Flame Retardancy- a Comprehensive Review of Mechanism, Material, and Fire Testing

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Abstract— **The goal of this review is to make the field better and easily approachable of “flame-retardants for polymeric material.” As a different element/compound that emerges with the polymeric materials and influences the properties of that material. It is a revolutionary development in material science and technology. These additives are affecting the mechanical, and thermal properties and flame-retardant performance. Flame retardant materials and their mechanism along with the fire testing methods are reviewed. First, the mechanism of flame-retardant material involves combustion and formation of deferent layers. Then, Flame-retardant materials like metal, halogenated compounds, and phosphorus-based materials with their fire testing processes. The most widely used additives like Metal hydroxides, and metal carbonates also the behavior and performance of the fire are described in this review. As a result, high-performance flame-retardant polymer composites may be extendable and implemented in the production of polymeric materials.**

Keywords—Flame-mechanism, ammonium polyphosphate (APP), alumina trihydrate (ATH), limiting oxygen index (LOI%)

I. INTRODUCTION

Today's world is reliant on synthetic polymers, which are present almost everywhere. Natural polymers like wood, cotton, and natural rubber, as well as more conventional materials like metals and ceramics, are being swiftly replaced by synthetic polymer materials nowadays. In daily life, the use of artificial polymeric materials delivers many benefits to the community. But still, these materials have a unique set of qualities, including low weight, ease of production, and relatively high flammability [1]. In terms of polymers' fire resistance and response to fire, safety regulations are currently becoming more and more important for many industries. Instead of that, we can use an inorganic material, halogenated and phosphorus-based flame-retardant compounds [2]. These compounds have an impact on ‘the condensed-phase combustion process. Mostly, the polymer's chemical structure determines the extent of impact. The flame-retardant effect is particularly evident when these compounds are applied to materials with a high oxygen concentration, such as polyesters, polyurethanes, cellulose, or epoxies [3] [4].

The flame-retardant mechanism results in different areas including the char layer, molten polymer zone, flame zone, and underlaying zone. These different areas of fire show the degradation or decomposition process of polymeric and synthetic materials. The most current findings on the utilization of different materials to create multifunctional flame-retardant polymers are reviewed in this review article. The mechanism of flame-retardant is important in optimizing the resultant polymer composites' structure. This review article consists of fire tests as the Limiting Oxygen Index (LOI) test and cone calorimeter which can used to find flame retardancy for different polymers and flame-retardant compounds like metal, halogenated, and phosphorus-based compounds [5]. Also, there are a variety of mineral-based flame-retardant additives available like hydroxides and carbonates with higher rates of flame retardancy. The most commonly used additives are alumina trihydrate (ATH) and ammonium polyphosphate (APP) which can produce a protective layer against fire propagation.

II. THE MECHANISM OF FLAME RETARDANT

Considering that burning is a known complicated both a chemical and physical process, multiple mechanical concepts operate concurrently, making it challenging to pinpoint a single dominant mechanism. The most successful mechanism of flame retardancy has been known for years to be both the condensed and gas phase effects. An example of the mechanism of flame-retardant is shown in Fig. 1. [5]

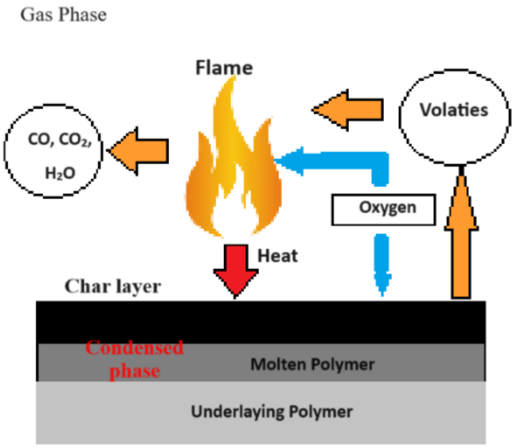


Fig. 1. Different layers of fire in gas-condensed phase

As a result, multiple zones can be distinguished, including the flame zone, char layer, molten polymer, and underlying polymer. Within the flame zone, volatiles resulting from the decomposition of polymers combine with atmospheric oxygen to produce a variety of flames and release heat [2].

The char layer regulates heat and mass fluxes between the condensed and gas phases, making it a crucial region in the polymer's combustion process. The decomposition volatiles originate in the molten polymer, also known as the thermally decomposed zone, and then move via the layer of microporous char to the flame zone. While being near the hot polymer zone, the base polymer zone is unbroken. The gas phase is designated by the flame zone, while the condensed phase is shown by the remaining zones. A flame retardant is referred to as a gas-phase mechanism if it disrupts combustion methods in the gas phase by radical absorption. On the other hand, the condensed-phase process entails the usage of a flame-retardant to facilitate char formation on the outer layer. This creates a barrier that prevents volatiles that catch fire from flowing into the flame and protects the polymer from heat and air. This portion aims to give detailed information on some of the fundamental ideas, working theories, and modes of operation of flame-retardants [6] [7].

The purpose of flame-retardant systems is to stop or block the polymer-burning process that was previously discussed. Because of the way they behave, fire retardant systems can react chemically (in the condense or gaseous phase) or physically (by chilling, forming a protective layer, or diluting fuel). They can block the different steps in the combustion of polymers, including heating, pyrolysis, ignition, and the spread of thermal degradation. Above is a report and discussion of flame-retardant systems' primary ways of action [8].

III. Flame Retardant Materials

A. Inorganic flame-retardant

1. Metal hydroxides:

Metal hydroxides must break down with the required heat and produce water at a temperature that is greater than or equal to the polymer's temperature of breakdown to be used as polymeric flame retardants [2].

The two mineral flame retardants that are most frequently employed are magnesium di-hydroxide (MDH) and aluminum tri-hydroxide (ATH). Mineral fillers for flame retardants have a distinct activity in the vapor/condensed phase and belong to the endothermic cooling system of flame retardancy. In particular, the mineral filler undergoes endothermic breakdown when exposed to heat in a fire. This slows the polymer's thermal breakdown by cooling the condensed phase. Additionally, because the mineral filler's breakdown products are not combustible, the leftover residue from the thermal breakdown (typically a metal oxide) reduces the full amount of polymeric material fuel that is available (condensed phase), and the mineral filler's release of gas that is non-flammable, aids in the dilution of the fuel that is available for ignition in the vapor phase [9].

2. Aluminium-based metal hydroxides:

Between 180^0 and 200^0 C, aluminum tri-hydroxide (Al $(OH)_3$) undergoes an endothermic reaction, which releases water and produces alumina and the heat is 1050 Kj / Kg [10].

$$2Al\ (OH)_3 \rightarrow Al_2O_3 + 3H_2O$$

These days, metal carbonates and metal hydroxides are the widely used mineral fillers as flame-retardants. It involves the commonly used hydroxides of magnesium (Mg $(OH)_2$) and alumina (Al $(OH)_3$). Due to the water being hydrated rather than Al-OH bonds predominating on the aluminum oxide surface, aluminum hydroxide is sometimes referred to as "alumina trihydrate (ATH)" (Al_2O_3. $3H_2O$). However, the term "net stoichiometry" is used interchangeably in discussions of flame-retardant chemistry.

$$Al_2O_3.3H_2O + \text{Heat } (300\text{-}200\ ^0C) \rightarrow Al_2O_3 + 3H_2O\ (g)$$

3. Magnesium based hydroxides

Magnesium di-hydroxides (Mg $(OH)_2$) function similarly to Al $(OH)_3$, but they degrade endothermically at temperatures above 300 ^0C, where heat is 1300 kj / kg [10].

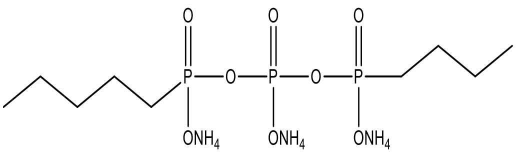
$$2Mg\ (OH)_2 \rightarrow 2MgO + 2H_2O$$

For the carbonates, but calcium carbonate is frequently used with other fillers, such as silicone, and activating elements to function as an active flame-retardant for wire and cable components, magnesium carbonate is occasionally used. Hydro magnesite, a somewhat other type of magnesium carbonate that can release CO_2 and water at lower temperatures, is also employed. While mineral fillers are not usually used in combination with synergistic agents, they are occasionally mixed with other flame-retardants to lessen emissions discharge.

$$Mg\ (OH)_2 + \text{Heat } (300\text{-}320\ ^0C) \rightarrow MgO + H_2O\ (g)$$

When a fire occurs, water and ammonia (NH_3) are eliminated by an intumescent ammonium polyphosphate (APP) stirred by the heat source. Ultra phosphate is then formed, which may serve as a barrier to stop the spread of the fire.

(a)APP



(b)ATH

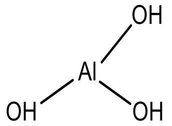


Fig. 2. Chemical structure of APP and ATH

For several reasons, the combined action of APP/ATH led to better fire-extinguishing behavior [11].

- The first is that the production of aluminum phosphate stops the volatility of phosphorous from evaporating. The second is the simplicity of ATH, which facilitates proton exchange and makes the evolution of water and ammonia gas easier.
- Lastly, the glassy ultra-phosphate structure of Al-P-O is changed by its crystalline shape, allowing gases to pass through the solid surface.

B. Halogen-based agents

As their name implies, halogenated flame retardants are compounds that contain F, Cl, Br, and I, elements found in the halogen group of the periodic table. Their chemical structures can differ greatly, ranging from aromatic to volatile carbon substrates that have undergone per-halogenation (halogen replacing all hydrogen) or can be inorganic; however, organohalogen compounds are the most effective when added to polymers to act as flame retardants. The usage of organobromine compounds can be easily explained by the fact that the C-Br bond works perfectly to put out flame. That bond is sufficiently steady enough for exposure to the environment and yet sufficiently brittle that heat can readily break down the connection, releasing the bromine when exposed to fire to stop the free radical reactions related to combustion. Because of their specific bonding strengths, halogen-based flame retardants are most effective in the vapor phase, where they prevent burning [12].

Halogen radicals generated from the Flame-Retardants eliminate (scavenge) high-energy OH* and H* radicals formed during combustion [13].

$RX \rightarrow R^* + X^*$

$X^* + R'H \rightarrow R'^* + HX$

$HX + H^* \rightarrow H_2 + X^*$

1. Brominated compounds:

Electronics, furniture, and textiles have all made extensive use of brominated flame retardants, like polybrominated diphenyl ethers (PBDEs) and tetra-bromo-bisphenol (TBBPA) [13].

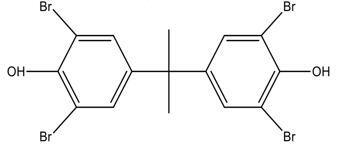
These PBDEs were most commonly employed in the past, but several nations have restricted or outright banned their usage because of their continued use, bioaccumulation, and possible health risks.

2. Chlorinated compounds:

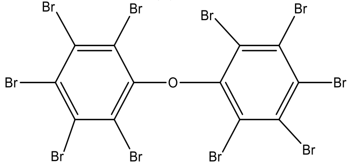
In a variety of industries, including textiles, rubber, and plastics, chlorinated flame retardants—particularly chlorinated paraffin—are utilized.

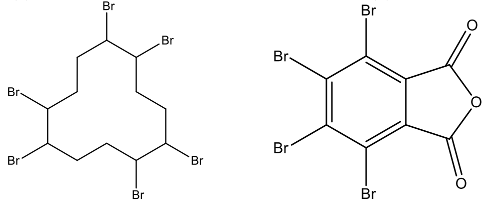
Similar to brominated flame retardants, certain chlorinated flame retardants have come under study because of their long half-lives in the environment and possible health hazards [13].

(a)TBBPA



(b) PBDE




(c) BCHD

(d) TBPA

Fig. 3. Halogenated compounds

C. Phosphorus-based flame-retardant

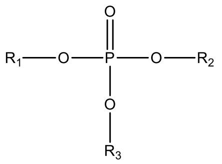
1. Red phosphorus:

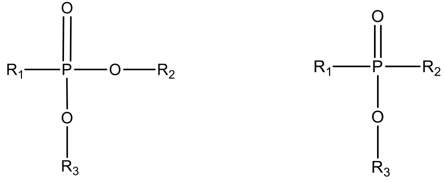
The most intense source of phosphorus for retardancy is red phosphorus. When applied less than 10% it performs well on polymers like polyesters, polyamides, and polyurethanes. The majority of scientists and researchers now believe that red phosphorus undergoes thermal oxidation in phosphorus polymers containing nitrogen or oxygen, which heats up to produce polyphosphoric acid. This acid catalyzes the polymer end-chain dehydration process, which results in the creation of char [14].

2. Inorganic phosphates:

An inorganic salt of ammonia and polyphosphoric acid is called ammonium polyphosphate (APP). It is well known that APPs are non-volatile, stable substances. At temperatures higher than 300 ^{0}C, long-chain APPs start to break down into ammonia and polyphosphoric acid. The breakdown of short-chain APPs starts as the temperature rises above 150 ^{0}C. Therefore, it is crucial to adjust the APP's crystalline shape to the temperature at which the polymer decomposes [15].

(a) Organic Phosphate




(b) Phosphonates

(c) Phosphinates

Fig. 3. Phosphorus-based compounds [2]

D. Natural Fibers

It's critical to look at the composition and structure of natural fibers to comprehend their characteristics. It mostly depends on where the fibers are sourced from. These sources consist of minerals, plants, and animals. Animal fibers are largely made of protein and can be extracted from hair, wool, or silk. Hemicellulose, cellulosic microfibrils, and lignin matrix form the majority of plant fibers [16].

1. Wool and its blends

Wool's chemical and physical structures are complicated, and it has amide connections that contain nitrogen, which makes it a naturally non-flammable fiber. Its low ignition temperature, which is roughly 680 °C is accompanied by a comparatively high LOI value of approximately 25% [17]. Wool is also suggested as a fire-resistant covering in specific situations [15].

Hexa-fluoro-titanate or hexa-fluoro-zirconate treatment of wool fiber is one of the most widely used Flame retardant methods. The mechanism involves the interaction of positively charged wool fibers with negatively charged complex ions of zirconium or titanium in an acidic environment (pH <3) at 60 °C. The best acids are those that are citric, acetic, formic, or hydrochloric [18]. The intumescent char forms as a result of this system.

(a) $\text{Wool-NH2} + H^+ \rightarrow [\text{Wool-NH}_3]$

(b) $[ZrF_6]^{2-}$ or $[TiF_6]^{2-} + 2\ [\text{Wool-NH}_3]^+ \rightarrow$

$[\text{Wool-NH}_3]_2[ZrF_6]$ or $[\text{Wool-NH}_3]_2[TiF_2]$

2. Silk Fibers

Generally speaking, silk is a protein made up of nearly eighteen residues of amino acids with different reactive functional groups like OH and NH_2. Unmodified silk can still function as a fuel source in fibers even though its high N concentration (LOI value is approx 23) causes it to show relatively low flammability [16]. The most common compounds utilized to provide silk Flame retardant qualities are those based on phosphorus [19]. For instance, urea and phosphoric acid treatment of silk fabric resulted in a moderate loss of tensile strength and an increase in LOI value up to 28, however, the fabric's washing strength was restricted [20].

E. Synthetic Fibers

The two main categories of polymeric matrices are thermoset and thermoplastic polymers. The polymeric matrix and the manufacturing techniques have a significant impact on the characteristics of composites. In general, the matrix helps to sustain the reinforcements from shear and compression. However, polymeric matrices are not very strong against heat loading or flame propagation [21]. Many articles about the flammability of polymers or polymer composites have been presented [22] [23] [24].

1. Polyesters

Polyester, or PET as it is more widely known, is a synthetic fiber made via the polymerization of organic dibasic acid and dihydric alcohol. Developed as the first wide range of synthetic fibers, it was invented in 1941 and is now widely utilized in many industries, including household textiles, clothing, car seats, tire manufacturing, and more [25].

2. Polyamides

The naturally occurring flame retardant properties of aromatic fiber-forming polyamides, with LOIs of approximately 29, and their substantial char yields upon burning, result from their aromatic structures and comparatively low hydrogen atom contents. The main polyamides that produce aliphatic fibers, nylon 6 and nylon 6.6, have LOIs of approximately 21, which indicates that they are not as flame-resistant as they could be [16].

IV. FIRE TESTING METHODS

Polymers are classified as flammable based on their heat release, flame-spread rate, and ignitability. At least one of these flammability criteria needs to be determined by suitable testing for flammability, depending on the use of the polymeric substance. At the industrial or academic level, flammability tests can be conducted on a small--, medium--, or large-scale basis for testing produced items or screen materials during product development [2].

The fire-retardant qualities of the different additives in the formulation of the synthetic materials were determined using two standard test techniques.

One common method for estimating the flammability of organic polymers and composite materials is the limiting oxygen index (LOI). The least oxygen content required to maintain flame combustion is known as the LOI, and it can be utilized to determine how easy a burning material is to extinguish on its own [9]. A vertically mounted specimen is burned downward as part of the Limiting Oxygen Index (LOI) test, which measures how easy material is to burn in an oxygen-nitrogen environment. The test process is generally repeatable to within + or - 0.5% of the original value and provides a useful assessment of the relative flammability of different materials. Greater LOI values correspond to better flame retardancy [26]. The LOI value is defined as the minimum concentration of oxygen $[O_2]$ in a mixture of oxygen/nitrogen $[O_2/N_2]$.

The LOI is expressed as [5]:

$$\text{LOI}= \frac{[O_2]}{[O_2]+[N_2]} * (100)$$

Table–I lists flash and self-ignition temperature parameters for various polymers along with their LOI values. Also, the heat release rate for each polymer is mentioned there.

The cone calorimeter simulates A range of fire temperatures through the application of heat fluxes ranging from 10 to 100 kW/m to test specimens using a truncated conical heating element. It has been proven that the approach gives data with good correlations to full-scale fire test results. It is fire testing technology used with cone calorimeter and heat flux [26]. The most significant and popular experiments for investigating and developing the fire behavior of polymeric materials have been cone calorimeter studies. Moreover, one of the best bench-scale tools for simulating actual fire conditions is the cone calorimeter. Through the investigation of characteristics such as time to ignition (TTI), heat release rate (HRR), total heat released (THR), residual mass, smoke, and CO/CO_2 release rates, the cone calorimeter tests can produce quantitative analysis to materials flammability study [27].

TABLE I. TEMPERATURES OF FLASH-IGNITION, SELF-IGNITION, AND CORRESPONDING LOI VALUES FOR DIFFERENT POLYMERS

Polymers	**temperature (^{0}C) of Flash-ignition [2]**	**temperature (^{0}C) of Self-ignition [2]**	**Heat Release Rate (W.cm^{-2})**	**LOI (%) [2]**
Polyethylene	340	350	140.8	18
Polypropylene	320	350	150.9	18
Polystyrene	350	490	110.1	18
Poly (vinyl chloride)	390	490	17.5	42

TABLE II. CORRELATED LOI VALUES FOR SELECTED FLAME-RETARDANT MATERIALS

Flame-retardant compound	**LOI (%)**
Aluminium hydroxides	30
Magnesium hydroxides	40
Halogenated compounds	20-30
Red phosphorus	40

CONCLUSION

In many sectors where polymeric materials are used, the usage of flame retardants in these materials is a crucial part of maintaining worker safety. To improve knowledge and encourage more developments in the sector, this study has examined the types, methods, and uses of flame retardants. To reduce the risk of fire, flame retardants work through both gas-phase and condensed-phase mechanisms, influencing various stages of combustion. Inorganic flame retardants, like phosphorus-based compounds and metal hydroxides, are effective at lowering flammability and forming protective barriers. While halogenated compounds can effectively interfere with combustion processes, they are frequently used, especially the brominated and chlorinated kinds. However, research into substitute flame retardant compounds must continue due to worries about their environmental durability and possible health dangers. Mineral flame retardants, such as carbonates and metal hydroxides, are viable ways to improve polymeric materials' fire resistance. They release non-flammable gases and break down endothermically, which lowers the amount of fuel available for burning. Natural fibers with flame-retardant qualities, such as silk and wool, are valuable materials in several applications. Treatments like hexa-fluoro-titanate or hexa-fluoro-zirconate treatment improve their fire resistance even more and provide eco-friendly substitutes for synthetic fibers. Flame retardants are beneficial in improving the fire safety profile of synthetic fibers, such as polyester. To create high-performance flame-retardant materials, it is essential to comprehend how flame retardants interact with polymeric matrices. To conclude up, flame retardant technology development must continue since it is critical to tackling fire safety issues in a variety of industries. Researchers can keep improving the fire resistance of polymeric materials and contribute to a safer and more sustainable future by utilizing novel materials and methods.

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