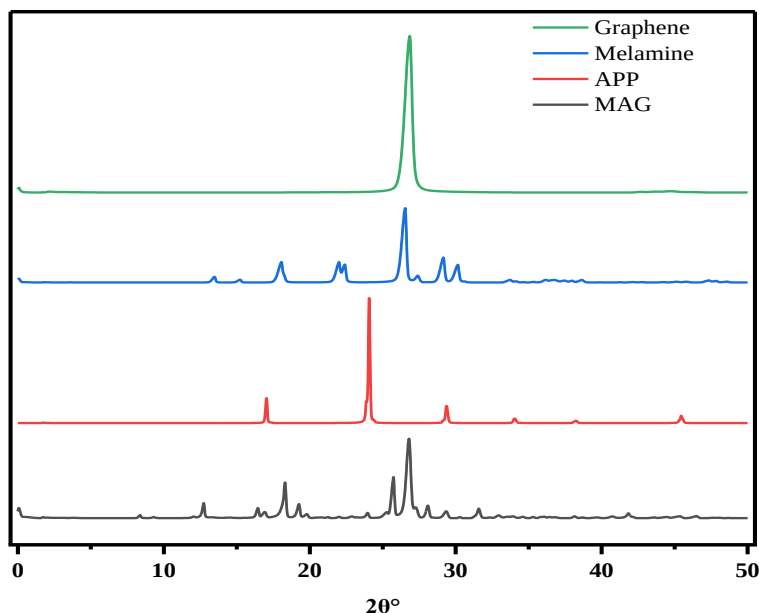


Figure 6 XRD pattern of M,A,G and MAG.

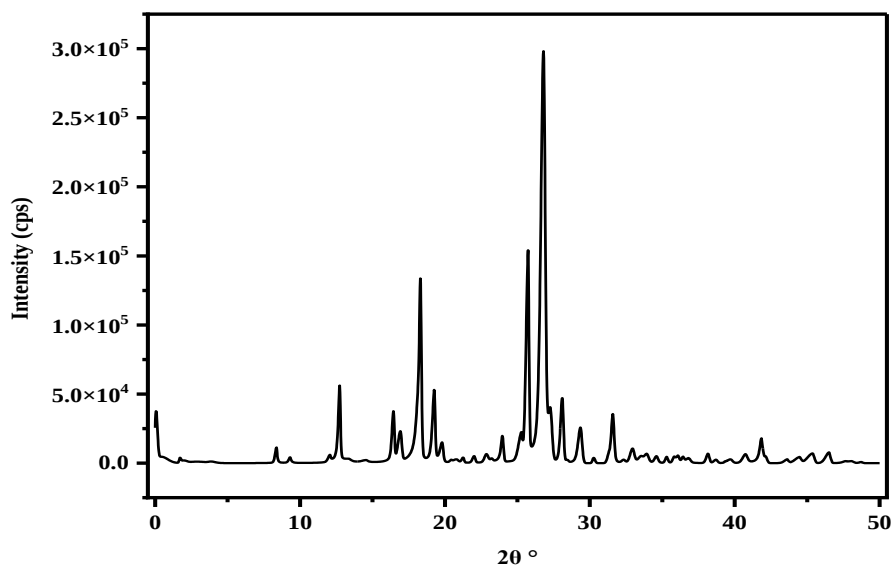


Figure 7 XRD pattern of MAG.

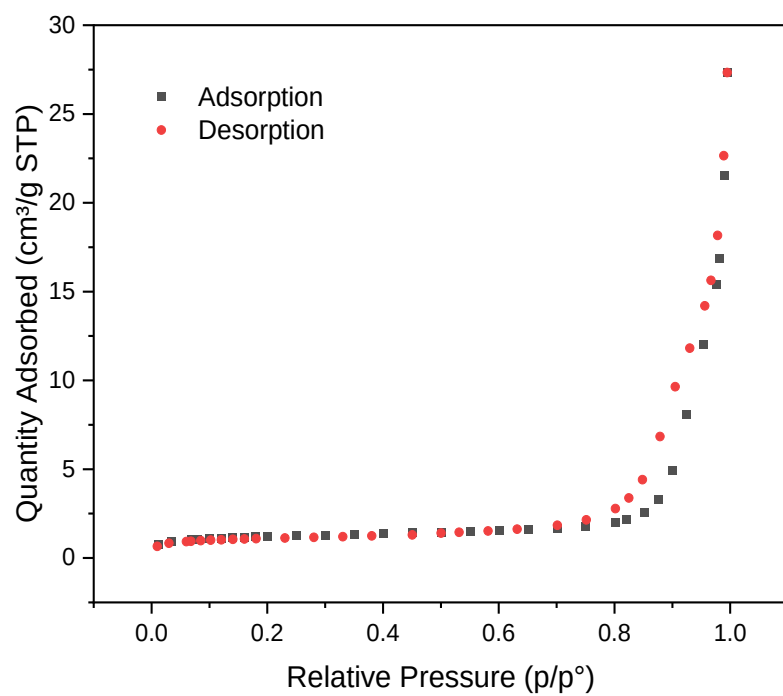


Figure 8 N<sub>2</sub> adsorption-desorption of MAG

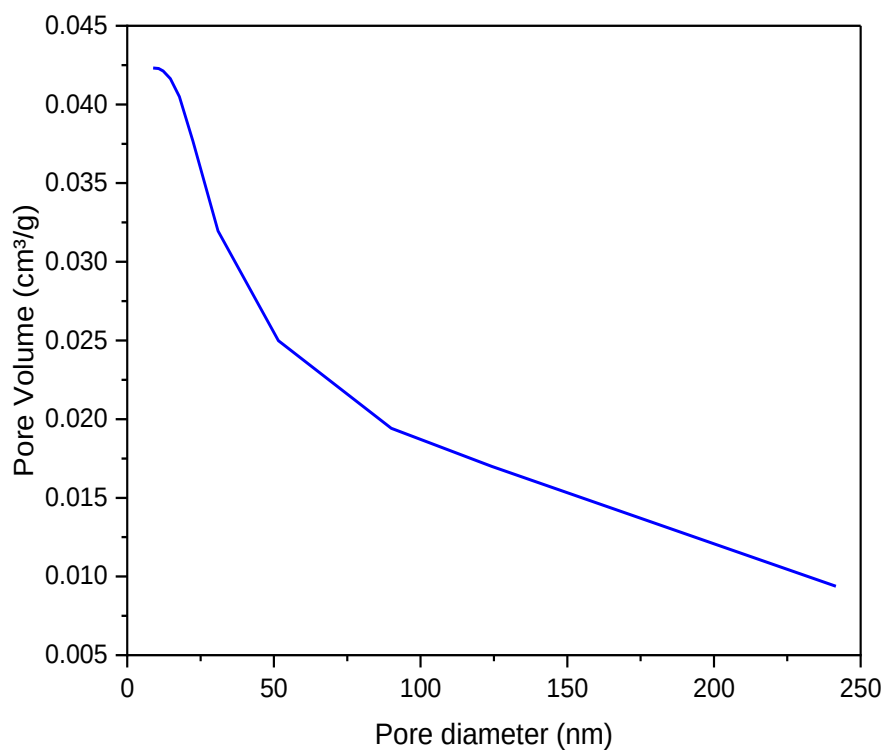


Figure 9 Pore size distribution of MAG

Using nitrogen adsorption/desorption isotherms at  $-195.747^{\circ}\text{C}$ , the porosity properties were analyzed. The Brunauer–Emmett–Teller (BET) analysis revealed that MAG has a specific surface area of  $4.3820\text{m}^2/\text{g}$ , a pore volume of  $0.042313\text{ cm}^3/\text{g}$ , a pore diameter of  $21.72206\text{ nm}$ , and an average particle size of  $11042.3551\text{ nm}$ . Figure 8 has demonstrated the  $\text{N}_2$  adsorption/desorption isotherms. The average pore size distribution is shown in Figure 9. The  $\text{N}_2$  isotherms of MAG, indicates the reversible nitrogen adsorption isotherms which exhibit minimal hysteresis, indicating a Type-IV behavior that is commonly associated with mesoporous materials [117], [118]. The presence of the porous structure in MAG is crucial and beneficial, as it enables an effective suppression of the harmful emissions, such as carbon monoxide ( $\text{CO}$ ) and carbon dioxide ( $\text{CO}_2$ ), which can easily access the porous network of composites after combustion [119].

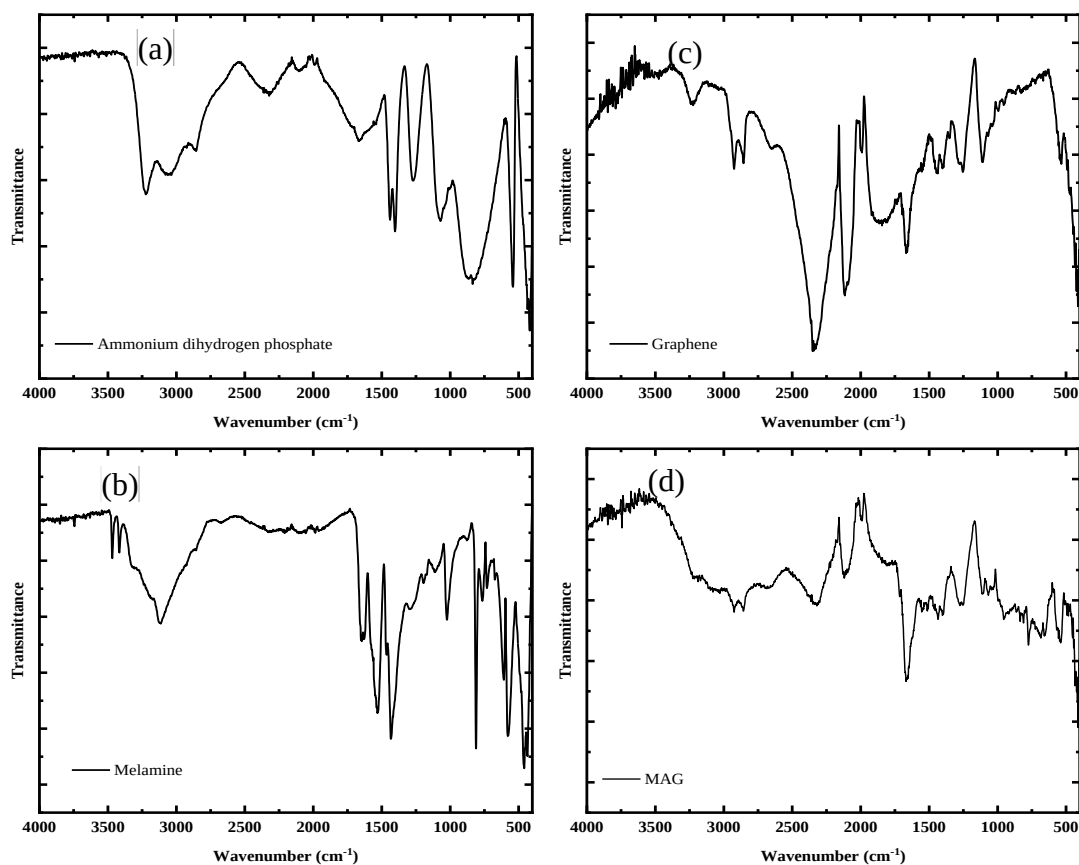


Figure 10 FTIR of (a) Ammonium dihydrogen phosphate, (b) melamine, (c) Graphene, (d) MAG

FTIR spectra of MAG and its precursors were used to examine its chemical structure as demonstrated in Figure 10. The major peak of ammonium dihydrogen phosphate was observed in range of 300-3400  $\text{cm}^{-1}$  which is mainly attributed to OH stretching vibration, the weak band at 1400  $\text{cm}^{-1}$  is assigned to the P=O stretching vibration of the phosphate group, a broad peak between 800-1000  $\text{cm}^{-1}$  is related to the P–OH and O–P–O bonds which grafted phosphate groups [120]. These peaks are still maintained after ammonium dihydrogen phosphates reacted with melamine due to the presence of these groups attached to the MAG. For melamine, the major peak was observed in the range of 3100-3400  $\text{cm}^{-1}$ , which is associated with the symmetric stretching vibration of N-H in the  $\text{NH}_2$  group, that is attached to the melamine structure [121]. But in the spectrum of MAG, it shifted, and there is a new broad peak at 3100 and 3300  $\text{cm}^{-1}$  which are attributed to the stretching vibration absorption of  $-\text{NH}_3$  and  $-\text{NH}_2$  [122]. While for graphene, there is a broad peak at 2300  $\text{cm}^{-1}$  which is attributed to the stretching vibration of C–H. This peak was shifted to 1600  $\text{cm}^{-1}$ , as a result of the stretching vibration C–O on MAG structure. These absorption peaks demonstrate that condensation of melamine and ammonium dihydrogen phosphate does occur.

#### **4.1.2 Surface Morphology and Elemental Analysis**

The surface morphology of MAG was analyzed using SEM and TEM as indicated in Figures 11 a&b respectively, the formation of nanosheets structure was observed with thickness at range of 40-60nm. Figure 11a indicates that there are a large number of nanosheets layer stacked layer after layer, the  $\pi$ – $\pi$  stacking configuration between MAG layers is a sandwich-like arrangement. Also, Figure 11b demonstrates how the graphene nanolayer lies on top of the ammonium polyphosphate layer, this indicates that the

hydrothermal reaction leads to the formation of a book like nanolayers. In order to examine the compatibility between PS and MAG. SEM was used to analyze the morphology of the PS-MAG10 blend, as demonstrated in Figure 11c. which has shown a fine morphology of the PS blend. The nanosheet was well dispersed on PS matrix which serves as nano-enhancer that reduces the deterioration of PS's mechanical properties caused by adding filler. It can be seen that there is a uniform distribution of the PS bead profile.

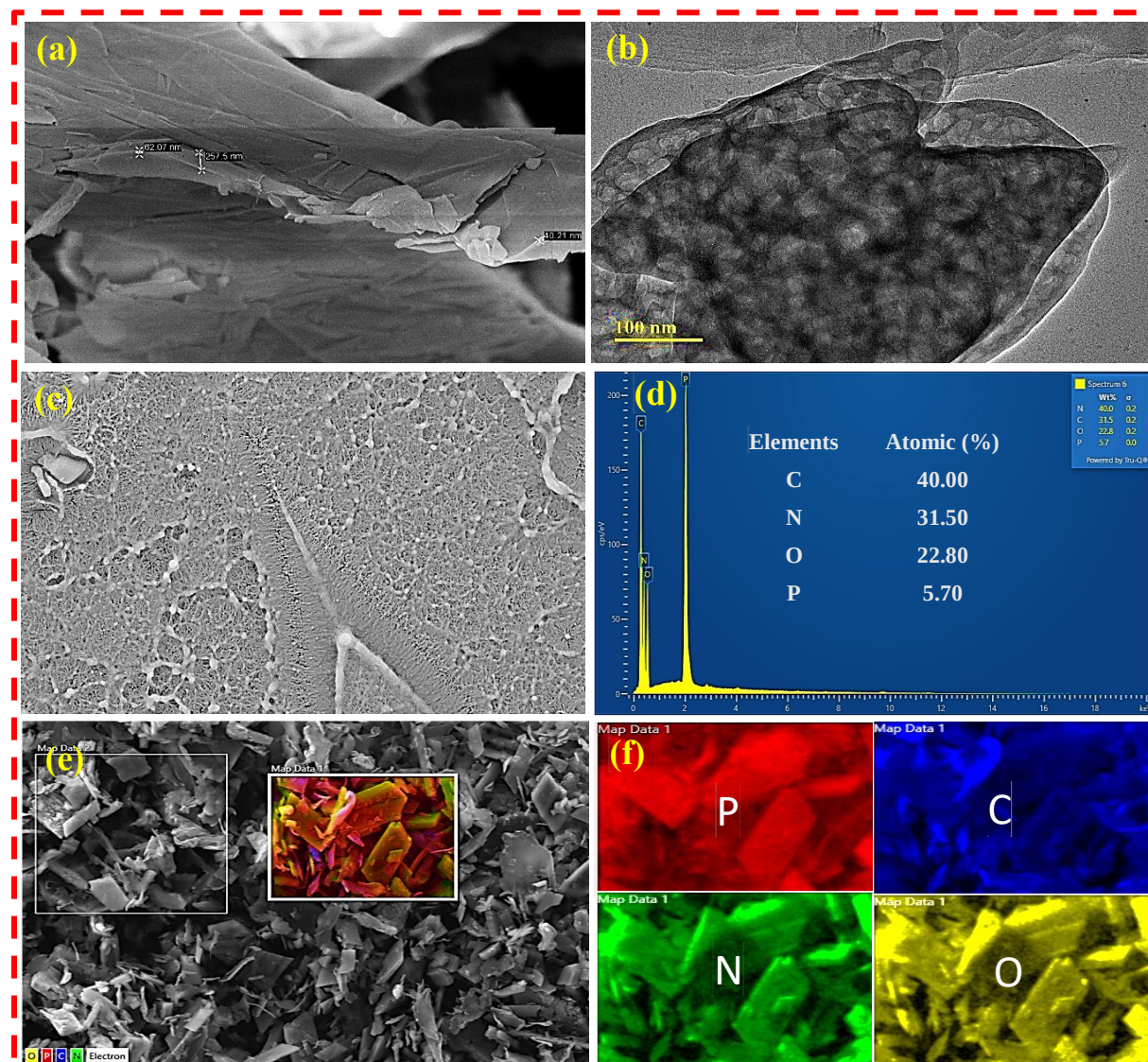


Figure 11(a) SEM image of MAG, (b) TEM of MAG, (c) SEM image of PS-MAG10, (d-f) EDS mapping images of MAG

Therefore, an in-situ dispersion was achieved, with no formation of agglomeration. Because of the proper dispersion of this material in PS. While the elemental distribution of MAG was highlighted in Figure 11d-f. This has shown the main elemental composition of MAG which indicated that there is a synergy effect between ammonium dihydrogen phosphate, melamine, and graphene.

#### **4.1.3 Thermal Stability**

The thermal analysis of the MAG nanosheets, PS and PS composites was analyzed using TG and DTG curves as shown in Figure 12 a&b, respectively. Moreover, the matching parameters are summarized in Table 4. The thermal degradation temperature of MAG nanosheets and PS when weight loss was 5 wt% are 224 and 365 °C respectively. The maximum thermal decomposition temperatures are 277 and 420 °C respectively. This indicates that the nanosheet has lower  $T_{5\%}$  and  $T_{\max}$  than PS. Moreover, increase in MAG loads decreases PS  $T_{5\%}$  and  $T_{\max}$  as shown in Table 2. However, the rate of thermal degradation of MAG is 0.37 %/°C which is lower than 2.77 %/°C of pure PS. This indicates that MAG has a lower thermal degradation rate compared to the pure PS. Furthermore, integrating it with the PS has significantly slowed down the decomposition rate of PS.

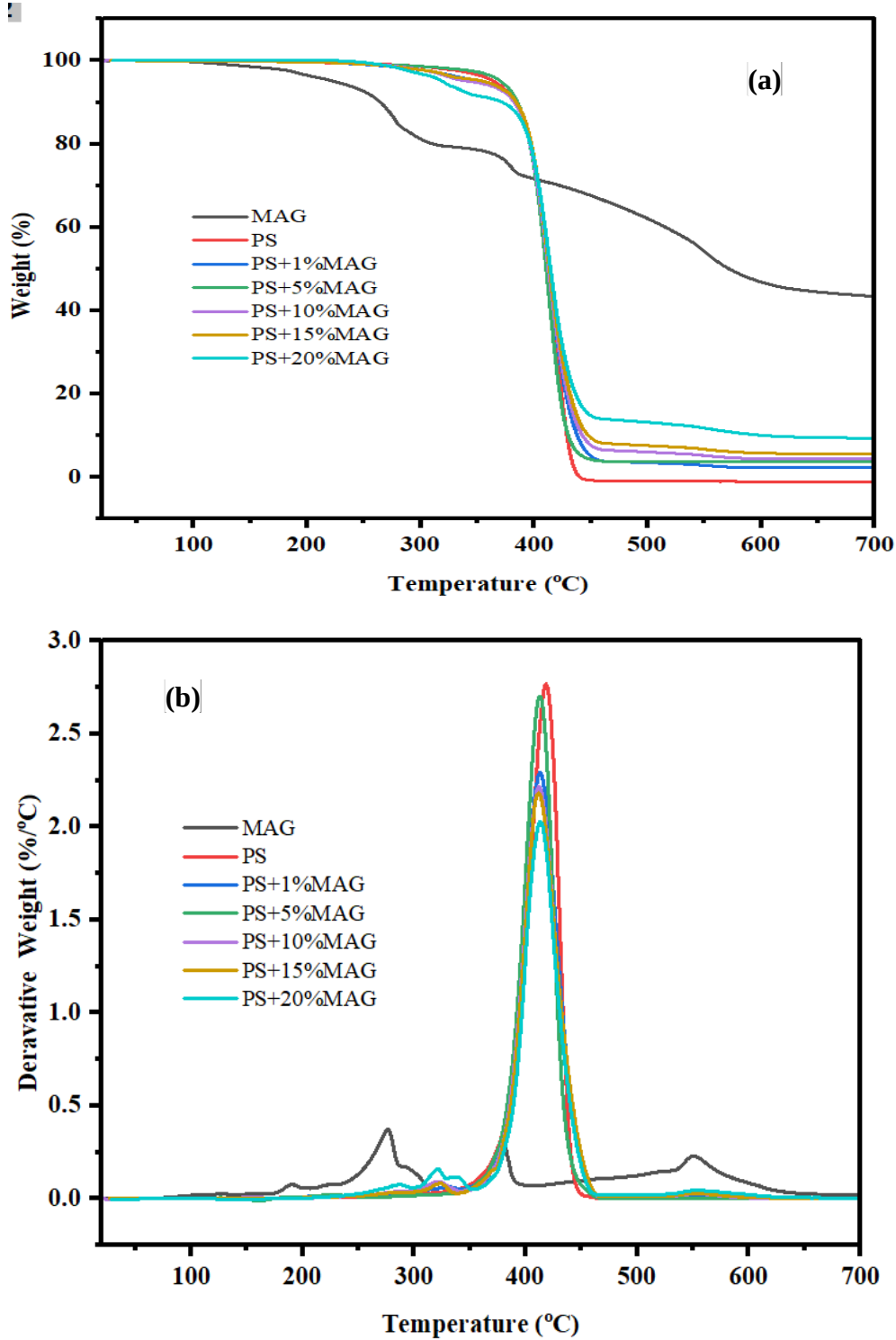


Figure 12 (a) TG and (b) DTG curves of MAG, PS and PS composites

**Table 4 TGA and DTG curves parameters of MAG, PS, and PS composites**

| <b>Sample</b> | <b>T<sub>5%</sub> (°C)</b> | <b>T<sub>max</sub> (°C)</b> | <b>R<sub>max</sub> (%/°C)</b> | <b>Residue at 450 °C (%)</b> | <b>Residue at 700 °C (%)</b> |
|---------------|----------------------------|-----------------------------|-------------------------------|------------------------------|------------------------------|
| PS            | 365.00                     | 420.00                      | 2.77                          | /                            | /                            |
| MAG           | 224.00                     | 277.00                      | 0.37                          | 67.62                        | 43.37                        |
| PS-MAG1       | 353.00                     | 414.00                      | 2.29                          | 5.07                         | 2.22                         |
| PS-MAG5       | 371.00                     | 413.00                      | 2.70                          | 4.25                         | 3.77                         |
| PS-MAG10      | 344.00                     | 413.00                      | 2.22                          | 7.70                         | 4.33                         |
| PS-MAG15      | 356.00                     | 411.00                      | 2.18                          | 9.39                         | 5.45                         |
| PS-MAG20      | 320.00                     | 413.00                      | 2.03                          | 14.77                        | 9.33                         |

T<sub>5%</sub>: thermal degradation temperature when weight loss was 5 wt%, T<sub>max</sub>: thermal degradation temperature when weight loss was at its maximum and R<sub>max</sub>: maximum mass loss rate.

Thus, MAG has demonstrated a high thermal stability due to its high char rate production as shown in Table 2. PS has completely decomposed at a higher temperature of 450 °C without any residue. While MAG has a char residue of 67.62 and 43.37% at 450 and 700 °C respectively. Similarly, increase in MAG loads increases the char yield of the PS, this indicates that addition of MAG can significantly enhance both thermal stability and char residue. The substantial enhancement in the char residue is primarily related to the generation of polyphosphoric acid resulting from the decomposition of MAG during the combustion process, which could catalyze cellulose into char, as a result of the excellent thermal stability of graphene the char residue was further increased [123]. In summary, the catalytic effect of MAG in promoting carbon formation. which results in a flame, heat, and oxygen blocking effect contributed to the thermal stability of the PS composites. Therefore, it is obvious that the thermal degradation rate and char residue of the PS composites were greatly improved. Indicating that MAG play a good role in flame retardancy.

#### 4.1.4 Flammability

The LOI and combustion analysis was examined using Figure 13. The LOI value of pure PS was 17.99, indicating its dripping and extreme flammability, but by adding just 1wt% of MAG the LOI value increased significantly to 18.51. A higher LOI of 21.01% was achieved in the case of PS-MAG20, this indicates a higher oxygen concentration requirement for the combustion of the composites. Furthermore, as the load of MAG increases the LOI of the PS composites increase, due to a good flame retardancy of the nanosheets. MAG contains characteristics peaks of P–O, NH<sub>3</sub>, NH<sub>2</sub>, OH as has shown in Figure 10. upon combustion it releases a noncombustible volatile gas such as NH<sub>3</sub>, NH<sub>2</sub>, PO<sub>x</sub>, etc. which dilutes the surrounding oxygen and combustible gases. Also, it has a charring effect that serves as a shield to the oxygen and flaming zone upon combustion. In contrast to the PS which has a higher burning rate (less thermal stability) without char formation. Therefore, this high flame retardancy effect in PS-MAG (1-20) was attributed to the effectiveness of MAG as flame retardancy, non-combustible gas producer and charring forming agent which enables formation char barrier layer during combustion.

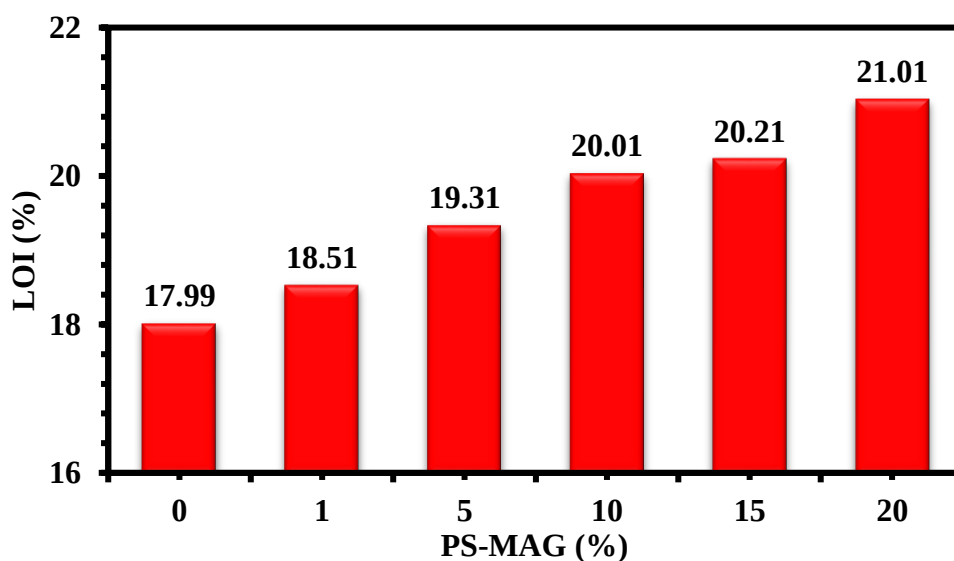


Figure 13 LOI of PS and PS-MAG

#### 4.1.5 Dynamic Mechanical Analysis

Figure 14-16 and Table 5 summarize the dynamic mechanical properties of pure PS and its nanocomposites. Figure 10a demonstrated the variation of the amount of energy dissipated (loss modulus  $E''$ ) when heated, this response is attributed to the viscoelastic behavior exhibited by pure PS and its composites. At low temperature PS and its composites have relatively the same and linear value of  $E''$ . Though, as the temperature approaches  $T_g$  of PS value of  $E''$  has increased drastically. Also, there is increase in  $E''$  of composites compare to the pure PS. Thus, the increase in MAG loads increases  $E''$  of PS. The hindrance in material flow caused by internal molecular frictions at the matrix-filler interphase leads to increased energy dissipation in the form of force. Furthermore, at glass transition phase exponential decrease in  $E''$  was observed, as the material transitioned into the rubbery region and exhibited a viscous behavior, a distinct peak was observed [124].

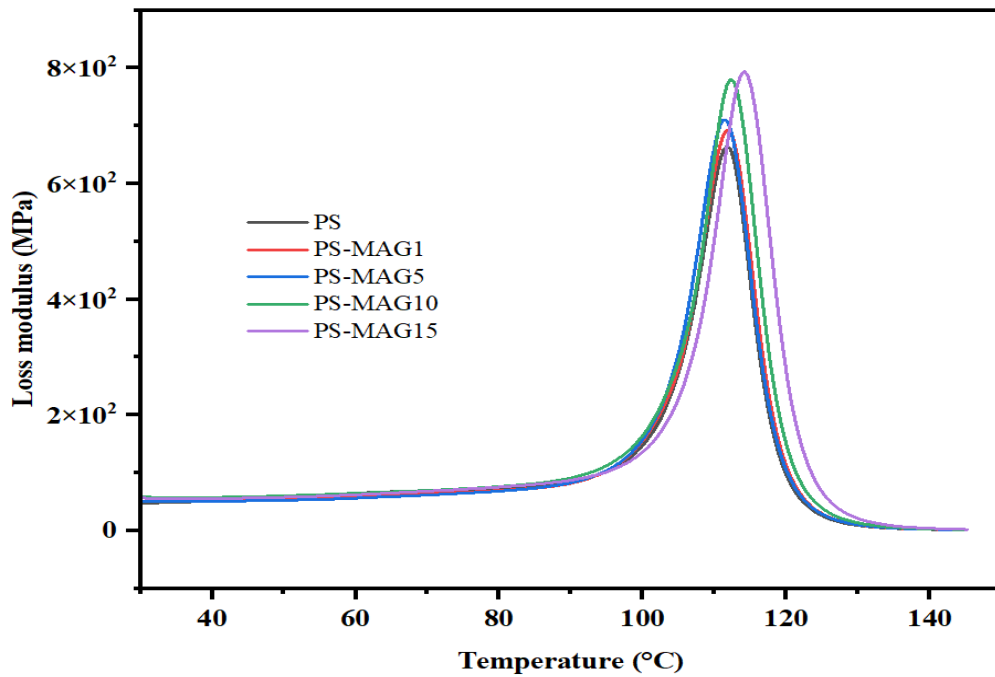


Figure 14 Figure 10 Loss modulus of PS and its composites with MAG

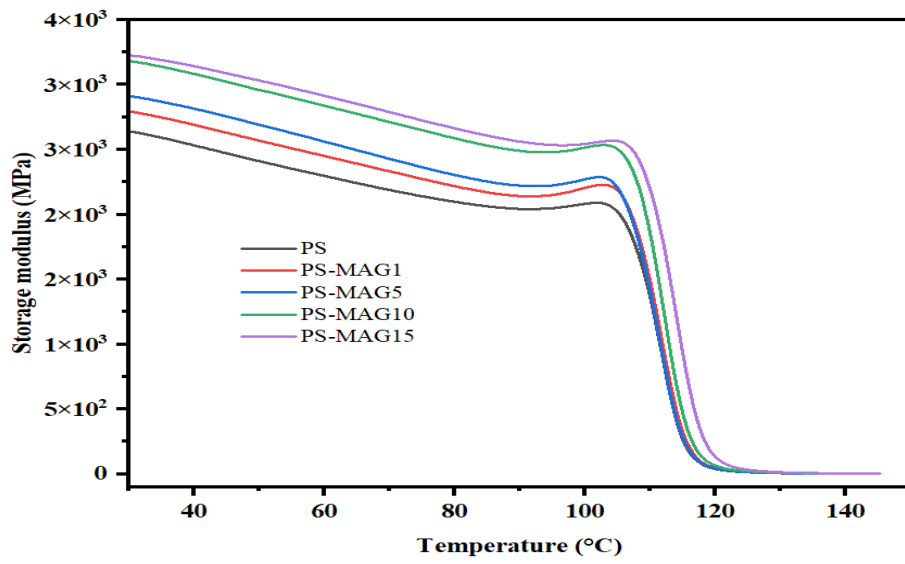


Figure 15 Storage modulus of PS and its composites with MAG

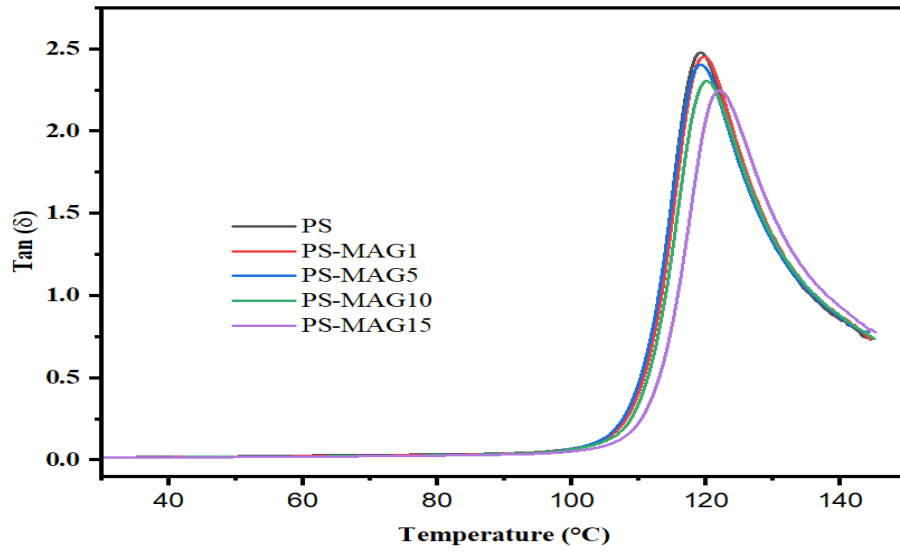


Figure 16 Damping factor of PS and its composites with MAG

Table 5 DMA parameters of PS and PS composites with MAG

| Sample   | Loss Modulus       |                 | Storage Modulus   |                 | Damping Factor |                 |
|----------|--------------------|-----------------|-------------------|-----------------|----------------|-----------------|
|          | $E''_{\max}$ (MPa) | $T_{\max}$ (°C) | $E'_{\max}$ (MPa) | $T_{\max}$ (°C) | $\tan(\delta)$ | $T_{\max}$ (°C) |
| PS       | 665.06             | 111.77          | 2084.37           | 102.91          | 2.48           | 119.36          |
| PS-MAG1  | 692.55             | 112.03          | 2223.44           | 103.64          | 2.46           | 119.61          |
| PS-MAG5  | 710.15             | 111.24          | 2285.31           | 102.86          | 2.41           | 119.35          |
| PS-MAG10 | 780.33             | 112.23          | 2561.68           | 102.81          | 2.31           | 120.33          |
| PS-MAG15 | 794.05             | 114.16          | 2563.73           | 105.29          | 2.25           | 122.22          |

$E'_{\max}$ : maximum storage modulus,  $E''_{\max}$ : maximum loss modulus and  $T_{\max}$ : maximum temperature

Variation in the composites' ability to store energy (storage modulus  $E'$ ) elastically was demonstrated in Figure 15. Also, it shows the three phases transition which are; glassy, glass transition and rubbery phases. At first phase the values of  $E'$  are higher as a result of the rigid molecular structure, but declines at the second phase down to  $T_g$  because the polymeric chains are flexible at higher temperature. At a temperature beyond  $T_g$  value of  $E'$  decreased drastically, which can be clarified by the easy flexibility of polymeric chains since this affects the interfacial adhesion caused by reinforcement and the viscoelastic behavior of nanocomposites [125]. Generally, the decline in the value of  $E'$  with rising temperature can be attributed to a decrease in intermolecular forces and reduced hindrance to molecular movement. However, it increased with material loads, which is directly connected with improved compatibility at the interphase between the PS matrix and filler. Hence, the incorporation of MAG into PS resulted in an enhancement of crystallinity, resulting to increased rigidity, stiffness, and a reduction in the mobility of polymeric chains [126]. Figure 10c has indicated the ratio between loss modulus and storage modulus which is damping factor ( $\tan \delta$ ). This property describes the ability of the material to dissipate or store energy in response to the viscoelastic behavior of PS composites [127]. It was observed that the peak of  $\tan \delta$  for the PS was sharp and high, which subsequently decreased by adding MAG. Also, it indicates an excellent compatibility between the nanomaterial and matrix of PS due to substantial intermolecular interactions as has shown in Figure 11c. Moreover, it was noted that the value of  $T_g$  decreased in all the modified samples, causing a shift of the  $\tan$  peak toward higher temperatures. This shift can be attributed to the increased mobility of the active molecules and then eventually reduced approaching zero. The value of  $T_g$  was affected by several factors, such as the closely

packed intermolecular structure or linear structure, as well as the type and amount of reinforcement or filler content [128].

#### **4.1.6 Thermal conductivity**

Generally, PS has a good thermal insulation performance, because of its lower thermal conductivity. However, its thermal conductivity ( $\lambda$ ) increased linearly as the temperature increases as shown in Figure 17. At ambient temperature the value of  $\lambda$  of PS, PS-MAG1, PS-MAG5, PS-MAG10 and PS-MAG15 are; 0.1327, 0.1342, 0.1393, 0.1329 and 0.1523  $\text{Wm}^{-1}\text{K}^{-1}$  respectively. This indicates a slight increase in thermal conductivity as filler loads increases, although these composites are at acceptable range compare to 0.14  $\text{Wm}^{-1}\text{K}^{-1}$  thermal conductivity of commercial PS for thermal insulation application [129]. At higher temperature 50°C and higher filler load 15wt% the linear increase in thermal conductivity reached 0.1577  $\text{Wm}^{-1}\text{K}^{-1}$ . The increment in  $\lambda$  is mostly due to a substantial increase in radiant thermal conductivity's contribution to overall thermal conductivity at high temperatures. Heat insulation is specifically affected by factors such as pore structure on a broad scale. The porous nature of MAG provides a good thermal insulation performance for PS. Consequently, heat transfer in MAG at room temperature predominantly includes the conduction of heat within the solid framework and through the pores [130].

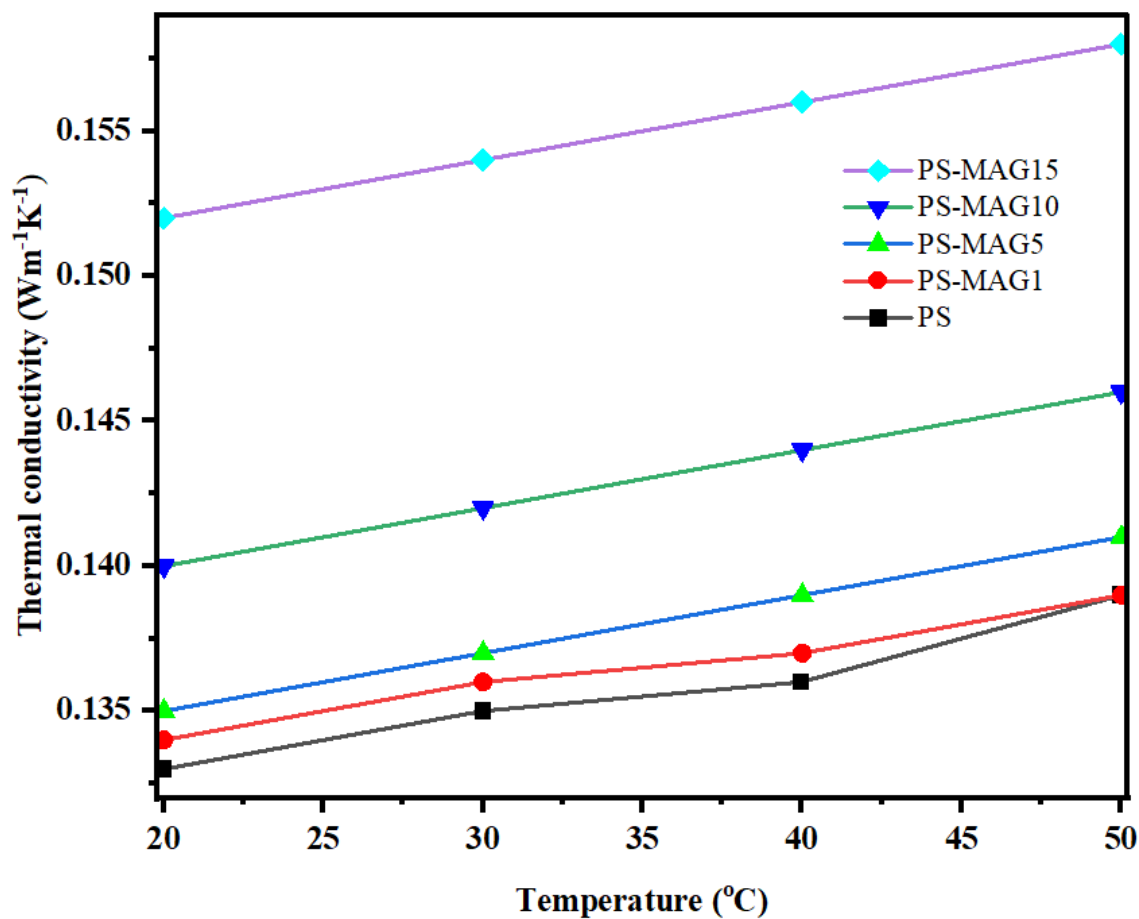


Figure 17 thermal conductivity of PS and its composites.

## 4.2 ZnAl-LDH and Its composites Flame retardant

### 4.2.1 X-Ray Diffraction (XRD)

XRD spectrum of calcined ZnAl-LDH, graphene, ZnAl-G, and ZnAl-G-PCL are shown in Figure 18. The graphene peaks can be seen in the ZnAl-G and ZnAl-G-PCL zoom region at  $2\theta \approx 26^\circ$  already reported in our previous work [112]. Calcination is done under nitrogen environment in tubular furnace at  $450^\circ\text{C}$  in 4 hrs. The peaks of ZnAl at C (003 and 006) disappear due to calcination. After calcination, layered structure is then transformed to mixed metal oxide structure which is obvious from figure and is well in compliance with the literature [131], [132].

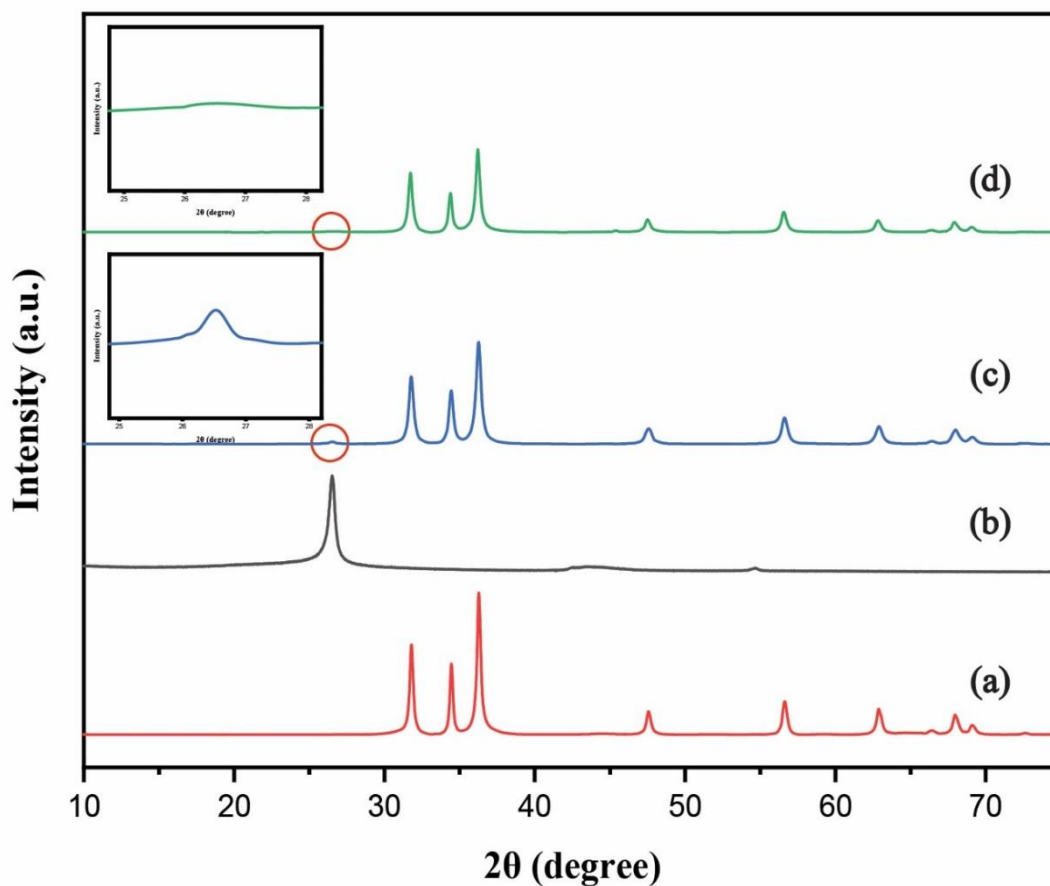


Figure 18 XRD spectrum of calcined (a) ZnAl-LDH, (b) graphene, (c) ZnAl-G, and (d) ZnAl-G-PCL

#### 4.2.2 FE-SEM analysis

The morphological characteristics and surface study of the calcined LDH and its composites were analyzed using field emission scanning electron microscopy (FE-SEM) at different resolutions. From Figure 19 it is clear that, the graphene has planner structure Figure 19a however, ZnAl has aggregate structure evident from Figure 19b. The FE-SEM images for ZnAL-G and ZnAl-G-LDH shown both planner and aggregate structures, showing the existence of both graphene sheets and LDH [112], [133], [134].

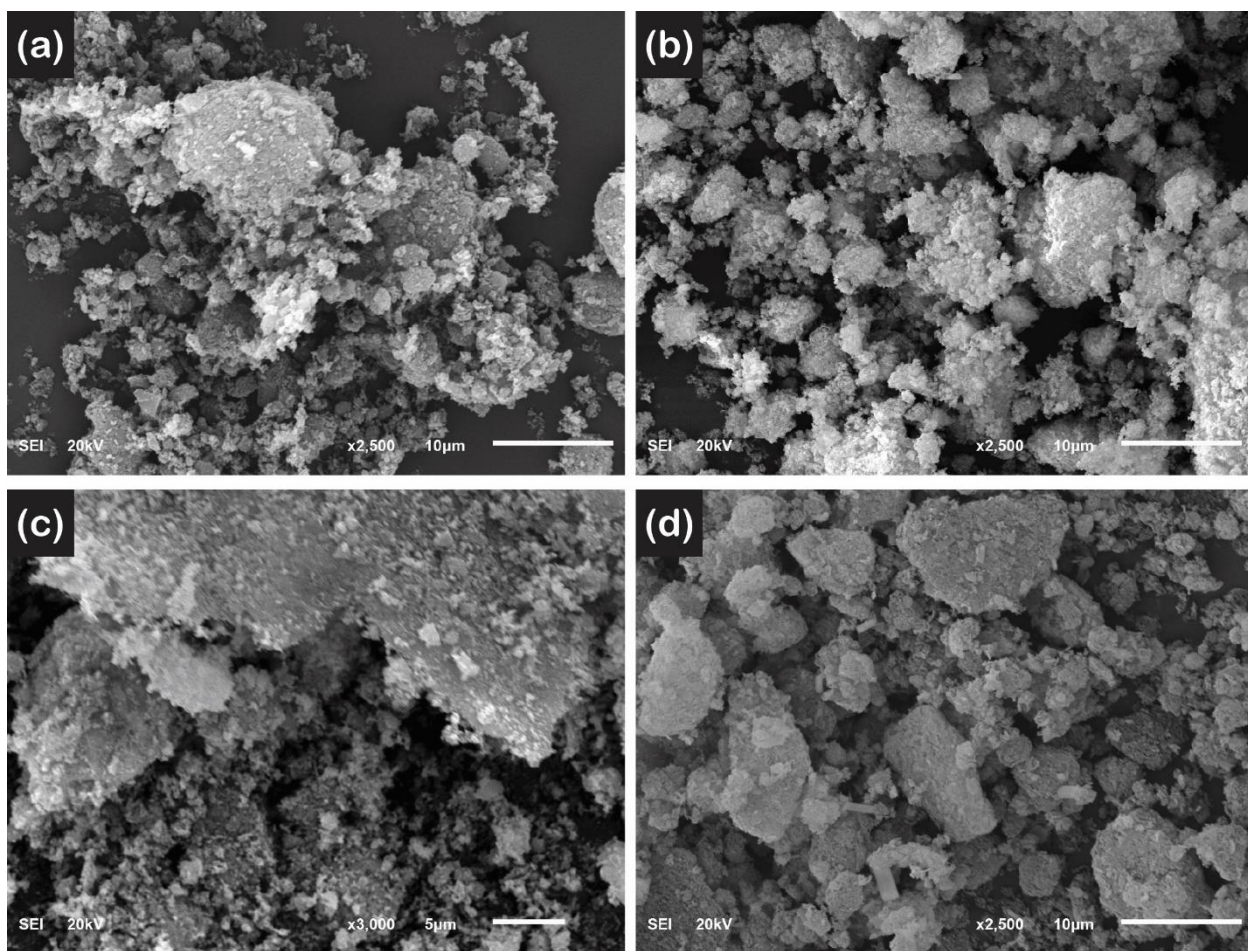


Figure 19 FE-SEM images of (a) graphene, (b) ZnAl-LDH, (c) ZnAl-G, and (d) ZnAl-G-PCL

### 4.2.3 TEM analysis

The structure of nanocomposites synthesized by co-precipitation methods for graphene, LDH, and its composites is shown in the Transmission electron microscope images represented in Figure 20. Sharp hexagonal structure possessed by ZnAl-LDH can be seen from Figure 20b. The nanocomposite composed of ZnAl-G and ZnAl-G-PCL has hexagonal structures under the umbrella of graphene nanosheets in accordance with previously illustrated research work [135]. Further, homogeneous dispersion and synergistic effect of graphene inside the nanofiller is evident from Figure 20c and 20d.

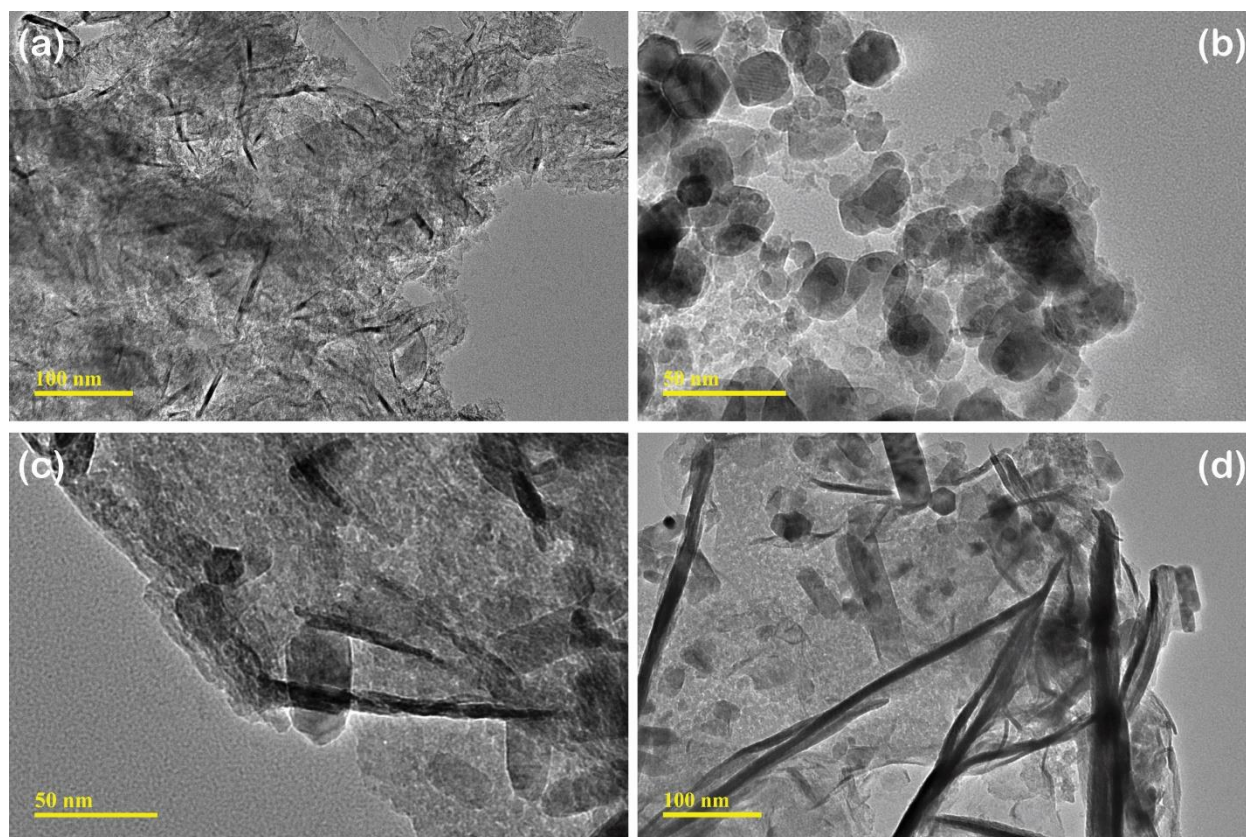


Figure 20 HR-TEM images of (a) graphene, (b) ZnAl-LDH, (c) ZnAl-G, and (d) ZnAl-G-PCL

#### 4.2.4 Thermal stability

The thermal stability of ZnAl, ZnAl-G and ZnAl-G-PCL under nitrogen flow was studied using thermogravimetry (TG), and derivative thermogravimetry (DTG) curves were plotted, as illustrated in Figure 21 a&b where ZnAl-LDH pristine shows a higher thermal stability compare to its composite, due to the presence of potent van der Waals forces between the layers. But by intercalating graphene and ionic liquid into the interlayer of ZnAl-LDHs has reduced the thermal stability of the LDHs due the decrease in forces between the laminates [136]. ZnAl-LDH pristine has shown three main weight loss stages, the initial phase of weight reduction took place between 50 and 220 °C, where the main weight loss that occurred at temperature below 220 °C was ascribed to the release of water molecules that were physically attached to the surface and interlaced within the LDHs-C layers. Also, weigh loss between 190 ~ 220 °C primarily involved the elimination of minor quantities of -OH and  $\text{CO}_3^{2-}$  resulting from electrostatic bond [137]. While the second stage weight occurred between 400 – 600 °C as a result of the removal of interlayer crystallization water. The last weight reduction results from the dehydroxylation and deionization processes of LDHs. As the temperature rises (600-900 °C), hydrotalcite has the potential to fully transform into a dense metal oxide [138]. Also, it can be observed that the ZnAl composites follows the same weight loss pattern with ZnAl-LDH pristine due to the release of absorbed water and crystallization water molecule. The major cause of loss weight in ZnAl-G is primarily attributed to dehydroxylation, deionization of  $\text{CO}_3^{2-}$  and the presence of graphene. While for ZnAl-G-PCL the TGA curve differs from that of ZnAl and ZnAl-G-LDH because the thermal stability of metal phosphine oxides is less than that

of volatile anion  $\text{CO}_3^{2-}$ , this indirectly demonstrates that phosphorous from phosphonium ionic liquid has successfully replaced  $\text{CO}_3^{2-}$  of ZnAl-LDH [27].

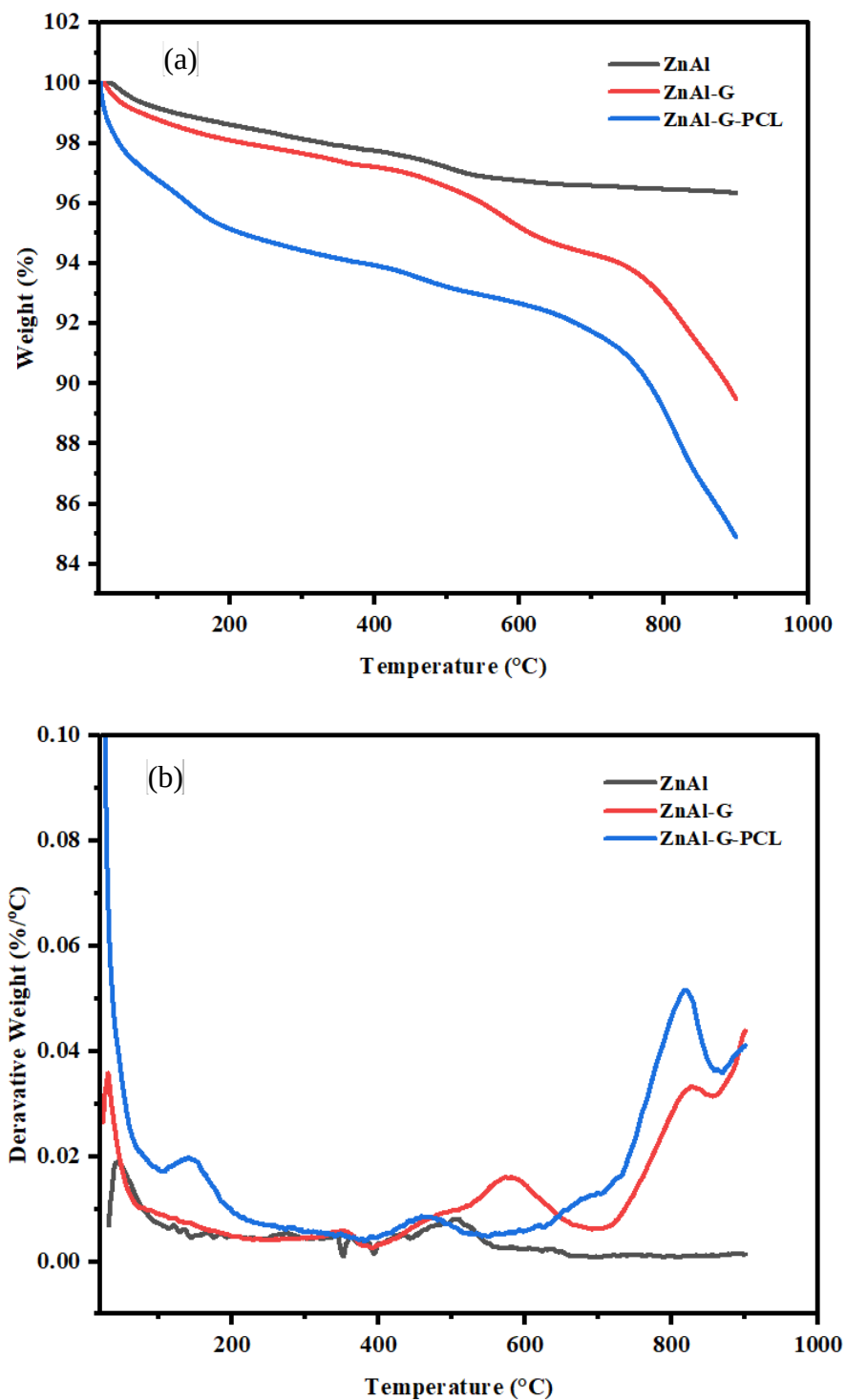


Figure 21 (a) TG and (b) DTG curves of ZnAl, ZnAl-G and ZnAl-G-PCL.

Generally, the materials are highly thermally stable. The specific values of the TG and DTG curves of the ZnAl-LDH pristine and its composites are itemized in Table 6. The nanofillers residue at 500 °C are; 97.2, 96.55 and 93.22 wt% for ZnAl, ZnAl-G and ZnAl-G-PCL respectively. This specifies that these materials could serve as an effective component for flame retardation due to their outstanding ability to carbonize. Also, the weight loss at higher temperature 700 °C are only 3.41, 5.69 and 8.25 wt% of ZnAl, ZnAl-G and ZnAl-G-PCL with maximum mass loss rate  $R_{max}(\%/^{\circ}\text{C})$  of 0.01, 0.03 and 0.05  $\%/^{\circ}\text{C}$  respectively. The outstanding thermal stability of ZnAl-G-PCL plays a critical role in minimizing the fire threat associated with polystyrene.

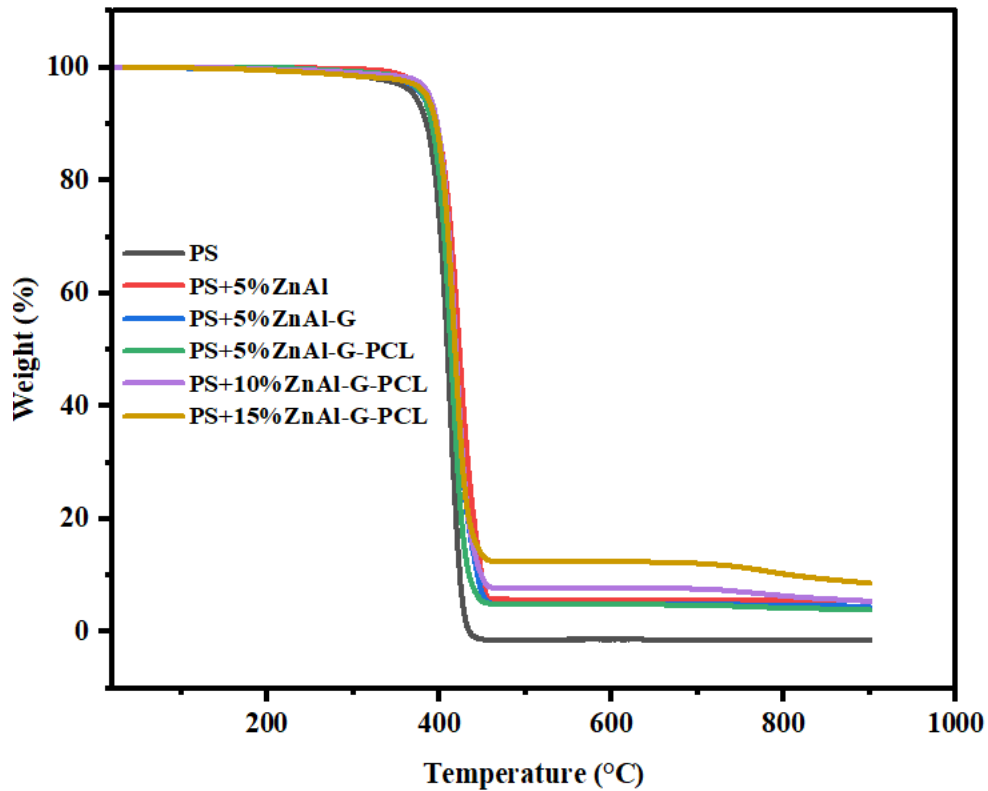


Figure 22 TG curves of PS and PS composites

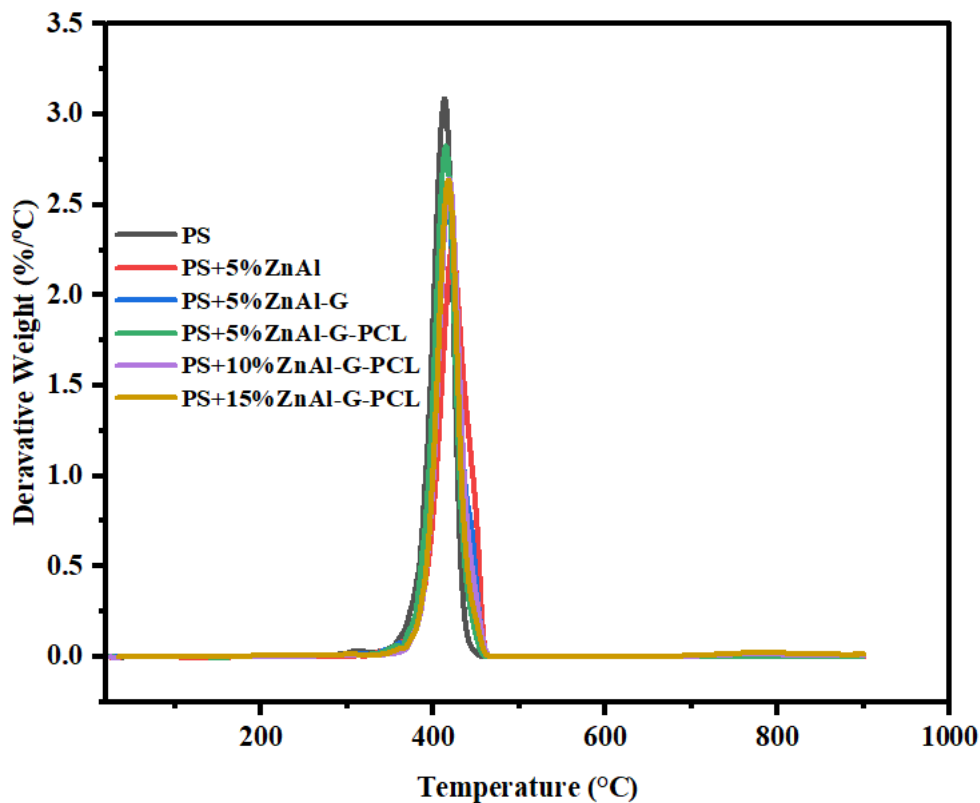


Figure 23 DTG curves of PS and PS composites.

The thermal stability of the pure PS and its composites was analyzed using Figure 22 and 23 where TG, DTG specific values and char yield parameters are evaluated in Table 6. Generally, the figure indicates that there is a clear enhancement in PS thermal stability. The thermal degradation temperature of pure PS when the weight loss was 5 wt% ( $T_{5\%}$ ) is 371°C, the maximum degradation rate temperature ( $T_{max}$ ) is 413 °C with high mass loss rate of 3.09%/°C. but at the temperature above 430 °C the PS has completely degraded with no residue remain. This indicates that PS has low thermal stability. By incorporating 5wt% of ZnAl, ZnAl-G and ZnAl-G-PCL on PS matrix,

**Table 6 TGA and DTG curves parameters of ZnAl hybrids, PS, and PS composites**

| <b>Sample</b>    | <b>T<sub>5%</sub><br/>(°C)</b> | <b>T<sub>max</sub><br/>(°C)</b> | <b>R<sub>max</sub><br/>(%/°C)</b> | <b>Residue at<br/>500 °C (%)</b> | <b>Residue at<br/>700 °C (%)</b> |
|------------------|--------------------------------|---------------------------------|-----------------------------------|----------------------------------|----------------------------------|
| PS               | 371                            | 413                             | 3.09                              | /                                | /                                |
| ZnAl             | /                              | 510                             | 0.01                              | 97                               | 96.59                            |
| ZnAl-G           | 616                            | 829                             | 0.03                              | 96                               | 94.31                            |
| ZnAl-G-PCL       | 217                            | 817                             | 0.05                              | 93                               | 91.75                            |
| PS/5%ZnAl        | 384                            | 422                             | 2.25                              | 6.75                             | 5.62                             |
| PS/5%ZnAl-G      | 380                            | 417                             | 2.55                              | 5.50                             | 5.09                             |
| PS/5%ZnAl-G-PCL  | 381                            | 415                             | 2.83                              | 5.20                             | 4.80                             |
| PS/10%ZnAl-G-PCL | 388                            | 418                             | 2.64                              | 9.00                             | 8.02                             |
| PS/15%ZnAl-G-PCL | 385                            | 418                             | 2.62                              | 13.56                            | 12.15                            |

T<sub>5%</sub>: thermal degradation temperature when the weight loss was 5 wt%, T<sub>max</sub>: thermal degradation temperature when the weight loss was at its maximum and R<sub>max</sub>: maximum mass loss rate.

The T<sub>5%</sub> has drastically increased to 384, 380 and 381 °C also the T<sub>max</sub> has increased to 422, 417 and 415 °C respectively. This indicates that there is an improvement in T<sub>5%</sub> and T<sub>max</sub> of PS due to the excellent thermal stability of these nanofillers which enhanced thermal stability of the pure PS. Also, decrease in weight loss rate of PS composites was observed from 3.09 to 2.25, 2.55 and 2.83 %/°C for PS/5%ZnAl, PS/5%ZnAl-G and PS/5%ZnAl-G-PCL respectively. One could observe that the carbonaceous residue of pure PS is 0 wt% at 500 °C. while with a 5wt% of ZnAl, ZnAl-G and ZnAl-G-PCL into the PS matrix the char residue of PS composite at 500 °C increased to 6.75, 5.50 and 5.20 wt% respectively, this has shown that both materials can effectively enhance the carbonization process of PS while burning. As anticipated, the introduction of ZnAl pristine has generate more char residue followed by ZnAl-G and ZnAl-G-PCL, this because of the presence of strong van der Waals forces between the ZnAl-LDH laminates which make it highly thermal stable. By intercalating graphene and phosphonium based ionic liquid on ZnAl-LDH has

decreased the force between laminates which improve LOI by promoting char formations as demonstrated on Figures 22 and 23.

#### 4.2.5 Limiting Oxygen Index (LOI) of PS and its composites

The burning behavior of PS and its composites was observed using the LOI, which is a fundamental method employed to study the flammability properties of polymers [139]. The LOI values for the pure PS, PS/ZnAl, PS/ZnAl-G and PS/ZnAl-G-PCL has demonstrated in Figure 24. The initial information about flame resistance for PS nanocomposites was provided by the value of LOI [140]. Pure PS has LOI value of 17.98-18.0 which is extremely flammable that can easily be combustible in air, by incorporating ZnAl-LDHs and its composites the values of LOI has increased significantly and show no dripping during burning. With addition of 5wt% of ZnAl, ZnAl-G and ZnAl-G-PCL the LOI values has increased to 18.51, 18.71 and 19.11 respectively. Therefore, with the addition of LDHs nanocomposites the burning behavior of PS has increased in comparison with the pure PS.

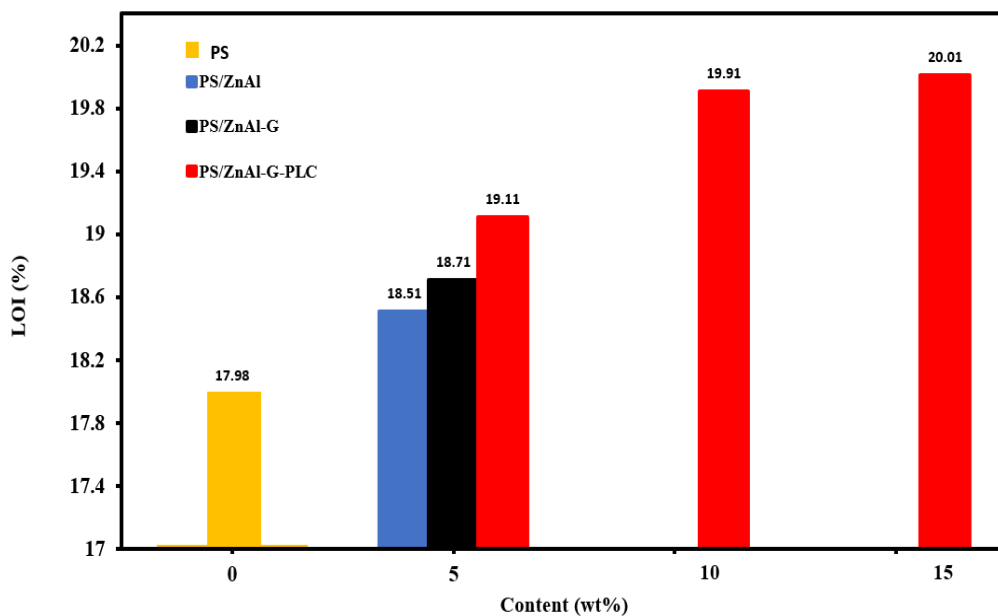


Figure 15 LOI of PS and PS composites with ZnAl.

Pure PS burns continuously, similar to a candle, with a consistent flow of melting drips until the entire sample is depleted. The combustion of PS/ZnAl nanocomposites exhibited distinct behavior, with these samples displaying three regions on the combustion surface. These regions included skin layers comprising char, and then molten layers supported by a solid surface. As the loading level of all LDHs was only 5 wt.% the increase in LOI value of ZnAl-G-PCL was highest followed by ZnAl-G and then ZnAl. This can be interlinked with the intercalation of graphene and phosphonium based ionic liquid into the interlayer of ZnAl-LDHs. Furthermore, by incorporating 10 wt% and 15 wt% of ZnAl-G-PCL with PS the LOI value has increased to 19.91 and 20.01 respectively. Therefore, ZnAl-LDH modification has a positive impact on pure PS resulting in an alteration of the LOI value of PS nanocomposites. This is because the incorporation of ZnAl-G-PCL nanocomposites will reduce the content of oxygen because of the formation of phosphorus-oxygen bonds content in ZnAl-G-PCL-LDH which is lower than that in ZnAl-G and ZnAl. The phosphorus-oxygen bond plays a crucial role in enhancing flame retardancy, as it can establish bridging bonds with the metal ions present in LDH and improve a synergistic effect on promoting char formation [141]. Also, at presence of air phosphonium based ionic liquid tends to generate phosphine oxides, which is not combustible gas that can dilute the oxygen presence on the PS surface [142]. The dense residual char that develops during pyrolysis has the ability to adhere to the polymer's surface, which, in turn, reduces heat transfer and the penetration of oxygen. This, consequently, results in a decreased emission of combustion gases. It was also observed that the ignition of pure PS leads to a rapid-fire propagation and is accompanied by the generation of molten drips, without substantial self-extinguishing behavior. Conversely, PS composites do not generate molten droplets during

combustion and exhibit self-extinguishing behavior. The most prominent flame retardant property is displayed by those that can self-extinguish shortly after ignition and produce the least amount of smoke throughout combustion. Clearly, the addition of ZnAl-G-PCL enhances the flame retardant characteristics of PS composites.

#### **4.2.6 Dynamic Mechanical Thermal Analysis**

The mechanical properties of polystyrene composites are a critical factor related to their practical utility. Typically, an increased loading quantity and poor interfacial compatibility between nanofiller and polymer matrix may results in a degradation of the mechanical performance of polymer composites [143]. DMA was conducted to examine the viscoelastic behavior of the PS and its nanocomposites from room temperature to 140°C, the dependency of storage modulus, loss modulus and damping factor on these temperature range are shown in Figures 25,26 and 227 respectively. Figure 25 has shown the variations of the storage modulus over the range of these temperature. The Figure indicates that the storage moduli of the PS and its composites decreases with increase in temperature, this is attributed to the energy dissipation phenomenon that involves the coordinated movements of the polymer chains as the temperature rises [144]. However, incorporating LDHs and its hybrids into PS matrix elevated the storage modulus across the entire temperature spectrum. At glassy state temperature 40°C in which molecules are frozen [145], addition of 5wt% of ZnAl, ZnAl-G and ZnAl-G-PLC resulted in a substantial enhancement of the storage modulus by 119, 160 and 248 MPa respectively. This substantial improvement in storage modulus can be related to the reinforcement provided by the LDHs layer, which enhanced the interfacial interaction between the nanofiller and the polymer matrix, and restricted the mobility of the polymer chains [146], [147]. Generally, it can be observed

that incorporation of ZnAl-LDH on PS matrix has a positive impact on storage modulus. But the modified LDH has higher impact on the storage modulus due to higher compatibility between ZnAl-LDH composites and PS matrix compare to pristine ZnAl-LDH. The specific values of the storage modulus parameters of the ZnAl-LDH pristine and its composites are presented in Table 7.

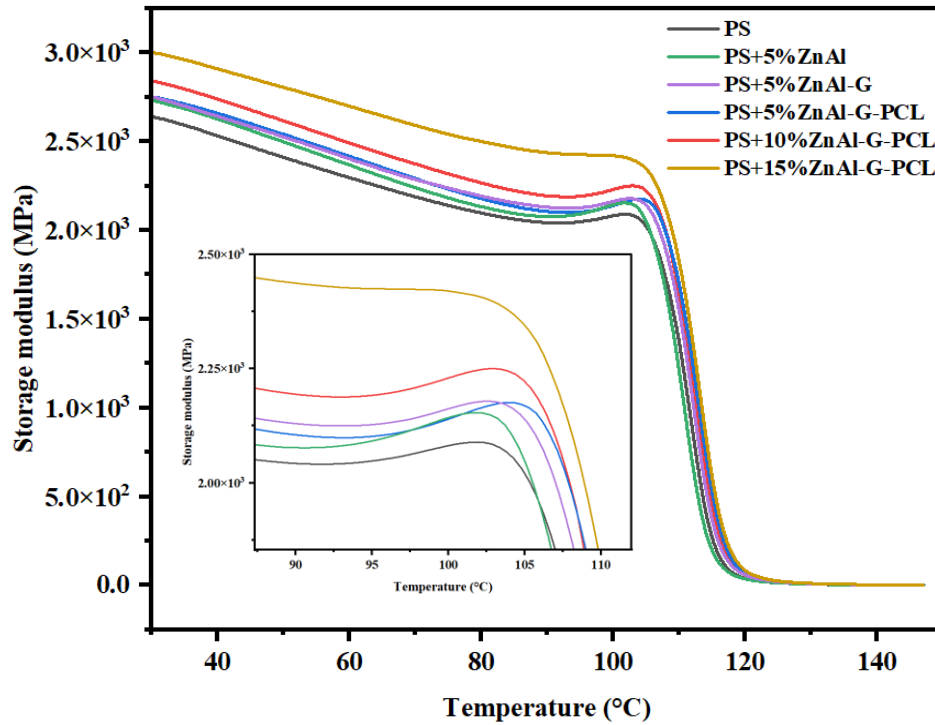


Figure 25 Storage modulus of PS and its nanocomposites with ZnAl

Table 7 Storage modulus of PS and its composites with ZnAl

| Sample           | Storage Modulus (MPa) |        |
|------------------|-----------------------|--------|
|                  | 50 °C                 | 100 °C |
| PS               | 2400                  | 2000   |
| PS/5%ZnAl        | 2495                  | 2150   |
| PS/5%ZnAl-G      | 2525                  | 2170   |
| PS/5%ZnAl-G-PCL  | 2559                  | 2210   |
| PS/10%ZnAl-G-PCL | 2714                  | 2334   |
| PS/15%ZnAl-G-PCL | 2853                  | 2518   |

**Table 8 DMA parameters of PS and its PS composites with ZnAl**

| Sample           | Storage Modulus         |                       | Loss Modulus             |                       | Damping Factor |                       |
|------------------|-------------------------|-----------------------|--------------------------|-----------------------|----------------|-----------------------|
|                  | E' <sub>max</sub> (MPa) | T <sub>max</sub> (°C) | E'' <sub>max</sub> (MPa) | T <sub>max</sub> (°C) | tan (δ)        | T <sub>max</sub> (°C) |
| PS               | 2084                    | 102                   | 665                      | 112                   | 2.48           | 119                   |
| PS/5%ZnAl        | 2154                    | 103                   | 680                      | 113                   | 2.41           | 121                   |
| PS/5%ZnAl-G      | 2179                    | 103                   | 685                      | 111                   | 2.40           | 120                   |
| PS/5%ZnAl-G-PCL  | 2176                    | 105                   | 698                      | 113                   | 2.37           | 118                   |
| PS/10%ZnAl-G-PCL | 2250                    | 103                   | 700                      | 112                   | 2.22           | 121                   |
| PS/15%ZnAl-G-PCL | 2490                    | 103                   | 731                      | 113                   | 2.17           | 120                   |

E'<sub>max</sub>: maximum storage modulus, E''<sub>max</sub>: maximum loss modulus and T<sub>max</sub>: maximum temperature

The loss factor curves for both pure PS and its composites are also depicted in Figure 26. The temperature corresponding to the point where the curve reaches its highest peak was identified as the glass transition temperature (T<sub>g</sub>). Obviously, when compared to pure PS, the T<sub>g</sub> for the PS/LDHs nanocomposites exhibited a substantial increase. The T<sub>g</sub> of the nanocomposites was approximately 158°C higher than that of the pure PS. It is commonly accepted that the reasonably uniform dispersion of LDH layers within the nanocomposites can enable improved interfacial interaction between the sheets and the polymer matrix, thereby significantly limits the segmental motion of polymer chains. This, in turn, results in a notable increase in the shift of the T<sub>g</sub> [148]. Also, one can notice that there is an obvious increase in loss modulus by introducing 5wt% of ZnAl-LDH pristine and its composites. This could be due to an increase in the amorphous region due to the decrease crystallinity. The loss modulus of the nanocomposites is higher than that of pure PS, this is attributed to the role of L LDH in decreasing crystallinity of PS.

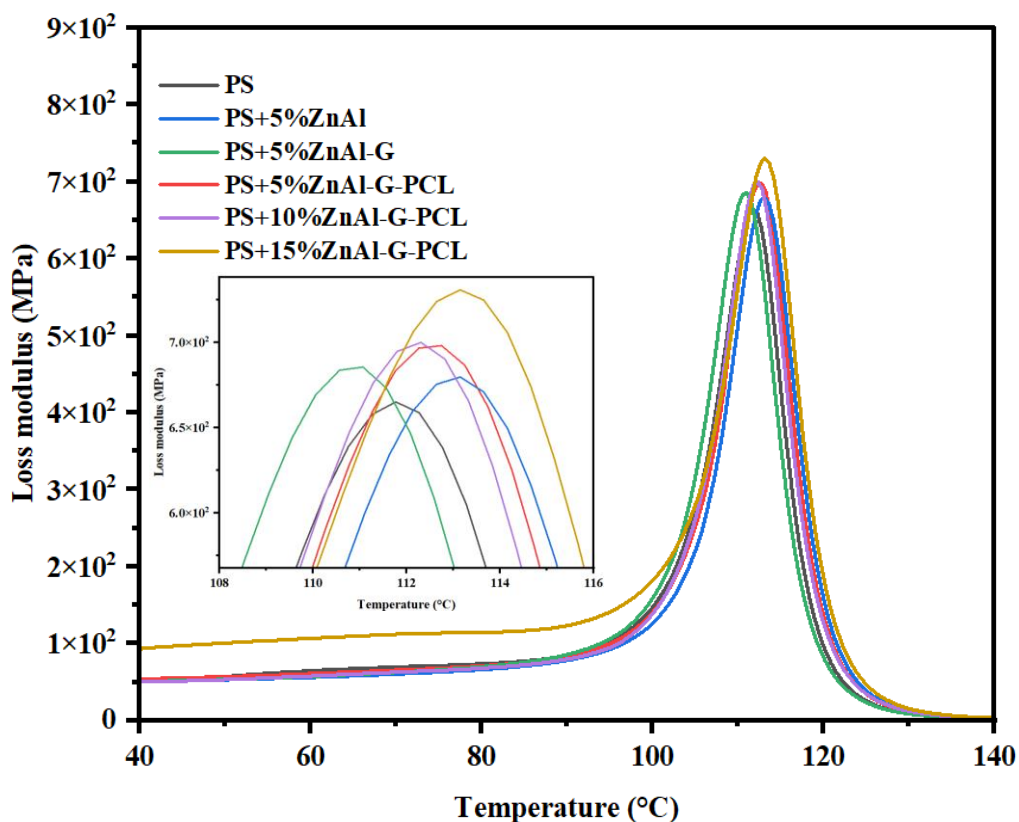


Figure 26 Loss modulus of PS and its nanocomposites with ZnAl

The effect of loss damping factor  $\tan(\delta)$  on temperature curves for pure PS and its composites are shown Figure 27. It can be observed that pure PS has higher loss factor, while addition of ZnAl-LDH pristine and its composites decreases damping factor due to good interaction between PS and LDH phases which leads to an increase in physical intertwining among the macromolecules. [149]

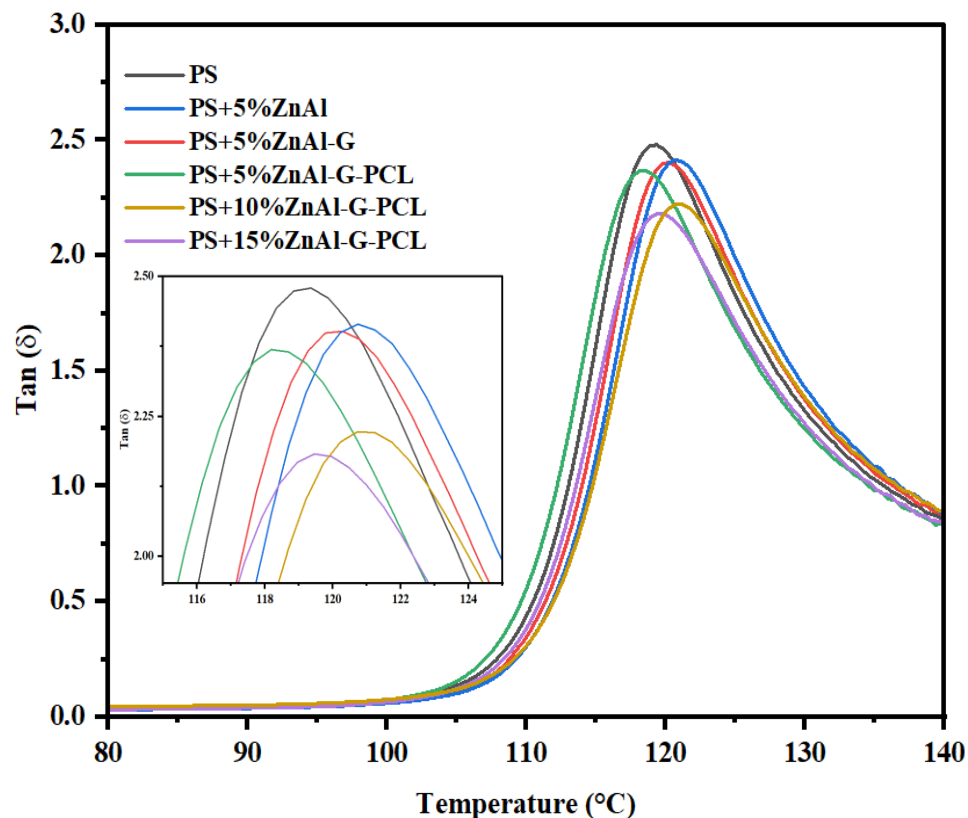


Figure 27 Damping factor of PS and its nanocomposites with ZnAl

The peak that appears in the  $\tan(\delta)$  curve between 115-125°C is attributed with the glass transition of the PS matrix. The  $\tan(\delta)$  value indicates an equilibrium between the elastic and viscous phases within the polymer's structure. The damping factor of PS nanocomposites films is influenced by the addition of reinforcements, and these factors are lower than that observed in pure PS. However, the relaxation process diminished when ZnAl-LDH composites were incorporated into the PS matrix [150]. This change is attributed to a decrease in the quantity of the material's matrix, which is responsible for its damping properties, in other words, a decrease in the number of mobile units involved in the relaxation process, and the movement of polymer molecules is restricted from the hydrogen bonds between the PS chains, ZnAl-LDH, ZnAl-G and ZnAl-G-PCL. In simpler terms, it's widely recognized that the unique interactions between polymer chains and filler

particles can create a distinct layer of polymer around each particle. This layer has features that are different from those of the bulk material [151]. If the particles in the dispersed phase are assumed to be rigid the polymer layer that contributes to the effective filler volume fraction within the composite must be a stationary one. Since energy dissipation occurs at the interface between the filler and the matrix, a stronger interface is identified by reduced energy dissipation. Consequently, lower  $\tan \delta$  peak values show improved interfacial adhesion [152].

#### **4.2.7 Thermal Conductivity**

Thermal conductivity is a crucial parameter for assessing the thermal insulation ability of energy-efficient building materials [153]. Figure 28 indicates thermal conductivity of pure PS and its composites from ambient to higher temperature. Generally, PS has a lower thermal conductivity compared to many polymers which make a good thermal insulator. The thermal conductivity of the PS and its composites have increased linearly due to the increase in temperature as indicated in Figure 28. Initially, at low temperature 30 °C the thermal conductivity of PS, PS+5%ZnAl, PS+5%ZnAl-G and PS+%ZnAl-G-PCL are 0.1364, 0.1316, 0.1337 and 0.1356 W/mK respectively. However, at higher temperature 90 °C the thermal conductivity has increased to 0.1512, 0.1570, 0.1529 and 0.1529 W/mK for PS, PS+5%ZnAl, PS+5%ZnAl-G and PS+%ZnAl-G-PCL respectively. This indicates that at higher temperature ZnAl-LDH has higher thermal conductivity. Which is attributed to the radiant thermal conductivity to total thermal conductivity at elevated temperatures. Because heat transfer in ZnAl at higher temperature primarily comprises heat conduction within the solid framework. But by intercalation of graphene and phosphonium ionic liquid has lower the thermal conductivity, porous nature of graphene and ionic liquid provides an

effective thermal insulation performance for PS. Precisely, parameters such as pore structure exert a comprehensive impact on thermal insulation. The reduced pore size and the continuous three-dimensional porous structure of ZnAl-G and ZnAl-G-PCL contribute to the elongation of the heat conduction path. Thereby leads to lower thermal conductivity and enhances flame resistance [154].

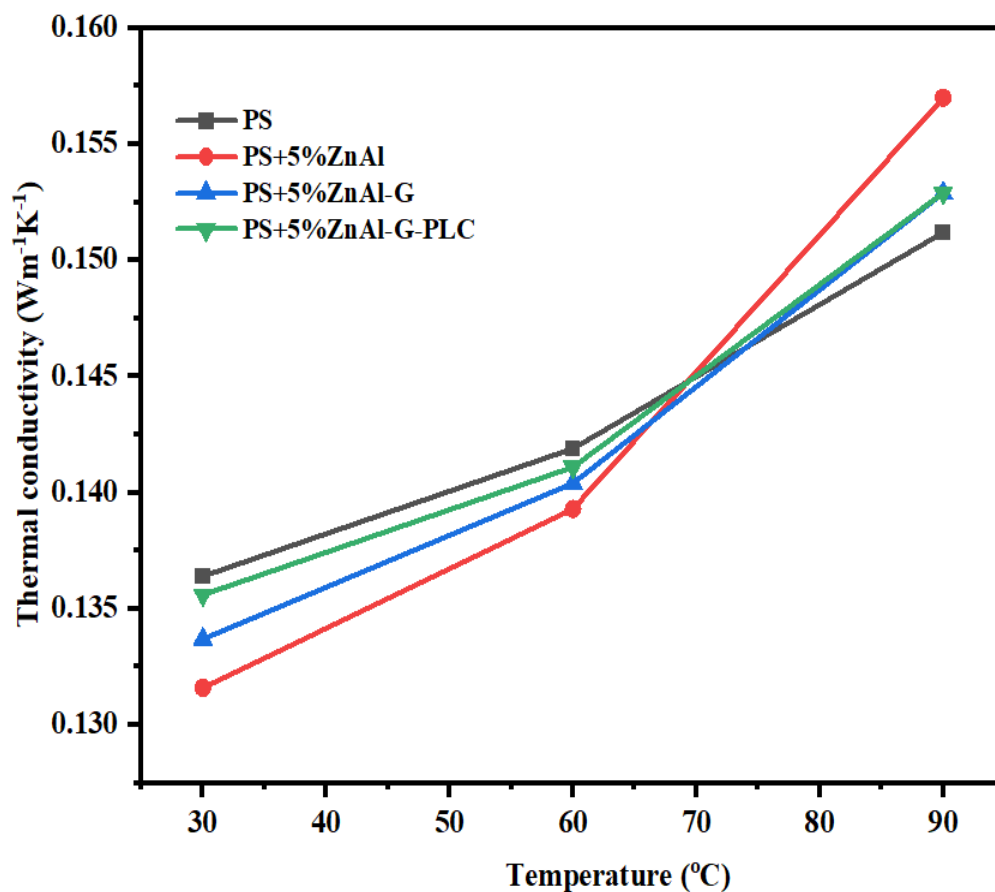


Figure 28 Thermal conductivity of PS and its composites with ZnAl.

## CHAPTER 5

### CONCLUSION

In an effort to enhance the thermal stability, mechanical properties, and flame retardancy of materials. In this research, two novel environmentally friendly flame retardants were successfully synthesized. The first flame retardant, a nanolayered intumescent flame retardant (MAG), demonstrated a significant increase in thermal stability with higher char residue. This was evidenced by a higher decomposition temperature, indicating that polystyrene treated with MAG could withstand higher temperatures before starting to break down. It also demonstrated higher flame retardancy due to its ability to release incombustible gases, which dilute the concentration of oxygen and flammable gases, and a high limiting oxygen index was observed. The second flame retardant, ZnAl-LDH and its composites, not only enhanced flame retardancy but also enhanced the mechanical properties of the treated materials due to the synergistic effect of the material. This resulted in polystyrene composites that were more durable and resistant to wear and tear while also being safer in the event of a fire. Moreover, this material does not increase thermal conductivity of the polystyrene. Furthermore, this material is a Type-IV mesoporous materials which has the ability to suppress the released gases such as; CO<sub>2</sub>, CO etc. In conclusion both the two materials represent promising advancements in the field of flame retardants, offering improved safety and durability for a wide range of materials. Further studies are underway to optimize their synthesis and application processes.

## References

- [1] S. B. Sadineni, S. Madala, and R. F. Boehm, “Passive building energy savings: A review of building envelope components,” *Renewable and Sustainable Energy Reviews*, vol. 15, no. 8, pp. 3617–3631, Oct. 2011, doi: 10.1016/j.rser.2011.07.014.
- [2] O. Gencel *et al.*, “Development, characterization and thermo-regulative performance of microencapsulated phase change material included-glass fiber reinforced foam concrete as novel thermal energy effective-building material,” *Energy*, vol. 257, p. 124786, Oct. 2022, doi: 10.1016/j.energy.2022.124786.
- [3] Y. Xu, “Introductory Chapter: Flame Retardant and Thermally Insulating Polymers,” in *Flame Retardant and Thermally Insulating Polymers*, IntechOpen, 2021. doi: 10.5772/intechopen.99111.
- [4] Y. Shi, C. Liu, L. Fu, F. Yang, Y. Lv, and B. Yu, “Hierarchical assembly of polystyrene/graphitic carbon nitride/reduced graphene oxide nanocomposites toward high fire safety,” *Compos B Eng*, vol. 179, p. 107541, Dec. 2019, doi: 10.1016/j.compositesb.2019.107541.
- [5] N. F. Attia and M. Zayed, “Nanoparticles Decorated on Resin Particles and Their Flame Retardancy Behavior for Polymer Composites,” *J Nanomater*, vol. 2017, pp. 1–8, 2017, doi: 10.1155/2017/7381787.
- [6] K. Dybka-Stępień, H. Antolak, M. Kmiotek, D. Piechota, and A. Koziróg, “Disposable Food Packaging and Serving Materials—Trends and Biodegradability,” *Polymers (Basel)*, vol. 13, no. 20, p. 3606, Oct. 2021, doi: 10.3390/polym13203606.
- [7] M. Bar, R. Alagirusamy, and A. Das, “Flame retardant polymer composites,” *Fibers and Polymers*, vol. 16, no. 4, pp. 705–717, Apr. 2015, doi: 10.1007/s12221-015-0705-6.
- [8] K. Salmeia, J. Fage, S. Liang, and S. Gaan, “An Overview of Mode of Action and Analytical Methods for Evaluation of Gas Phase Activities of Flame Retardants,” *Polymers (Basel)*, vol. 7, no. 3, pp. 504–526, Mar. 2015, doi: 10.3390/polym7030504.
- [9] N. Amarnath, D. Appavoo, and B. Lochab, “Eco-Friendly Halogen-Free Flame Retardant Cardanol Polyphosphazene Polybenzoxazine Networks,” *ACS Sustain*

*Chem Eng*, vol. 6, no. 1, pp. 389–402, Jan. 2018, doi:  
10.1021/acssuschemeng.7b02657.

- [10] S. Gao, X. Zhao, and G. Liu, “Synthesis of an integrated intumescent flame retardant and its flame retardancy properties for polypropylene,” *Polym Degrad Stab*, vol. 138, pp. 106–114, Apr. 2017, doi:  
10.1016/j.polymdegradstab.2016.05.007.
- [11] C. Bao *et al.*, “Graphite oxide, graphene, and metal-loaded graphene for fire safety applications of polystyrene,” *J Mater Chem*, vol. 22, no. 32, p. 16399, 2012, doi:  
10.1039/c2jm32500d.
- [12] N. F. Attia, “Sustainable and efficient flame retardant materials for achieving high fire safety for polystyrene composites,” *J Therm Anal Calorim*, vol. 147, no. 10, pp. 5733–5742, May 2022, doi: 10.1007/s10973-021-10948-3.
- [13] H. Vahabi, F. Laoutid, M. Mehrpouya, M. R. Saeb, and P. Dubois, “Flame retardant polymer materials: An update and the future for 3D printing developments,” *Materials Science and Engineering: R: Reports*, vol. 144, p. 100604, Apr. 2021, doi: 10.1016/j.mser.2020.100604.
- [14] N. F. Attia, S. E. A. Elashery, A. M. Zakria, A. S. Eltaweil, and H. Oh, “Recent advances in graphene sheets as new generation of flame retardant materials,” *Materials Science and Engineering: B*, vol. 274, p. 115460, Dec. 2021, doi:  
10.1016/j.mseb.2021.115460.
- [15] S. Chang, T. Xie, and G. Yang, “Effects of interfacial modification on the thermal, mechanical, and fire properties of high-impact polystyrene/microencapsulated red phosphorous,” *J Appl Polym Sci*, vol. 110, no. 4, pp. 2139–2144, Nov. 2008, doi:  
10.1002/app.28814.
- [16] Y.-W. Yan, J.-Q. Huang, Y.-H. Guan, K. Shang, R.-K. Jian, and Y.-Z. Wang, “Flame retardance and thermal degradation mechanism of polystyrene modified with aluminum hypophosphite,” *Polym Degrad Stab*, vol. 99, pp. 35–42, Jan. 2014, doi: 10.1016/j.polymdegradstab.2013.12.014.
- [17] W. Lyu, Y. Cui, X. Zhang, J. Yuan, and W. Zhang, “Fire and thermal properties of PA 66 resin treated with poly-N-aniline-phenyl phosphamide as a flame retardant,” *Fire Mater*, vol. 41, no. 4, pp. 349–361, Jun. 2017, doi: 10.1002/fam.2385.
- [18] C. Feng, M. Liang, J. Jiang, J. Huang, and H. Liu, “Synergistic effect of a novel triazine charring agent and ammonium polyphosphate on the flame retardant properties of halogen-free flame retardant polypropylene composites,”

- Thermochim Acta*, vol. 627–629, pp. 83–90, Mar. 2016, doi: 10.1016/j.tca.2015.11.003.
- [19] Y.-F. Ai, L. Xia, F.-Q. Pang, Y.-L. Xu, H.-B. Zhao, and R.-K. Jian, “Mechanically strong and flame-retardant epoxy resins with anti-corrosion performance,” *Compos B Eng*, vol. 193, p. 108019, Jul. 2020, doi: 10.1016/j.compositesb.2020.108019.
  - [20] Z.-J. Cao, W. Liao, S.-X. Wang, H.-B. Zhao, and Y.-Z. Wang, “Polyurethane foams with functionalized graphene towards high fire-resistance, low smoke release, superior thermal insulation,” *Chemical Engineering Journal*, vol. 361, pp. 1245–1254, Apr. 2019, doi: 10.1016/j.cej.2018.12.176.
  - [21] W. Rao, J. Shi, C. Yu, H.-B. Zhao, and Y.-Z. Wang, “Highly efficient, transparent, and environment-friendly flame-retardant coating for cotton fabric,” *Chemical Engineering Journal*, vol. 424, p. 130556, Nov. 2021, doi: 10.1016/j.cej.2021.130556.
  - [22] C. Yu, T. Wu, F. Yang, W. Rao, H.-B. Zhao, and Z. Zhu, “Construction of hetero-structured nanohybrid relying on reactive phosphazene towards flame retardation and mechanical enhancement of epoxy resins,” *Eur Polym J*, vol. 167, p. 111075, Mar. 2022, doi: 10.1016/j.eurpolymj.2022.111075.
  - [23] A.-N. Zhang *et al.*, “Construction of durable eco-friendly biomass-based flame-retardant coating for cotton fabrics,” *Chemical Engineering Journal*, vol. 410, p. 128361, Apr. 2021, doi: 10.1016/j.cej.2020.128361.
  - [24] J.-S. Wang, D.-Y. Wang, Y. Liu, X.-G. Ge, and Y.-Z. Wang, “Polyamide-enhanced flame retardancy of ammonium polyphosphate on epoxy resin,” *J Appl Polym Sci*, vol. 108, no. 4, pp. 2644–2653, May 2008, doi: 10.1002/app.27522.
  - [25] M. Qin, X. Hu, and J. Guo, “Preparation of a New Type of Expansion Flame Retardant and Application in Polystyrene,” *Coatings*, vol. 13, no. 4, p. 733, Apr. 2023, doi: 10.3390/coatings13040733.
  - [26] B. Cao *et al.*, “The flammability of expandable polystyrene foams coated with melamine modified urea formaldehyde resin,” *J Appl Polym Sci*, vol. 134, no. 5, Feb. 2017, doi: 10.1002/app.44423.
  - [27] S. Yuan, W. Chen, and G. Liu, “Effects of two kinds of THEIC-based charring agents on flame-retardant properties of polylactide,” *J Appl Polym Sci*, vol. 132, no. 24, p. n/a-n/a, Jun. 2015, doi: 10.1002/app.42086.
  - [28] Y.-W. Yan, L. Chen, R.-K. Jian, S. Kong, and Y.-Z. Wang, “Intumescence: An effect way to flame retardance and smoke suppression for polystyrene,” *Polym*

- Degrad Stab*, vol. 97, no. 8, pp. 1423–1431, Aug. 2012, doi: 10.1016/j.polymdegradstab.2012.05.013.
- [29] Q. Tai, Y. Kan, L. Chen, W. Xing, Y. Hu, and L. Song, “Morphologies and thermal properties of flame-retardant polystyrene/ $\alpha$ -zirconium phosphate nanocomposites,” *React Funct Polym*, vol. 70, no. 6, pp. 340–345, Jun. 2010, doi: 10.1016/j.reactfunctpolym.2010.02.008.
- [30] J.-Y. Si *et al.*, “Functionalization of MXene Nanosheets for Polystyrene towards High Thermal Stability and Flame Retardant Properties,” *Polymers (Basel)*, vol. 11, no. 6, p. 976, Jun. 2019, doi: 10.3390/polym11060976.
- [31] M. W. Beach *et al.*, “Studies of degradation enhancement of polystyrene by flame retardant additives,” *Polym Degrad Stab*, vol. 93, no. 9, pp. 1664–1673, Sep. 2008, doi: 10.1016/j.polymdegradstab.2008.06.010.
- [32] H. Lu and C. A. Wilkie, “Synergistic effect of carbon nanotubes and decabromodiphenyl oxide/Sb<sub>2</sub>O<sub>3</sub> in improving the flame retardancy of polystyrene,” *Polym Degrad Stab*, vol. 95, no. 4, pp. 564–571, Apr. 2010, doi: 10.1016/j.polymdegradstab.2009.12.011.
- [33] F. Yang and G. L. Nelson, “Combination effect of nanoparticles with flame retardants on the flammability of nanocomposites,” *Polym Degrad Stab*, vol. 96, no. 3, pp. 270–276, Mar. 2011, doi: 10.1016/j.polymdegradstab.2010.06.003.
- [34] M. W. Beach *et al.*, “Studies of degradation enhancement of polystyrene by flame retardant additives,” *Polym Degrad Stab*, vol. 93, no. 9, pp. 1664–1673, Sep. 2008, doi: 10.1016/j.polymdegradstab.2008.06.010.
- [35] F. Yang and G. L. Nelson, “Combination effect of nanoparticles with flame retardants on the flammability of nanocomposites,” *Polym Degrad Stab*, vol. 96, no. 3, pp. 270–276, Mar. 2011, doi: 10.1016/j.polymdegradstab.2010.06.003.
- [36] Y. Xue *et al.*, “Effects of heterionic montmorillonites on flame resistances of polystyrene nanocomposites and the flame retardant mechanism,” *J Compos Mater*, vol. 52, no. 10, pp. 1295–1303, May 2018, doi: 10.1177/0021998317724861.
- [37] M. Sabet, H. Soleimani, E. Mohammadian, and S. Hosseini, “The Effect of Graphene Oxide on Flame Retardancy of Polypropylene and Polystyrene,” *Mater Perform Charact*, vol. 9, no. 1, p. 20190256, Jan. 2020, doi: 10.1520/MPC20190256.

- [38] N. H. Ramli Sulong, S. A. S. Mustapa, and M. K. Abdul Rashid, "Application of expanded polystyrene (EPS) in buildings and constructions: A review," *J Appl Polym Sci*, vol. 136, no. 20, May 2019, doi: 10.1002/app.47529.
- [39] Y. Wang *et al.*, "Study on the effect of PolyFR and its FR system on the flame retardancy and foaming behavior of polystyrene," *RSC Adv*, vol. 9, no. 1, pp. 192–205, 2019, doi: 10.1039/C8RA09680E.
- [40] W.-J. Hu, Y.-M. Li, Y.-Y. Pang, Y.-R. Li, and D.-Y. Wang, "The preparation of phosphorus and nitrogen-containing structure towards the enhancement of flame retardancy for thermoplastic polyurethane elastomer," *Colloids Surf A Physicochem Eng Asp*, vol. 656, p. 130375, Jan. 2023, doi: 10.1016/j.colsurfa.2022.130375.
- [41] H. Jiang *et al.*, "Construction of polyphosphazene-functionalized Ti3C2TX with high efficient flame retardancy for epoxy and its synergetic mechanisms," *Chemical Engineering Journal*, vol. 456, p. 141049, Jan. 2023, doi: 10.1016/j.cej.2022.141049.
- [42] L. Jianjun and O. Yuxiang, *Theory of Flame Retardation of Polymeric Materials*. De Gruyter, 2019. doi: 10.1515/9783110349351.
- [43] A. Dasari, Z. Z. Yu, G. P. Cai, and Y. W. Mai, "Recent developments in the fire retardancy of polymeric materials," *Prog Polym Sci*, vol. 38, no. 9, pp. 1357–1387, 2013, doi: 10.1016/j.progpolymsci.2013.06.006.
- [44] N. F. Attia and M. Zayed, "Nanoparticles Decorated on Resin Particles and Their Flame Retardancy Behavior for Polymer Composites," *J Nanomater*, vol. 2017, pp. 1–8, 2017, doi: 10.1155/2017/7381787.
- [45] Y. Shi, C. Liu, L. Fu, F. Yang, Y. Lv, and B. Yu, "Hierarchical assembly of polystyrene/graphitic carbon nitride/reduced graphene oxide nanocomposites toward high fire safety," *Compos B Eng*, vol. 179, p. 107541, Dec. 2019, doi: 10.1016/j.compositesb.2019.107541.
- [46] J. Shen, J. Liang, X. Lin, H. Lin, J. Yu, and S. Wang, "The flame-retardant mechanisms and preparation of polymer composites and their potential application in construction engineering," *Polymers (Basel)*, vol. 14, no. 1, 2022, doi: 10.3390/polym14010082.
- [47] W. Zhang, Y. Lei, X. Li, H. Shao, W. Xu, and D. Li, "A facile, environmentally and friendly flame-retardant: Synergistic flame retardant property of polyurethane rigid foam," *Mater Lett*, vol. 267, p. 127542, May 2020, doi: 10.1016/j.matlet.2020.127542.

- [48] I. S. Wichman, “Material flammability, combustion, toxicity and fire hazard in transportation,” *Prog Energy Combust Sci*, vol. 29, no. 3, pp. 247–299, Jan. 2003, doi: 10.1016/S0360-1285(03)00027-3.
- [49] N. Amarnath, D. Appavoo, and B. Lochab, “Eco-Friendly Halogen-Free Flame Retardant Cardanol Polyphosphazene Polybenzoxazine Networks,” *ACS Sustain Chem Eng*, vol. 6, no. 1, pp. 389–402, Jan. 2018, doi: 10.1021/acssuschemeng.7b02657.
- [50] T. Zhang *et al.*, “Improved cathode materials for microbial electrosynthesis,” *Energy Environ. Sci.*, vol. 6, no. 1, pp. 217–224, 2013, doi: 10.1039/C2EE23350A.
- [51] K. Dybka-Stępień, H. Antolak, M. Kmiotek, D. Piechota, and A. Koziróg, “Disposable Food Packaging and Serving Materials—Trends and Biodegradability,” *Polymers (Basel)*, vol. 13, no. 20, p. 3606, Oct. 2021, doi: 10.3390/polym13203606.
- [52] C. A. Wilkie, “Fire retardancy of polymers,” *Materials Today*, vol. 12, no. 4, p. 46, Apr. 2009, doi: 10.1016/S1369-7021(09)70137-3.
- [53] A. B. Morgan and J. W. Gilman, “An overview of flame retardancy of polymeric materials: application, technology, and future directions,” *Fire Mater*, vol. 37, no. 4, pp. 259–279, Jun. 2013, doi: 10.1002/fam.2128.
- [54] B. J. Holland and J. N. Hay, “The thermal degradation of poly(vinyl alcohol),” *Polymer (Guildf)*, vol. 42, no. 16, pp. 6775–6783, Jul. 2001, doi: 10.1016/S0032-3861(01)00166-5.
- [55] R. A. Ilyas *et al.*, “Polymer Composites Filled with Metal Derivatives: A Review of Flame Retardants,” *Polymers (Basel)*, vol. 13, no. 11, p. 1701, May 2021, doi: 10.3390/polym13111701.
- [56] J. P. da Costa, P. S. M. Santos, A. C. Duarte, and T. Rocha-Santos, “(Nano)plastics in the environment – Sources, fates and effects,” *Science of The Total Environment*, vol. 566–567, pp. 15–26, Oct. 2016, doi: 10.1016/j.scitotenv.2016.05.041.
- [57] A. Castrovinci and G. Camino, “Fire-Retardant Mechanisms in Polymer Nano-Composite Materials,” in *Multifunctional Barriers for Flexible Structure*, Berlin, Heidelberg: Springer Berlin Heidelberg, pp. 87–108. doi: 10.1007/978-3-540-71920-5\_5.
- [58] L. Ahmed, “Thermal, Mechanical and Flammability Studies of Flame-retardant Polymer Nanocomposites,” 2018.

- [59] G. Malucelli, F. Carosio, J. Alongi, A. Fina, A. Frache, and G. Camino, “Materials engineering for surface-confined flame retardancy,” *Materials Science and Engineering: R: Reports*, vol. 84, pp. 1–20, Oct. 2014, doi: 10.1016/j.mser.2014.08.001.
- [60] A. B. Morgan, “The Future of Flame Retardant Polymers – Unmet Needs and Likely New Approaches,” *Polymer Reviews*, vol. 59, no. 1, pp. 25–54, Jan. 2019, doi: 10.1080/15583724.2018.1454948.
- [61] S. Shahari, M. Fathullah, M. M. A. B. Abdullah, Z. Shayfull, M. Mia, and V. E. Budi Darmawan, “Recent developments in fire retardant glass fibre reinforced epoxy composite and geopolymer as a potential fire-retardant material: A review,” *Constr Build Mater*, vol. 277, p. 122246, Mar. 2021, doi: 10.1016/j.conbuildmat.2021.122246.
- [62] Y. Hou *et al.*, “A review on metal-organic hybrids as flame retardants for enhancing fire safety of polymer composites,” *Compos B Eng*, vol. 221, p. 109014, Sep. 2021, doi: 10.1016/j.compositesb.2021.109014.
- [63] X.-M. Li and R.-J. Yang, “Study on blooming of tetrabromobisphenol a bis(2,3-dibromopropyl ether) in blends with polypropylene,” *J Appl Polym Sci*, vol. 101, no. 1, pp. 20–24, Jul. 2006, doi: 10.1002/app.23089.
- [64] A. E. Simond, M. Houde, V. Lesage, R. Michaud, and J. Verreault, “Metabolomic profiles of the endangered St. Lawrence Estuary beluga population and associations with organohalogen contaminants,” *Science of The Total Environment*, vol. 717, p. 137204, May 2020, doi: 10.1016/j.scitotenv.2020.137204.
- [65] M. Sharkey, S. Harrad, M. Abou-Elwafa Abdallah, D. S. Drage, and H. Berresheim, “Phasing-out of legacy brominated flame retardants: The UNEP Stockholm Convention and other legislative action worldwide,” *Environ Int*, vol. 144, p. 106041, Nov. 2020, doi: 10.1016/j.envint.2020.106041.
- [66] C. M. Tai and R. K. Y. Li, “Mechanical properties of flame retardant filled polypropylene composites,” *J Appl Polym Sci*, vol. 80, no. 14, pp. 2718–2728, Jun. 2001, doi: 10.1002/app.1386.
- [67] A. M. Montalbano *et al.*, “Cytotoxic and genotoxic effects of the flame retardants (PBDE-47, PBDE-99 and PBDE-209) in human bronchial epithelial cells,” *Chemosphere*, vol. 245, p. 125600, Apr. 2020, doi: 10.1016/j.chemosphere.2019.125600.

- [68] S. Sinha Ray and M. Kuruma, *Halogen-Free Flame-Retardant Polymers*, vol. 294, in Springer Series in Materials Science, vol. 294. Cham: Springer International Publishing, 2020. doi: 10.1007/978-3-030-35491-6.
- [69] A. M. Vuong, K. Yolton, K. M. Cecil, J. M. Braun, B. P. Lanphear, and A. Chen, “Flame Retardants and Neurodevelopment: an Updated Review of Epidemiological Literature,” *Curr Epidemiol Rep*, vol. 7, no. 4, pp. 220–236, Dec. 2020, doi: 10.1007/s40471-020-00256-z.
- [70] G. Martinez, J. Niu, L. Takser, J.-P. Bellenger, and J. Zhu, “A review on the analytical procedures of halogenated flame retardants by gas chromatography coupled with single quadrupole mass spectrometry and their levels in human samples,” *Environmental Pollution*, vol. 285, p. 117476, Sep. 2021, doi: 10.1016/j.envpol.2021.117476.
- [71] M. Giulivo *et al.*, “Occurrence of halogenated and organophosphate flame retardants in sediment and fish samples from three European river basins,” *Science of The Total Environment*, vol. 586, pp. 782–791, May 2017, doi: 10.1016/j.scitotenv.2017.02.056.
- [72] G. Martinez, J. Niu, L. Takser, J.-P. Bellenger, and J. Zhu, “A review on the analytical procedures of halogenated flame retardants by gas chromatography coupled with single quadrupole mass spectrometry and their levels in human samples,” *Environmental Pollution*, vol. 285, p. 117476, Sep. 2021, doi: 10.1016/j.envpol.2021.117476.
- [73] C. Bevington *et al.*, “Development of a Flame Retardant and an Organohalogen Flame Retardant Chemical Inventory,” *Sci Data*, vol. 9, no. 1, p. 295, Jun. 2022, doi: 10.1038/s41597-022-01351-0.
- [74] A. Beaugendre *et al.*, “Flame retardant and weathering resistant self-layering epoxy-silicone coatings for plastics,” *Prog Org Coat*, vol. 136, p. 105269, Nov. 2019, doi: 10.1016/j.porgcoat.2019.105269.
- [75] M. D. Albaqami, S. F. Shaikh, and A. Nafady, “Utilization of hybrid silicone rubber/Exolit AP 422 composite for the fabrication of mechanically flexible, flame-retardant and superhydrophobic polyurethane foams,” *Mater Chem Phys*, vol. 273, p. 125133, Nov. 2021, doi: 10.1016/j.matchemphys.2021.125133.
- [76] H. Liu, S. Wang, J. Sun, and X. Gu, “biopolymers Improving flame retardant and mechanical properties of ethylene – vinyl acetate by cured compound silicone decorated magnesium hydroxide,” *J Mater Sci*, vol. 57, no. 3, pp. 2243–2256, 2022, doi: 10.1007/s10853-021-06751-y.

- [77] W. Zhong, Y. Cui, R. Li, R. Yang, Y. Li, and L. Zhu, "Distribution and sources of ordinary monomeric and emerging oligomeric organophosphorus flame retardants in Haihe Basin, China," *Science of The Total Environment*, vol. 785, p. 147274, Sep. 2021, doi: 10.1016/j.scitotenv.2021.147274.
- [78] W. Zhao, H. B. Zhao, J. B. Cheng, W. Li, J. Zhang, and Y. Z. Wang, "A green, durable and effective flame-retardant coating for expandable polystyrene foams," *Chemical Engineering Journal*, vol. 440, no. November 2021, p. 135807, 2022, doi: 10.1016/j.cej.2022.135807.
- [79] Z. Fang, Z. Guo, H. Ma, Q. Chen, and Y. Wu, "Study of a halogen-free flame-retarded Polypropylene composition with balanced strength and toughness," *International Journal of Materials and Product Technology*, vol. 37, no. 3/4, p. 350, 2010, doi: 10.1504/IJMPT.2010.031434.
- [80] J. Yan, P. Xu, P. Zhang, and H. Fan, "Surface-modified ammonium polyphosphate for flame-retardant and reinforced polyurethane composites," *Colloids Surf A Physicochem Eng Asp*, vol. 626, p. 127092, Oct. 2021, doi: 10.1016/j.colsurfa.2021.127092.
- [81] Y. Liu, Y. Gao, Z. Zhang, and Q. Wang, "Preparation of ammonium polyphosphate and dye co-intercalated LDH/polypropylene composites with enhanced flame retardant and UV resistance properties," *Chemosphere*, vol. 277, p. 130370, Aug. 2021, doi: 10.1016/j.chemosphere.2021.130370.
- [82] M. C. Mata, V. Castro, J. B. Quintana, R. Rodil, R. Beiras, and L. Vidal-Liñán, "Bioaccumulation of organophosphorus flame retardants in the marine mussel *Mytilus galloprovincialis*," *Science of The Total Environment*, vol. 805, p. 150384, Jan. 2022, doi: 10.1016/j.scitotenv.2021.150384.
- [83] X. Zhao *et al.*, "Biomimetic construction peanut-leaf structure on ammonium polyphosphate surface: Improving its compatibility with poly(lactic acid) and flame-retardant efficiency simultaneously," *Chemical Engineering Journal*, vol. 412, p. 128737, May 2021, doi: 10.1016/j.cej.2021.128737.
- [84] M. Cui *et al.*, "Intumescent flame retardant behavior of triazine group and ammonium polyphosphate in waterborne polyurethane," *Polym Degrad Stab*, vol. 183, p. 109439, Jan. 2021, doi: 10.1016/j.polymdegradstab.2020.109439.
- [85] H. Li, W. Zeng, J. Shi, N. Wen, Z. Yang, and Z. Lei, "Effects of novel functionalized magnesium phosphate monomers on the flame retardancy and mechanical properties of polyethylene terephthalate copolymers," *Chemosphere*, vol. 288, p. 132648, Feb. 2022, doi: 10.1016/j.chemosphere.2021.132648.

- [86] Y. Liu, J. Li, and Q. Wang, "Preparation of High Loading Magnesium Hydroxide Flame Retardant Polypropylene by Solid State Shear Milling," *J Compos Mater*, vol. 41, no. 16, pp. 1995–2003, Aug. 2007, doi: 10.1177/0021998307074098.
- [87] B. B. Marosfoi, S. Garas, B. Bodzay, F. Zubonyai, and G. Marosi, "Flame retardancy study on magnesium hydroxide associated with clays of different morphology in polypropylene matrix," *Polym Adv Technol*, vol. 19, no. 6, pp. 693–700, Jun. 2008, doi: 10.1002/pat.1153.
- [88] X. Chen, J. Yu, S. Lu, H. Wu, S. Guo, and Z. Luo, "Combustion Characteristics of Polypropylene/Magnesium Hydroxide/Expandable Graphite Composites," *Journal of Macromolecular Science, Part B*, vol. 48, no. 6, pp. 1081–1092, Oct. 2009, doi: 10.1080/00222340903039396.
- [89] Q. Zhao-Lu, L. Ding-Hua, and Y. Rong-Jie, "Preparation of Ammonium Polyphosphate Coated with Aluminium Hydroxide and Its Application in Polypropylene as Flame Retardant," *Journal of Inorganic Materials*, vol. 30, no. 12, p. 1267, 2015, doi: 10.15541/jim20150243.
- [90] C. Wan, S. Liu, Y. Chen, and F. Zhang, "Facile, one-pot, formaldehyde-free synthesis of reactive N P flame retardant for a biomolecule of cotton," *Int J Biol Macromol*, vol. 163, pp. 1659–1668, Nov. 2020, doi: 10.1016/j.ijbiomac.2020.09.174.
- [91] J. Reuter, L. Greiner, P. Kukla, and M. Döring, "Efficient flame retardant interplay of unsaturated polyester resin formulations based on ammonium polyphosphate," *Polym Degrad Stab*, vol. 178, p. 109134, Aug. 2020, doi: 10.1016/j.polymdegradstab.2020.109134.
- [92] H. Nabipour, X. Wang, M. Z. Rahman, L. Song, and Y. Hu, "An environmentally friendly approach to fabricating flame retardant, antibacterial and antifungal cotton fabrics via self-assembly of guanazole-metal complex," *J Clean Prod*, vol. 273, p. 122832, Nov. 2020, doi: 10.1016/j.jclepro.2020.122832.
- [93] K. Wu, X. Wang, Y. Xu, and W. Guo, "Flame retardant efficiency of modified para-aramid fiber synergizing with ammonium polyphosphate on PP/EPDM," *Polym Degrad Stab*, vol. 172, p. 109065, Feb. 2020, doi: 10.1016/j.polymdegradstab.2019.109065.
- [94] Z. Zhang *et al.*, "Hydrothermal synthesis of  $4\text{ZnO} \cdot \text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$ /RGO hybrid material and its flame retardant behavior in flexible PVC and magnesium hydroxide composites," *Appl Surf Sci*, vol. 425, pp. 896–904, Dec. 2017, doi: 10.1016/j.apsusc.2017.07.101.

- [95] Y.-J. Geng and Z.-H. Liu, "Preparation and thermodynamic characterization of  $2\text{CaO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$  nanomaterials with enhanced flame retardant properties," *Colloids Surf A Physicochem Eng Asp*, vol. 522, pp. 563–568, Jun. 2017, doi: 10.1016/j.colsurfa.2017.03.044.
- [96] Á. Camargo and C. M. Ibañez, "Initial study of micronized zinc borate as flame retardant in *Eucalyptus grandis* from Uruguay," *MRS Adv*, vol. 3, no. 61, pp. 3551–3556, Dec. 2018, doi: 10.1557/adv.2018.585.
- [97] H. Durrani, V. Sharma, D. Bamoria, A. Shukla, S. Basak, and W. Ali, "Exploration of flame retardant efficacy of cellulosic fabric using in-situ synthesized zinc borate particles," *Cellulose*, vol. 27, no. 15, pp. 9061–9073, Oct. 2020, doi: 10.1007/s10570-020-03383-4.
- [98] M. Yurddaskal and E. Celik, "Effect of halogen-free nanoparticles on the mechanical, structural, thermal and flame retardant properties of polymer matrix composite," *Compos Struct*, vol. 183, pp. 381–388, Jan. 2018, doi: 10.1016/j.compstruct.2017.03.093.
- [99] X. Yue, C. Li, Y. Ni, Y. Xu, and J. Wang, "Flame retardant nanocomposites based on 2D layered nanomaterials: a review," *J Mater Sci*, vol. 54, no. 20, pp. 13070–13105, Oct. 2019, doi: 10.1007/s10853-019-03841-w.
- [100] R. A. McIntyre, "Common Nano-Materials and Their Use in Real World Applications," *Sci Prog*, vol. 95, no. 1, pp. 1–22, Mar. 2012, doi: 10.3184/003685012X13294715456431.
- [101] S. Lu, W. Hong, and X. Chen, "Nanoreinforcements of Two-Dimensional Nanomaterials for Flame Retardant Polymeric Composites: An Overview," *Advances in Polymer Technology*, vol. 2019, pp. 1–25, Dec. 2019, doi: 10.1155/2019/4273253.
- [102] X. Dong, J. Yang, X. Hua, S. Nie, and F. Kong, "Synthesis of a novel char-forming agent (PEIC): Improvement in flame retardancy, thermal stability, and smoke suppression for intumescent flame-retardant polypropylene composites," *J Appl Polym Sci*, vol. 137, no. 3, p. 48296, Jan. 2020, doi: 10.1002/app.48296.
- [103] D. A. Villamil Watson and D. A. Schiraldi, "Biomolecules as Flame Retardant Additives for Polymers: A Review," *Polymers (Basel)*, vol. 12, no. 4, p. 849, Apr. 2020, doi: 10.3390/polym12040849.
- [104] B. Tawiah *et al.*, "Highly efficient flame retardant and smoke suppression mechanism of boron modified graphene Oxide/Poly(Lactic acid) nanocomposites," *Carbon N Y*, vol. 150, pp. 8–20, Sep. 2019, doi: 10.1016/j.carbon.2019.05.002.

- [105] G. Cavallaro, S. Micciulla, L. Chiappisi, and G. Lazzara, “Chitosan-based smart hybrid materials: a physico-chemical perspective,” *J Mater Chem B*, vol. 9, no. 3, pp. 594–611, 2021, doi: 10.1039/D0TB01865A.
- [106] Z. Wang, Y. Liu, and J. Li, “Regulating Effects of Nitrogenous Bases on the Char Structure and Flame Retardancy of Polypropylene/Intumescent Flame Retardant Composites,” *ACS Sustain Chem Eng*, vol. 5, no. 3, pp. 2375–2383, Mar. 2017, doi: 10.1021/acssuschemeng.6b02712.
- [107] C. Jiao and X. Chen, “Flammability and thermal degradation of intumescent flame-retardant polypropylene composites,” *Polym Eng Sci*, vol. 50, no. 4, pp. 767–772, Apr. 2010, doi: 10.1002/pen.21583.
- [108] J.-C. Liu, M.-J. Xu, T. Lai, and B. Li, “Effect of Surface-Modified Ammonium Polyphosphate with KH550 and Silicon Resin on the Flame Retardancy, Water Resistance, Mechanical and Thermal Properties of Intumescent Flame Retardant Polypropylene,” *Ind Eng Chem Res*, vol. 54, no. 40, pp. 9733–9741, Oct. 2015, doi: 10.1021/acs.iecr.5b01670.
- [109] Q. Chen *et al.*, “Synthesis of a novel triazine-based intumescent flame retardant and its effects on the fire performance of expanded polystyrene foams,” *Polym Degrad Stab*, vol. 203, p. 110079, Sep. 2022, doi: 10.1016/j.polymdegradstab.2022.110079.
- [110] W.-J. Yuan, W. Zhao, G. Wu, and H.-B. Zhao, “A Phosphorus-Nitrogen-Carbon Synergistic Nanolayered Flame Retardant for Polystyrene,” *Polymers (Basel)*, vol. 14, no. 10, p. 2055, May 2022, doi: 10.3390/polym14102055.
- [111] W. Li, L. Qi, D. Ye, W. Cai, and W. Xing, “Facile modification of aluminum hypophosphate and its flame retardancy for polystyrene,” *Chin J Chem Eng*, Feb. 2023, doi: 10.1016/j.cjche.2023.02.001.
- [112] M. Daud, F. Shehzad, and M. A. Al-Harhi, “Metallocene-Catalyzed Copolymerization of Ethylene and 1-Hexene in the Presence of Graphene/MgAl LDH Nanofiller: Effect on the Activity, SCB, and Thermal Stability,” *Arab J Sci Eng*, vol. 43, no. 11, pp. 6021–6032, Nov. 2018, doi: 10.1007/s13369-018-3239-6.
- [113] S. Ahmad, M. B. Wazir, M. Daud, C. Kui Cheng, M. Ul Hassan Shah, and M. A. Al-Harhi, “Recent advancement in ionic liquid modified layered double hydroxide (IL-LDH): Progress, challenges, and future prospects,” *Inorg Chem Commun*, vol. 158, p. 111591, Dec. 2023, doi: 10.1016/j.inoche.2023.111591.
- [114] E. P. Barrett, L. G. Joyner, and P. P. Halenda, “The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen

- Isotherms,” *J Am Chem Soc*, vol. 73, no. 1, pp. 373–380, Jan. 1951, doi: 10.1021/ja01145a126.
- [115] W.-J. Yuan, W. Zhao, G. Wu, and H.-B. Zhao, “A Phosphorus-Nitrogen-Carbon Synergistic Nanolayered Flame Retardant for Polystyrene,” *Polymers (Basel)*, vol. 14, no. 10, p. 2055, May 2022, doi: 10.3390/polym14102055.
- [116] N. F. Attia, J. Park, and H. Oh, “Facile tool for green synthesis of graphene sheets and their smart free-standing UV protective film,” *Appl Surf Sci*, vol. 458, pp. 425–430, Nov. 2018, doi: 10.1016/j.apsusc.2018.07.066.
- [117] E. Lester, N. Hilal, and J. Henderson, “Porosity in ancient glass from Syria(c. 800AD) using gas adsorption and atomic force microscopy,” *Surface and Interface Analysis*, vol. 36, no. 9, pp. 1323–1329, Sep. 2004, doi: 10.1002/sia.1911.
- [118] A. Dahiru Shuaibu, A. Saeed Alzahrani, and Md. A. Aziz, “High-performance Supercapacitors Enabled by Highly-porous Date Stone-derived Activated Carbon and Organic Redox Gel Electrolyte,” *Asian J Org Chem*, Mar. 2023, doi: 10.1002/ajoc.202300050.
- [119] K. Sánchez-Zambrano *et al.*, “CO<sub>2</sub> Capture with Mesoporous Silicas Modified with Amines by Double Functionalization: Assessment of Adsorption/Desorption Cycles,” *Materials*, vol. 11, no. 6, p. 887, May 2018, doi: 10.3390/ma11060887.
- [120] C. Lin *et al.*, “High Leach-Resistant Fire-Retardant Modified Pine Wood ( *Pinus sylvestris* L. ) by In Situ Phosphorylation and Carbamylation,” *ACS Omega*, vol. 8, no. 12, pp. 11381–11396, Mar. 2023, doi: 10.1021/acsomega.3c00146.
- [121] H. Lu, D. Yi, H. Feng, B. Hou, and J. Hao, “Influence of the Crystal Structure of Melamine Trimetaphosphate 2D Supramolecules on the Properties of Polyamide 6,” *ACS Appl Mater Interfaces*, vol. 15, no. 9, pp. 12393–12402, Mar. 2023, doi: 10.1021/acsami.2c22760.
- [122] Y. Ren, D. Yuan, W. Li, and X. Cai, “Flame retardant efficiency of KH-550 modified urea-formaldehyde resin cooperating with ammonium polyphosphate on polypropylene,” *Polym Degrad Stab*, vol. 151, pp. 160–171, May 2018, doi: 10.1016/j.polymdegradstab.2018.03.014.
- [123] L. Liu, Z. Huang, Y. Pan, X. Wang, L. Song, and Y. Hu, “Finishing of cotton fabrics by multi-layered coatings to improve their flame retardancy and water repellency,” *Cellulose*, vol. 25, no. 8, pp. 4791–4803, Aug. 2018, doi: 10.1007/s10570-018-1866-4.

- [124] S. U. Rehman *et al.*, “Polystyrene-Sepiolite Clay Nanocomposites with Enhanced Mechanical and Thermal Properties,” *Polymers (Basel)*, vol. 14, no. 17, p. 3576, Aug. 2022, doi: 10.3390/polym14173576.
- [125] L. He, F. Xia, Y. Wang, J. Yuan, D. Chen, and J. Zheng, “Mechanical and Dynamic Mechanical Properties of the Amino Silicone Oil Emulsion Modified Ramie Fiber Reinforced Composites,” *Polymers (Basel)*, vol. 13, no. 23, p. 4083, Nov. 2021, doi: 10.3390/polym13234083.
- [126] M. Mittal and R. Chaudhary, “Effect of fiber content on thermal behavior and viscoelastic properties of PALF/Epoxy and COIR/Epoxy composites,” *Mater Res Express*, vol. 5, no. 12, p. 125305, Sep. 2018, doi: 10.1088/2053-1591/aae274.
- [127] W. Wei *et al.*, “Improving the Damping Properties of Nanocomposites by Monodispersed Hybrid POSS Nanoparticles: Preparation and Mechanisms,” *Polymers (Basel)*, vol. 11, no. 4, p. 647, Apr. 2019, doi: 10.3390/polym11040647.
- [128] G.-L. Zhu, D. Han, Y. Yuan, F. Chen, and Q. Fu, “Improving Damping Properties and Thermal Stability of Epoxy/Polyurethane Grafted Copolymer by Adding Glycidyl POSS,” *Chinese Journal of Polymer Science*, vol. 36, no. 11, pp. 1297–1302, Nov. 2018, doi: 10.1007/s10118-018-2145-4.
- [129] C. I. Idumah, “Recently emerging advancements in thermal conductivity and flame retardancy of MXene polymeric nanoarchitectures,” *Polymer-Plastics Technology and Materials*, vol. 62, no. 4, pp. 510–546, Mar. 2023, doi: 10.1080/25740881.2022.2121220.
- [130] X. Han, S. Ding, L. Zhu, and S. Wang, “Preparation and characterization of flame-retardant and thermal insulating bio-based composite aerogels,” *Energy Build*, vol. 278, p. 112656, Jan. 2023, doi: 10.1016/j.enbuild.2022.112656.
- [131] S. M. Gidado and İ. Akanyeti, “Comparison of Remazol Brilliant Blue Reactive Adsorption on Pristine and Calcined ZnAl, MgAl, ZnMgAl Layered Double Hydroxides,” *Water Air Soil Pollut*, vol. 231, no. 4, p. 146, Apr. 2020, doi: 10.1007/s11270-020-04522-0.
- [132] Z.-M. Ni, S.-J. Xia, L.-G. Wang, F.-F. Xing, and G.-X. Pan, “Treatment of methyl orange by calcined layered double hydroxides in aqueous solution: Adsorption property and kinetic studies,” *J Colloid Interface Sci*, vol. 316, no. 2, pp. 284–291, Dec. 2007, doi: 10.1016/j.jcis.2007.07.045.
- [133] T. S. Kazeem, M. Zubair, M. Daud, and M. A. Al-Harhi, “Enhanced Removal of Eriochrome Black T Using Graphene/NiMgAl-Layered Hydroxides: Isotherm,

- Kinetic, and Thermodynamic Studies,” *Arab J Sci Eng*, vol. 45, no. 9, pp. 7175–7189, Sep. 2020, doi: 10.1007/s13369-019-04327-2.
- [134] T. S. Kazeem, M. Zubair, M. Daud, N. D. Mu’azu, and M. A. Al-Harthi, “Graphene/ternary layered double hydroxide composites: Efficient removal of anionic dye from aqueous phase,” *Korean Journal of Chemical Engineering*, vol. 36, no. 7, pp. 1057–1068, Jul. 2019, doi: 10.1007/s11814-019-0284-0.
- [135] M. Sajid, C. Basheer, M. Daud, and A. Alsharaa, “Evaluation of layered double hydroxide/graphene hybrid as a sorbent in membrane-protected stir-bar supported micro-solid-phase extraction for determination of organochlorine pesticides in urine samples,” *J Chromatogr A*, vol. 1489, pp. 1–8, Mar. 2017, doi: 10.1016/j.chroma.2017.01.089.
- [136] K. Xu, G. Chen, and J. Shen, “Exfoliation and dispersion of micrometer-sized LDH particles in poly(ethylene terephthalate) and their nanocomposite thermal stability,” *Appl Clay Sci*, vol. 75–76, pp. 114–119, May 2013, doi: 10.1016/j.clay.2013.02.004.
- [137] H. Muire, J. H. Zietsman, and F. J. W. J. Labuschagné, “Thermochemical models and data of layered double hydroxides, a review,” *Chemical Thermodynamics and Thermal Analysis*, vol. 12, p. 100120, Dec. 2023, doi: 10.1016/j.ctta.2023.100120.
- [138] W. Wang *et al.*, “Fabrication of LDH nanosheets on  $\beta$ -FeOOH rods and applications for improving the fire safety of epoxy resin,” *Compos Part A Appl Sci Manuf*, vol. 80, pp. 259–269, Jan. 2016, doi: 10.1016/j.compositesa.2015.10.031.
- [139] B. Tawiah, Y. Zhou, R. K. K. Yuen, J. Sun, and B. Fei, “Microporous boron based intumescent macrocycle flame retardant for poly(lactic acid) with excellent UV protection,” *Chemical Engineering Journal*, vol. 402, p. 126209, Dec. 2020, doi: 10.1016/j.cej.2020.126209.
- [140] S. Naseem, S. Wießner, I. Kühnert, and A. Leuteritz, “Layered Double Hydroxide (MgFeAl-LDH)-Based Polypropylene (PP) Nanocomposite: Mechanical Properties and Thermal Degradation,” *Polymers (Basel)*, vol. 13, no. 19, p. 3452, Oct. 2021, doi: 10.3390/polym13193452.
- [141] W.-X. Li, H.-J. Zhang, X.-P. Hu, W.-X. Yang, Z. Cheng, and C.-Q. Xie, “Highly efficient replacement of traditional intumescent flame retardants in polypropylene by manganese ions doped melamine phytate nanosheets,” *J Hazard Mater*, vol. 398, p. 123001, Nov. 2020, doi: 10.1016/j.jhazmat.2020.123001.
- [142] C. Deferm, A. Van den Bossche, J. Luyten, H. Oosterhof, J. Fransaer, and K. Binnemans, “Thermal stability of trihexyl(tetradecyl)phosphonium chloride,”

*Physical Chemistry Chemical Physics*, vol. 20, no. 4, pp. 2444–2456, 2018, doi: 10.1039/C7CP08556G.

- [143] S. Khanal, W. Zhang, S. Ahmed, M. Ali, and S. Xu, “Effects of intumescent flame retardant system consisting of tris (2-hydroxyethyl) isocyanurate and ammonium polyphosphate on the flame retardant properties of high-density polyethylene composites,” *Compos Part A Appl Sci Manuf*, vol. 112, pp. 444–451, Sep. 2018, doi: 10.1016/J.COMPOSITESA.2018.06.030.
- [144] Q. P. Feng, X. J. Shen, J. P. Yang, S. Y. Fu, Y. W. Mai, and K. Friedrich, “Synthesis of epoxy composites with high carbon nanotube loading and effects of tubular and wavy morphology on composite strength and modulus,” *Polymer (Guildf)*, vol. 52, no. 26, pp. 6037–6045, Dec. 2011, doi: 10.1016/j.polymer.2011.10.049.
- [145] Y. Han *et al.*, “Preparation and flame retardancy of polystyrene nanocomposites based on layered double hydroxides,” *Polym Compos*, vol. 38, no. 8, pp. 1680–1688, Aug. 2017, doi: 10.1002/pc.23737.
- [146] L.-C. Tang *et al.*, “Creep and recovery of polystyrene composites filled with graphene additives,” *Compos Sci Technol*, vol. 91, pp. 63–70, Jan. 2014, doi: 10.1016/j.compscitech.2013.11.028.
- [147] L.-C. Tang *et al.*, “The effect of graphene dispersion on the mechanical properties of graphene/epoxy composites,” *Carbon N Y*, vol. 60, pp. 16–27, Aug. 2013, doi: 10.1016/j.carbon.2013.03.050.
- [148] T. F. Alhamada, M. A. Azmah Hanim, D. W. Jung, R. Saidur, A. Nuraini, and W. Z. W. Hasan, “MXene Based Nanocomposites for Recent Solar Energy Technologies,” *Nanomaterials*, vol. 12, no. 20, p. 3666, Oct. 2022, doi: 10.3390/nano12203666.
- [149] F. Rafiee *et al.*, “Thermal and dynamic mechanical properties of PP/EVA nanocomposites containing organo-modified layered double hydroxides,” *Compos B Eng*, vol. 103, pp. 122–130, Oct. 2016, doi: 10.1016/j.compositesb.2016.08.013.
- [150] M. Roohani, M. Shabanian, B. Kord, M. Hajibeygi, and H. A. Khonakdar, “New functional Fe<sub>3</sub>O<sub>4</sub> nanoparticles utilizing as adjuvant in the green PVA/cellulose whiskers nanocomposite,” *Thermochim Acta*, vol. 635, pp. 17–25, Jul. 2016, doi: 10.1016/j.tca.2016.04.020.
- [151] C. Bao, Y. Guo, L. Song, and Y. Hu, “Poly(vinyl alcohol) nanocomposites based on graphene and graphite oxide: a comparative investigation of property and

- mechanism,” *J Mater Chem*, vol. 21, no. 36, p. 13942, 2011, doi: 10.1039/c1jm11662b.
- [152] A. Raeisi, M. Shabanian, and K. Faghihi, “Preparation of  $\beta$ -cyclodextrin-ester network and new organo-modified LDH as dual additives of PVA: Thermal, dynamic-mechanical and migration study,” *Prog Org Coat*, vol. 111, pp. 402–415, Oct. 2017, doi: 10.1016/j.porgcoat.2017.06.022.
- [153] T. Xue, W. Fan, X. Zhang, X. Zhao, F. Yang, and T. Liu, “Layered double hydroxide/graphene oxide synergistically enhanced polyimide aerogels for thermal insulation and fire-retardancy,” *Compos B Eng*, vol. 219, p. 108963, Aug. 2021, doi: 10.1016/j.compositesb.2021.108963.
- [154] Z. Yu *et al.*, “Fire-Retardant and Thermally Insulating Phenolic-Silica Aerogels,” *Angewandte Chemie International Edition*, vol. 57, no. 17, pp. 4538–4542, Apr. 2018, doi: 10.1002/anie.201711717.

## Vitae

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Academic Background : I am a graduate engineer with a first-class honour in  
chemical Engineering with a strong background in both research and industrial  
experience. With interest in problem solving in a team, skillful in modelling and  
simulation of engineering processes. With research experience in wastewater  
treatment, Bioprocess and synthesis and characterization of nanomaterials in  
application to flame retardants for polymeric materials. |

| INSTITUTION                                         | DATES       | QUALIFICATION               |
|-----------------------------------------------------|-------------|-----------------------------|
| King Fahd University of Petroleum and Minerals, KSA | 2021-23     | MSc Chemical Engineering    |
| Bayero University, Kano, Nigeria                    | 2015 – 2021 | B.Eng. Chemical Engineering |
| Government Secondary School Stadium                 | 2008 - 2014 | SSCE Certificate            |
| Gobirawa Project Primary School                     | 2003 - 2008 | Primary certificate         |

## **PROFESSIONAL MEMBERSHIPS & CERTIFICATIONS**

- Nigerian Society of Engineers (NSE) student member
- Nigerian society of chemical engineers (NSChE)
- International Association of Engineers (IAENG membership)
- Diploma in Computer maintenance and Repairs
- Nigerian Universities Engineering Students' Association
- Nigerian Society of Chemical Engineers (Student Chapter)

## **RESEARCH EXPERIENCE**

**Research Assistant:** Department of chemical engineering and Center for Refining and Advance Chemicals, King Fahd University of Petroleum & Minerals 2022-present

**Advisor:** Prof. Mamdouh Al-Harhi

I developed a flame resistance polystyrene in building applications.

- Synthesized nanolayered layered double hydroxide (ZnMgAl-LDH), and functionalized graphene with (MgAl-LDH) and ionic liquid.
- Synthesized nanolayered layered double hydroxide (ZnAl-LDH), and functionalized graphene with (ZnAl-LDH) and ionic liquid.
- Synthesized nanolayered intumescent flame retardants
- Characterized the materials using BET, XRD, SEM, TEM, FT-IR, TGA, DMA, LOI, DSC, Raman scattering, and TA
- Used the materials to for development flame resistance polystyrene.

**Undergraduate research:** Department of chemical and petroleum engineering, Bayero university, Kano. 2020-2021

**Supervisor:** Dr. Adamu A Rasheed

- Research Project: Removal of zinc and copper from wastewater using banana peel.
- Design Project: Design of 60000tons/year of formaldehyde production plant.
- Bioreactor design: Design of bioreactor that convert cow dug and slaughter house waste into natural gas.

## **SKILLS**

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**Chemical Engineering Design:** I have mastery in Detailed design process design and simulation

**Relevant Modules:** Chemical reaction engineering, modelling and process simulation, Sustainable Energy Conversion Processes, Advanced Thermodynamics, Advanced Transport Phenomena, Computational Numerical Methods, Design of Experiments, risk assessment, and loss prevention.

**Computer skills:** Aspen plus, Aspen HYSYS, MATLAB, Visio, Microsoft suite, COMSOL, Origin, Mendeley, Zotero, and FOTRAN.

## **Publications**

**Isah. M.,** Mamdouh A. Al-harhi, and Farrukh Shehzad (2023). A novel nitrogen-phosphorus-graphene based synergistic nanosheet as an intumescent Flame Retardant for Polystyrene. (under review)

**Isah. M.,** Daud M., Mamdouh A. Al-harhi and Farrukh Shehzad (2023). Phosphonium based ionic liquid anchored with graphene functionalized ZnAl-LDH as nano-filler flame retardant for polystyrene. (under review)

**Mutawakkil Isah,** Wasif Farooq, Abdul Ahad Khan, and Abdul Gani Abdul Jameel (2023). Biological CO<sub>2</sub> Utilization; Current Status, Challenges, and Future Direction for Photosynthetic and Non-photosynthetic Route. (Submitted)

**Mutawakkil Isah,** Farrukh Shehzad, Mamdouh a. Al-Harhi (2023). Thermal stability and degradation kinetics of polystyrene-layered double hydroxide composites study for thermal insulation of buildings applications. RSC Chemical Nanoscience & Nanotechnology Group Annual Symposium: Nanotechnology for Energy, Environment and Biomedicine.

#### **Patent**

A novel nitrogen-phosphorus-graphene based synergistic nanosheet as an intumescence Flame Retardant for Polystyrene (filed)