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Research progress of emerging flame retardants for epoxy resin

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Epoxy resin (EP) has been widely used in many fields due to its excellent physical and chemical properties. However, its inherent flammability limits its application in some fields, and the development of efficient and environmentally friendly new flame retardants has become a research hotspot. In recent years, researchers have been committed to developing new flame retardants to improve the flame retardant properties of EP. The development of synergistic flame retardant systems, combined with the advantages of various flame retardants, has become a research trend. In this paper, the application progress of three kinds of new flame retardants in EP, including nano-materials, organic materials, and inorganic materials, is summarized. Their synthesis methods, structural design, and application prospects are compared, and a summary and prospect are given.

Keywords: Epoxy resin, Flame retardant, Nano-material, Organic material, Inorganic material.

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INTRODUCTION

Epoxy resin (EP) (Fig. 1) has been widely used in aerospace, electronic and electrical, construction, and other fields due to its excellent adhesion, mechanical properties, and chemical resistance. However, the flammability of EP limits its use in some cases with high safety requirements. To overcome this shortcoming, researchers are committed to developing various new flame retardants to improve the flame retardant properties of EP. In this paper, the research progress of three types of EP flame retardants, nano-materials, organic materials, and inorganic materials, is systematically summarized, and their design ideas and mechanism of action are discussed.

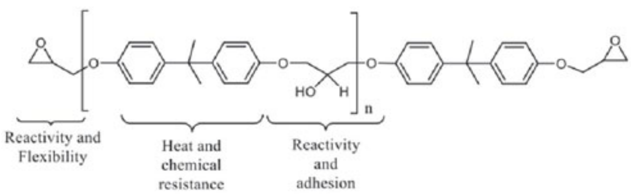

Figure 1. Structural characteristics of epoxy resin

In recent years, researchers have made significant progress by introducing different types of flame retardants. For example, Guo et al. developed a new environmentally friendly flame retardant based on phosphamide, which not only enhances the mechanical properties of EP, but also significantly improves its fire safety[1]. Qi et al. increased the length of the bridge chain through ingenious ester chain grafting technology, giving EP excellent thermal stability, smoke suppression ability, and mechanical properties[2]. In addition, inspired by the octopus tentacle structure, Zhong et al. prepared HPP @ PBA nanotubes, which successfully enhanced the mechanical properties and flame retardancy of EP nanocomposites[3]. These research results provide new ideas and methods for the flame retardant modification of EP. Phosphoamide-based flame retardants can not only improve the mechanical properties of EP, but also significantly improve its fire safety, providing more possibilities for the application of EP. Through ester chain grafting technology, Qi et al. successfully endowed EP with excellent thermal stability, smoke suppression ability, and mechanical properties, which provided a guarantee for the application of EP in high temperature environment. Zhong et al. successfully strengthened the mechanical properties and flame retardancy of EP nanocomposites by preparing HPP @ PBA nanotubes, which provided a new idea for the preparation and application of EP nanocomposites. These studies not only provide a new direction for the flame retardant modification of EP, but also provide strong technical support for the development and application of high-performance composites.

In terms of organic flame retardants, Yang et al. developed a flame retardant containing phosphorus/boron, which effectively improved the flame retardant properties of flax fiber reinforced epoxy resin (EP) composites by introducing phosphorus/boron elements[4]. These flame retardants can release phosphorus and boron compounds during combustion. These compounds can promote the formation of carbon layers and inhibit free radical reactions during combustion, thereby improving the flame retardant properties of composites. In addition, these flame retardants can also improve the mechanical properties of EP composites, providing more possibilities for their practical application.[4] Huan et al. synthesized a new P-N flame retardant based on DOPS / triazine-trione structure, which can effectively improve the flame retardancy of epoxy resin by introducing phosphorus/nitrogen elements[5]. These flame retardants can release phosphates and nitrides during combustion. These substances can inhibit free radical reactions during combustion and promote the formation of carbon layers, thereby improving the flame retardant properties of composites. In addition, these flame retardants can also improve the mechanical properties and thermal stability of EP, which provides more possibilities for its practical application. The application of nanomaterials has also achieved remarkable results. Jiang et al. successfully improved the fire safety and mechanical properties of epoxy resin by synthesizing linear polydichlorophosphazene and Ti3C2Tx MXene nanohybrid materials[6]. These nanomaterials not only have excellent thermal stability and catalytic combustion reaction ability, but also can improve the mechanical properties of the composites, which provides new ideas and methods for the flame retardant modification of EP[6]. Cheng et al. introduced ammonium phosphate and ionic liquid loaded with CuO--ZnO hollow spheres into epoxy resin composites, which enhanced their flame retardancy and thermal insulation properties[7]. These nanomaterials can release phosphates and nitrides during the combustion process, which can inhibit the free radical reaction during the combustion process and promote the formation of carbon layers, thereby improving the flame retardancy of the composites. The flame retardant properties of common mesh material-based flame retardants in EP are shown in Table 1. In addition, these nanomaterials can also improve the thermal stability of EP, which provides more possibilities for its practical application[8–9].

Through these studies, this paper not only summarizes the mechanism of various flame retardants but also provides valuable directions and ideas for the design and preparation of flame retardants in the future. These research results provide a new method to improve the flame retardant properties of epoxy resin composites and provide strong technical support for the development and application of high-performance composites. Future research can further explore the design and synthesis of new flame retardants to optimize their flame retardant efficiency and compatibility, and provide more possibilities for the application of epoxy resin composites.

APPLICATION OF NANOMATERIALS IN EPOXY RESIN COMPOSITES

Overview

With the rapid development of nanotechnology, the application of nanomaterials in epoxy resin composites has attracted more and more attention due to their unique physical and chemical properties. Nanomaterials have the characteristics of a large specific surface area, high chemical activity, and excellent mechanical properties, which make them show great potential in improving the flame retardancy of epoxy resin. The introduction of nanomaterials into epoxy resin can not only improve the flame retardancy of the material, but also effectively improve its mechanical, thermal, electrical, and other comprehensive properties [23–25]. In recent years, the application of nanomaterials in epoxy resin composites has made remarkable progress. For example, the halogen-free epoxy flame retardant and accelerator containing diimidazole skeleton developed by Liu et al. not only improves the overall performance of EP, but also provides a new direction for the research of environmentally friendly flame retardants[26]. Researchers have provided new ideas and methods for the modification of epoxy resin by designing and preparing different types of nano-flame retardants. These nano-flame retardants not only improve the flame retardancy of epoxy resin but also bring new possibilities for the design and application of composite materials.

Classification and Performance

MOFs

Metal-organic frameworks (MOFs) are a class of nanomaterials with high specific surface area, porous structure, and adjustable chemical properties (Fig. 2). The pore structure of MOFs can effectively capture and

Table 1. The fire behaviors of common mesh material-based flame retardants in EP composites

Sample	Adding amount (%)	Char yield (%)^a	UL-94	LOI (%)	pHRR reduction (%)^b	Reference
P-MOF	2.0	20	–	–	28	10
MOF@GO	2.0	17.0	–	29.0	30.0	11
PA-UiO_{66}-NH_2	5.0	24.3	V-1	29.1	41.0	12
Sn-MOF@PANI	2.0	19.5	–	–	42.0	13
ZIF-8@PA@SiO_2	5.0	30.9	V-1	28.8	38.3	14
W-Zr-MOF-DOPO	3.0	60.0	V-0	32.2	58.0	15
MXenes@MOF-B	2.0	16.5	–	–	42.5	16
UiO66-PDA-PBA	3.0	–	V-1	28.2	50.0	17
BN/PATP@Cu-MOF	2.0	25.7	–	–	55.9	18
Co-MOF@POSS	2.0	–	–	27.5	34.6	19
DOPO-COFs	3.2	–	–	25.0	18.4	20
AGO@COF	2.0	–	–	25.5	43.6	20
COF@PDA@CuO	2.0	14.8	–	–	31.9	21
HOF- FJU -1	9.0	25.9	V-1	29.2	38.5	22

a Measured by TGA under nitrogen (* under air.)
b Measured by cone calorimeter under 50 kW m^{-2}

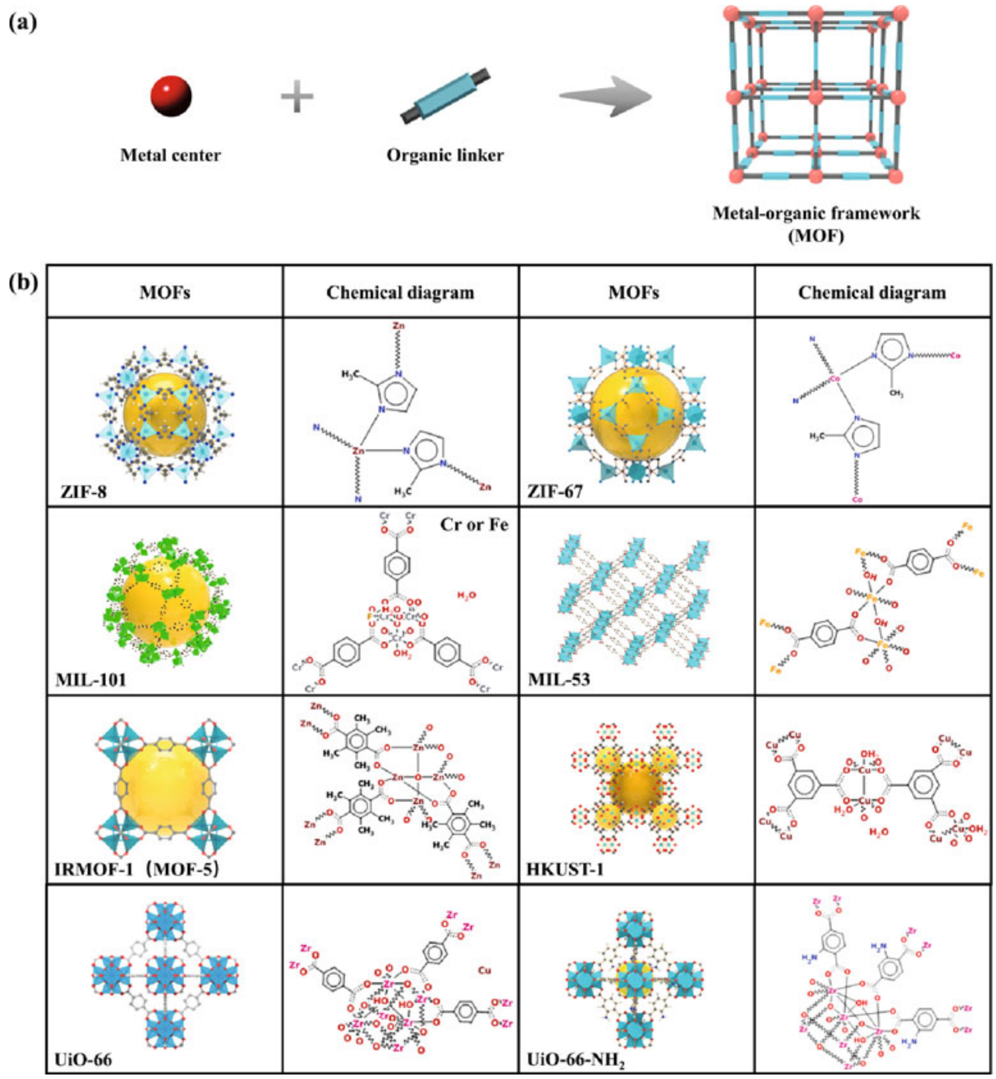

Figure 2. Schematic diagram of MOF synthesis (a); Crystal structure and chemical diagram of representative MOFs[27] (b). (Copyright 2023, Elsevier.)

block free radicals in flames, thereby inhibiting flame propagation[27–28]. Elashker et al. studied the application of metal-organic frameworks in polymers and pointed out their potential as new flame retardants[29]. The metal nodes and organic connectors in MOFs can provide additional thermal stability through chemical bonding, making the composites exhibit excellent flame retardancy at high temperatures. Studies have shown that the addition of MOFs can significantly improve the thermal stability and carbon residue rate of epoxy resin, thereby improving its flame retardant efficiency[27]. In addition, the pore structure of MOFs can also be used as an effective adsorbent to adsorb small molecule volatiles generated during combustion and reduce the generation of smoke. These properties make MOFs a promising choice for improving the flame retardancy of epoxy resin composites[30]. Li et al. developed an epoxy resin composite based on ZIF-67 (zinc-based metal-organic framework)[31]. They enhanced the formation ability of the carbon layer of the composite by modifying ZIF-67 in a rice ball-like manner and combining the crosslinking effect of carboxymethyl β-cyclodextrin[32–33]. This modified ZIF-67 not only improves the flame retardancy of epoxy resin[9–34], but also further improves the fire safety of the material by forming a denser carbon layer[35–36]. The application research status of nanomaterials in epoxy resin composites shows that the fire safety performance and other physical and chemical properties of epoxy resin can be significantly improved through precise design and modification of nanomaterials, which provides new possibilities for the application of polymer materials in a wider range of fields.

MXene

MXene is a two-dimensional transition metal carbide with excellent electrical conductivity and mechanical properties. The lamellar structure of MXene allows it to have good dispersion in epoxy resin, which is helpful in forming an effective flame retardant barrier. MXene can not only be used as a traditional thermal shielding material, but also promote the rapid emission of heat through its high thermal conductivity, reduce the surface temperature of the composite material, and thus slow down the spread of fire. For example, Jiang et al. successfully improved the fire safety and mechanical properties of epoxy resins by synthesizing linear polydichlorophosphazene and $Ti_3C_2T_x$ MXene nanohybrid materials[6]. The lamellar structure of MXene can also improve the mechanical strength and toughness of the composites, so that it can meet the requirements of high mechanical properties while maintaining flame-retardant properties. In addition, the surface of MXene can be functionally modified to make it have better compatibility and dispersibility with epoxy resin, thereby further improving the comprehensive performance of the composite material[35]. These properties make MXene a promising choice for improving the flame retardancy and mechanical properties of epoxy resin composites.

Other Related Nanomaterials

In addition to MOFs and MXenes, other nanomaterials have also been studied to improve the flame retardancy of epoxy resins. These nanomaterials include multifunctional ionic liquids, carbon nanotubes, nano-graphene, and nano-metal oxides. They have unique structures and properties, which can bring different flame retardant effects to epoxy resin composites. Xiao et al. developed a multifunctional ionic liquid, which can endow epoxy resin with excellent fire safety and mechanical properties, only with ultra-low load[37]. As a new type of green solvent, ionic liquid has good thermal stability and chemical stability. At the same time, its unique ionic structure makes it have good dispersibility in epoxy resin. By introducing ionic liquids, the combustion rate of epoxy resin can be effectively reduced, and a protective carbon layer can be formed, thereby improving the flame retardancy of the composites. Carbon nanotubes have been widely studied due to their unique structure and high thermal stability. Carbon nanotubes can form a network structure in epoxy resin to enhance the mechanical properties and thermal stability of the material[37]. This network structure can effectively prevent the spread of flame and inhibit the free radical reaction in the combustion process by forming a carbon layer, thereby improving the flame retardancy of the composite.

In addition, nano-graphene is also a potential flame retardant due to its excellent thermal conductivity and thermal stability. Its addition can significantly improve the flame retardancy of the composite material. Nano-graphene has good thermal conductivity, which can quickly dissipate heat and reduce the surface temperature of the composite material. At the same time, the lamellar structure of nanographene can form a dense carbon layer to isolate oxygen and heat, thereby improving the flame retardant properties of the composites. Finally, nano-metal oxides such as alumina and zirconia are also used as flame retardants due to their high melting point and ability to catalyze combustion reactions[29]. These nano-metal oxides can decompose to produce non-combustible gases such as carbon dioxide and water vapor during combustion, thereby diluting the oxygen concentration in the combustion region and slowing down the combustion reaction. In addition, these nano-metal oxides can also promote the formation of carbon layer and further improve the flame retardant properties of the composites.

In summary, the application of these nanomaterials provides a variety of choices for flame retardant modification of epoxy resins. The bio-based chitosan polymer electrolyte flame retardant containing phosphorus and nitrogen developed by Wu et al. effectively improved the flame retardancy and smoke suppression performance of epoxy resin[38]. These research results provide new ideas and methods for the flame retardant modification of epoxy resin composites, and provide strong technical support for the development and application of high--performance composites.

Mechanism of Nano-flame Retardants

The mechanism of action of nano-flame retardants in epoxy resin composites usually involves the following aspects: Nano-flame retardants can be used as a thermal shielding material to form a stable carbon layer on the surface of the composite material through their high thermal stability. This carbon layer can effectively isolate heat and oxygen, slow down the heat conduction rate, and thus prevent the spread of flame. For example, metal-organic frameworks (MOFs), due to their unique pore structure and thermal stability[39], can form a carbon layer at high temperatures to protect the lower epoxy resin from direct combustion[40–42]. Secondly, the addition of nano-flame retardants can change the combustion kinetics inside the composites[43]. During the combustion process, nano-flame retardants can release non-flammable gases, such as water vapor and carbon dioxide, which can dilute the concentration of combustible gases in the flame and reduce the rate of combustion reaction[19–25]. At the same time, the surface of nanomaterials may undergo catalytic reactions to further inhibit the formation of free radicals during combustion and slow down the chain propagation of combustion reactions. Finally, the physical and chemical properties of nano-flame retardants also have an important influence on their flame retardant effects in composites. For example, nanomaterials have a large specific surface area and high chemical activity[32], which helps them to form a uniform dispersion system in composites and improve the uniformity and stability of flame retardant properties. In addition, the interaction between nanomaterials and epoxy resin, such as the formation of chemical bonds or physical adsorption, also affects its flame retardant efficiency. For example, two-dimensional nanomaterials such as MXene, due to their good hydrophilicity, can enhance the interfacial bonding force by interacting with the hydroxyl group of epoxy resin, thereby providing more stable carbon layer protection during combustion[33–35]. Figure 3 shows

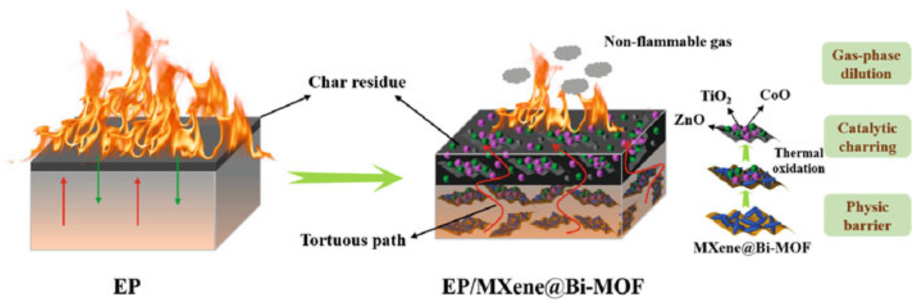

Figure 3. Proposed flame retardant mechanism of EP composites[44]. (Copyright 2022, Elsevier.)

the flame retardant mechanism of EP / MXene @ Bi--MOF. In summary, the flame retardant mechanism of nano-flame retardants is multifaceted, including thermal shielding, changes in combustion kinetics, and regulation of physical and chemical properties. These mechanisms work together to make epoxy resin composites exhibit higher flame-retardant properties in the face of fire.

APPLICATION OF ORGANIC MATERIALS IN EPOXY RESIN COMPOSITES

Overview

As a flame retardant for epoxy resin composites, organic materials can improve the flame retardancy of materials while maintaining the processing and mechanical properties of materials, which is due to their unique chemical structure and properties. These organic flame retardants have good compatibility and dispersibility, and can form a stable composite system with epoxy resin matrix. By introducing organic groups with flame retardant functions, such as aromatic rings, halogen atoms, phosphate groups, etc.[45–46], these organic materials can play a role in inhibiting flame propagation during combustion, thereby improving the overall flame retardant performance of epoxy resin composites. Aromatic compounds are one of the common organic flame retardants. These compounds usually have high thermal stability and can form a stable carbon layer during combustion, thereby preventing the transfer of heat and oxygen. For example, phosphate aromatic compounds can not only provide carbon layer protection, but also inhibit the production of free radicals by releasing phosphoric acid and phosphate, thus interrupting the combustion chain reaction. In addition, these compounds usually have good compatibility and can form a uniform dispersion system with the epoxy resin matrix without adversely affecting the mechanical properties of the composites.

Cyclic compounds are another common type of organic flame retardants, including halogenated cyclic compounds and phosphorus heterocyclic compounds. Halogenated cyclic compounds inhibit free radical reactions during combustion by releasing halogen gases, while phosphorus heterocyclic compounds prevent flame propagation by forming phosphate and carbon layers. These cyclic compounds usually have good thermal stability and chemical stability, and can maintain their structure in a high--temperature environment, thus providing long-term flame retardant protection for epoxy resin. However, the presence of halogen may cause some pollution to the environment, so there is some controversy in environmental protection. In addition to aromatic compounds and cyclic compounds, other types of organic materials are also used as flame retardants for epoxy resins. For example, organic compounds containing elements such as nitrogen and sulfur can release non-combustible gases such as nitrogen and sulfur dioxide during combustion, thereby reducing the concentration of combustion gases and slowing down the combustion rate. In addition, certain specific silicone compounds are also used as flame retardants due to their good thermal stability and charring properties, which can form a stable silicate carbon layer during combustion and provide effective thermal shielding. The design and selection of these organic flame retardants often require consideration of factors such as their compatibility with epoxy resins, cost-effectiveness, and environmental requirements.

The design and synthesis of organic flame retardants are also more flexible, and their flame retardant efficiency and compatibility can be optimized by molecular-level regulation, which provides a broad prospect for the application of epoxy resin composites. For example, by optimizing the molecular structure of organic flame retardants, their volatility and decomposition temperature during combustion can be reduced, thereby improving their flame retardancy. In addition, the compatibility and dispersion of organic flame retardants and epoxy resins can be improved by introducing specific functional groups, thereby improving the overall performance of the composites. These studies not only provide new ideas and methods for flame retardant modification of epoxy resin composites, but also provide effective solutions for fire prevention and control in practical applications.

Classification and Performance

Aromatic Compound

Aromatic compounds are widely used as flame retardants for epoxy resins due to their stable benzene ring structure. These compounds usually have high thermal stability and can form a stable carbon layer during combustion, thereby preventing the transfer of heat and oxygen. For example, Bessa et al.studied the thermal stability and flame retardant properties of phosphorylated microcrystalline cellulose reinforced polybenzoxazine / epoxy copolymers (Fig.4) and found that they had good flame retardant effects[47]. This polybenzoxazine / epoxy copolymer can form a dense carbon layer during

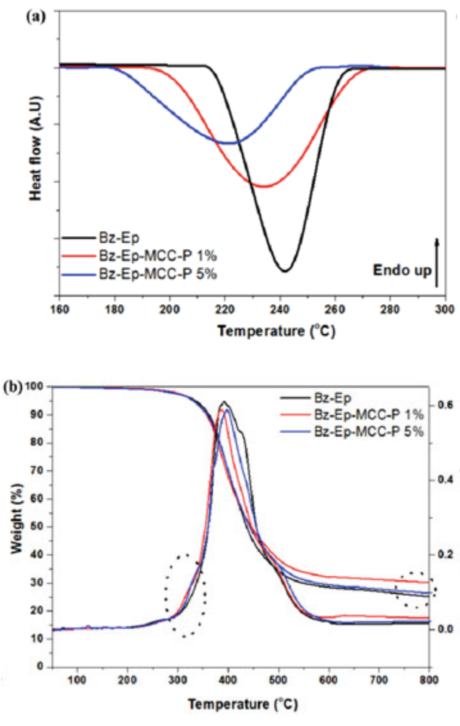

Figure 4. DSC studied the curing process of the Bz-Ep copolymer and its MCC-P-reinforced composites[47] (a). TGA/DTG studied the curing process of the Bz-Ep copolymer and its MCC-P-reinforced composites[47] (b). (Copyright 2024, Fibers.)

the combustion process, which effectively isolates the combustion area from the external environment and reduces the combustion rate, thereby improving the flame retardancy of the epoxy resin composite. In addition, these compounds usually have good compatibility and can form a uniform dispersion system with the epoxy resin matrix without adversely affecting the mechanical properties of the composites. Therefore, as an effective flame retardant, aromatic compounds provide a broad prospect for the application of epoxy resin composites.

Cyclic Compound

Cyclic compounds are another common type of organic flame retardants, including halogenated cyclic compounds and phosphorus heterocyclic compounds. Halogenated cyclic compounds inhibit free radical reactions during combustion by releasing halogen gases, while phosphorus heterocyclic compounds prevent flame propagation by forming phosphate and carbon layers. For example, Zhong et al. developed a bio-derived polyphosphate-modified halloysite nanotube as an environmentally friendly flame retardant (Fig. 5), which significantly reduced the smoke release of epoxy resin and enhanced its fire safety[48]. These halloysite nanotubes can release phosphorus heterocyclic compounds during combustion. These compounds can not only form phosphate and carbon layers, effectively preventing flame propagation, but also reduce smoke release and improve the fire safety of composites. In addition, these cyclic compounds usually have good thermal stability and chemical stability, and their structure can remain unchanged at high temperatures, thus providing long-term flame retardant protection for epoxy resins. Therefore, as an effective flame retardant, cyclic compounds provide more choices for the application of epoxy resin composites.

Other Organic Materials

In addition to aromatic compounds and cyclic compounds, other types of organic materials are also used as flame retardants for epoxy resins. These new flame retardants usually contain a variety of elements, such as phosphorus, nitrogen, silicon, zinc, etc., which can play a synergistic flame retardant role in the combustion process and improve the flame retardancy and smoke suppression performance of epoxy resin. For example, Li et al. developed a new type of hybrid flame retardant containing phosphorus/nitrogen/silicon/zinc to improve the flame retardancy and smoke suppression of epoxy resin[49]. By introducing a variety of elements, this mixed flame retardant can better play a synergistic flame retardant effect and improve the flame retardancy of epoxy resin. The application of these organic materials provides a variety of choices for flame retardant modification of epoxy resins, and also considers environmental protection requirements. In the design and synthesis of new flame retardants, researchers have continuously optimized the molecular structure of flame retardants to improve their flame retardant efficiency and compatibility. For example, Li et al. also studied the modification of epoxy resin based on DOPO-based flame retardants, and found that it can effectively improve the flame retardancy and mechanical properties of epoxy resin[50]. DOPO, as a phosphorus-containing flame retardant, can form phosphate and carbon layers during combustion, thereby inhibiting flame propagation. At the same time, DOPO can also improve the mechanical properties of epoxy resin, so that it has better performance in practical applications.

Tang et al. realized the flame retardant and toughening modification of epoxy thermosetting resin by synthesizing hyperbranched epoxy resin[51]. The hyperbranched structure helps to improve the crosslinking density and thermal stability of epoxy resin, thereby improving its flame retardancy. In addition, the hyperbranched structure can also improve the toughness of epoxy resin, so that it has better impact resistance in practical applications. Huang et al. synthesized a flame retardant based on biphenyl ether/vanillin, which enhanced the flame retardancy and mechanical properties of epoxy resin[52]. Diphenyl ether and vanillin groups have good thermal stability and charring properties, and can form a stable carbon layer during combustion, thereby improving the flame retardancy of epoxy resin. At the same time, these groups can also improve the mechanical properties of epoxy resin, so that it has better strength and toughness in practical applications. Deng et al. studied the flame retardant effect of phosphorus-nitrogen synergistic flame retardant on epoxy resin, and revealed its thermal decomposition and

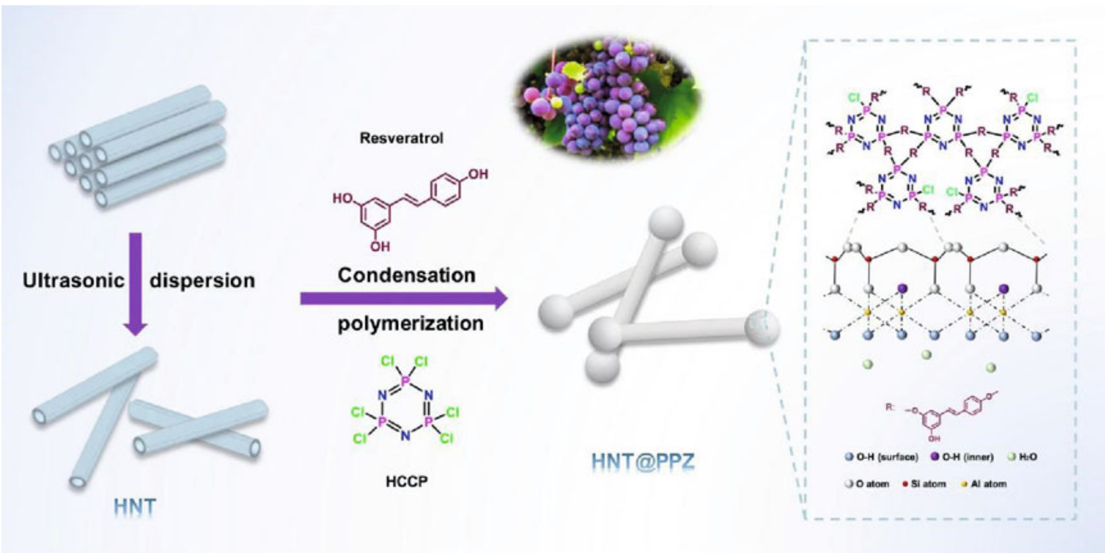

Figure 5. Schematic diagram of the synthetic route of HNT@PPZ[48]. (Copyright 2024, Elsevier.)

flame retardant mechanism[53]. By introducing phosphorus and nitrogen elements, phosphorus-nitrogen synergistic flame retardant can play a synergistic flame retardant effect and improve the flame retardancy of epoxy resin. In addition, the phosphorus-nitrogen synergistic flame retardant can also reduce the smoke release of epoxy resin and improve its environmental performance. These research results provide new ideas and methods for the flame retardant modification of epoxy resin composites, and provide strong technical support for the development and application of high-performance composites.

Mechanism of Organic Flame Retardants

The mechanism of action of organic flame retardants mainly involves two levels:gas phase and condensed phase. The two levels complement each other and jointly improve the flame retardant properties of epoxy resin composites. In the gas phase, organic flame retardants interrupt the chain reaction of combustion and reduce the combustion rate by releasing gases that can capture and neutralize free radicals, such as halogen gases, phosphoric acid gases, etc. This mechanism of action is to slow down the combustion process by reducing the number of free radicals, thereby effectively suppressing flame propagation. Taking the new halogen-free epoxy resin flame retardant synthesized by Yushuang et al. as an example, the flame retardant can release phosphoric acid gas during combustion, effectively interrupt the combustion chain reaction, and improve the flame retardant performance of the composite[54]. As an active gas, phosphoric acid gas can react with free radicals in the gas phase, thereby reducing the number of free radicals, slowing down the combustion process, and finally achieving the effect of inhibiting flame propagation.

In the condensed phase, organic flame retardants can promote the formation of a stable carbon layer. This carbon layer can not only isolate heat and oxygen, slow down heat conduction, but also reflect part of the heat and reduce the surface temperature of the composite material. The role of this carbon layer is similar to thermal shielding, which can effectively prevent heat from spreading into the interior of the composite material, thereby protecting the internal structure from high--temperature damage. Yan et al. used montmorillonite and ammonium dihydrogen phosphate to prepare an effective flame retardant, which can form a stable carbon layer during combustion, thereby improving the flame retardancy and smoke suppression performance of epoxy resin[55]. As a layered silicate mineral, montmorillonite has good thermal stability and chemical stability. During the combustion process, montmorillonite can form a dense carbon layer, which can effectively isolate the combustion area from the external environment and reduce the combustion rate. As a phosphorus-containing flame retardant, ammonium dihydrogen phosphate can release phosphoric acid gas during combustion and promote the formation of carbon layer. The carbon layer can not only isolate heat and oxygen, but also reflect part of the heat and reduce the surface temperature of the composite material. The flame retardant mechanism is shown in Figure 6, the application of this flame retardant provides a new idea and method for the flame retardant modification of epoxy resin composites. In summary, the organic flame retardants in the gas phase and condensed phase two levels of the role of mutual cooperation, together to improve the flame retardant properties of epoxy resin composites. By releasing gas and forming a carbon layer, these flame retardants effectively inhibit the propagation of flame and provide more possibilities for the application of epoxy resin composites.

In addition, organic flame retardants may undergo decomposition reactions at high temperatures, and the resulting decomposition products can further dilute the combustible gas and reduce the oxygen concentration required for the combustion reaction. This dilution effect helps to reduce the oxygen concentration in the combustion area, making the combustion reaction more difficult, thereby slowing down the flame propagation speed. The sulfur-phosphorus reactive flame retardant developed by Ma et al. can release a large amount of non--combustible gases during combustion, effectively dilute the combustible gases, and enhance the flame retardant properties of epoxy resin composites[56]. Through these combined effects, organic flame retardants effectively improve the flame retardancy of epoxy resin composites and reduce the risk of fire. At the same time, the design

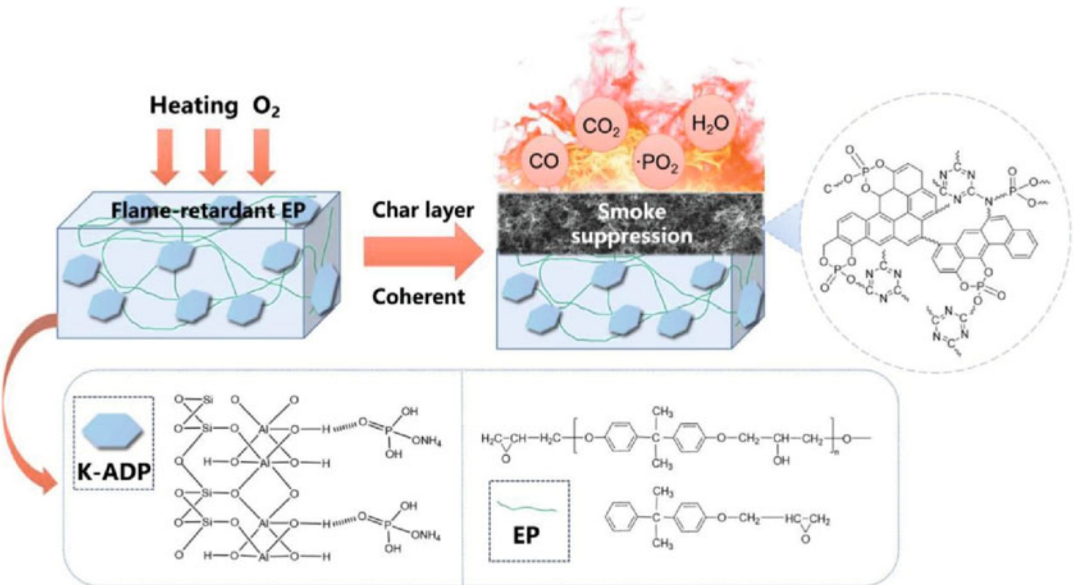

Figure 6. The possible flame-retardant mechanism of K-ADP in EP matrix[55]. (Copyright © 2023 Wiley Periodicals LLC.)

and synthesis of these flame retardants are also constantly optimized. For example, the multifunctional phosphorus--containing phthalocyanine dye developed by Wenjie Y et al. not only improves the flame retardancy of epoxy resin, but also improves its thermal stability, toughness and dielectric properties[57]. The P / N / S flame retardant developed by Yuzhao et al. based on DOPS-triazine group also significantly improved the flame retardancy, carbon formation and mechanical properties of epoxy resin[58]. These studies not only provide new ideas and methods for flame retardant modification of epoxy resin composites, but also provide effective solutions for fire prevention and control in practical applications.

APPLICATION OF INORGANIC MATERIALS IN EPOXY RESIN COMPOSITES

Overview

Inorganic materials are widely used in flame retardant modification of epoxy resin composites due to their excellent high temperature resistance, good chemical stability and high thermal stability. These inorganic flame retardants usually have high melting point and non-volatile properties, which can provide effective thermal protection for epoxy resins under extreme conditions[59]. The introduction of inorganic materials such as carbonates, sulfates, borates and metal oxides into epoxy resins can not only significantly improve the flame retardancy of composites, but also improve their mechanical strength and thermal stability, providing safety guarantee for high--performance composites in aerospace, electronics and other fields. The research and application of inorganic flame retardants have become an important direction to improve the safety of epoxy resin composites.

In recent years, researchers have made significant progress by introducing different types of inorganic flame retardants. For example, Shuailiang et al. prepared a novel flame retardant by coating polyphosphate on zinc oxide tin, which can effectively improve the fire safety and smoke suppression ability of epoxy resin[60]. Zhang et al. prepared a new type of phosphorus-nitrogen reactive flame retardant by a one-pot method, which can improve the flame retardancy of epoxy resin while improving its other properties[61]. In addition, Liu et al. synthesized a halogen-free epoxy resin flame retardant curing agent, which can significantly improve the flame retardant properties of epoxy resin[62]. Yifang et al. prepared a flame retardant epoxy resin with excellent light transmittance, mechanical properties, and anti-aging properties by introducing DOPO derivatives[63]. Junwei et al. developed a new type of phosphorus, nitrogen and sulfur multi-element flame retardant, which can effectively improve the fire safety of epoxy resin composites[64].

These studies not only provide new ideas and methods for flame retardant modification of epoxy resin composites, but also provide effective solutions for fire prevention and control in practical applications. For example, Hongyu et al. prepared a new flame retardant based on phosphorus/nitrogen modified lignin and metal organic framework, and applied it to epoxy resin, which significantly improved the flame retardant performance of epoxy resin[65]. These studies have shown that inorganic flame retardants play an important role in improving the flame retardancy of epoxy resin and provide strong technical support for the development and application of high-performance composite materials.

Classification and Performance

Inorganic materials play an important role in the flame retardant modification of epoxy resin composites due to their unique physical and chemical properties. The following is a detailed description of the classification and performance of several major types of inorganic flame retardants:

Carbonates

Carbonate inorganic flame retardants, such as calcium carbonate and magnesium carbonate, are widely used in flame retardant modification of epoxy resin composites due to their low cost, abundant sources, and good environmental protection performance. Cen et al. studied the flame retardant properties, dielectric properties, and thermal decomposition behavior of epoxy resin and cyanate ester composites containing new multifunctional flame retardants, and found that they had excellent flame retardant effects[66]. These carbonates can decompose at high temperatures to produce carbon dioxide gas, which helps to dilute combustible gases and reduce the oxygen concentration of combustion reactions, thereby exerting a flame retardant effect. In addition, the heat absorption effect of carbonate decomposition also helps to reduce the surface temperature of the composite material. However, the addition of carbonate may have a certain impact on the mechanical properties of the composites, so it is necessary to properly control its dosage and dispersion in practical applications.

Borates

Borates, inorganic flame retardants, including boric acid, borax, etc., have also been widely used in epoxy resin composites due to their high flame retardancy and low cost. Borate can form a glassy boric acid layer during combustion, which can isolate heat and oxygen, and promote the formation of a carbon layer, providing dual protection for the composite. The flame retardant effect of borate is also related to its dispersion and interaction in the composites. Good dispersion and interfacial bonding can significantly improve the flame retardant properties. For example, Shi et al. used zinc oxide tin/carbon nanotube hybrid materials as flame retardants and smoke inhibitors for epoxy resins, and achieved good results.[67]

Other Inorganic Materials

In addition to carbonates and borates, other inorganic materials are also used as flame retardants for epoxy resins. For example, metal oxides (such as alumina, zinc oxide, etc.) have attracted much attention due to their high thermal stability and ability to catalyze combustion reactions. These oxides can promote the formation of carbon layers at high temperatures and catalyze the free radical reactions generated by combustion, thereby inhibiting flame propagation. Sun et al. reviewed the new progress in the application of flame retardant modified epoxy resin and fire retardant coatings, which provided a new idea for the research and application of inorganic flame retardants[68].

In addition, silicate materials, such as diatomite and silica, are also used as flame retardants due to their good thermal stability and charring properties. The application of these inorganic materials not only improves the flame retardancy of epoxy resin composites but also provides additional mechanical and thermal performance improvements. For example, Pu et al. prepared a new phosphorus-nitrogen flame retardant through the synthesis of DOPO-DBAPh and applied it to epoxy resin composites, which significantly improved its flame retardant properties[69]. Based on a novel cyano-containing DOPO derivative, Yong et al. prepared a multifunctional epoxy resin with hydrophobicity, transparency, mechanical properties, and fire safety[70]. Vishal et al. synthesized a new type of phosphorus / nitrogen-containing flame retardant and applied it to epoxy/clay nanocomposites, which effectively improved the flame retardant, thermal and mechanical properties of the materials[71]. Tian et al. synthesized a functionalized Salen-Ni-based polyphosphazene flame retardant and studied its properties[72]. These studies have shown that inorganic flame retardants play an important role in improving the flame retardant properties of epoxy resin composites and provide strong technical support for the development and application of high-performance composites.

Mechanism of Inorganic Flame Retardants

The mechanism of action of inorganic flame retardants mainly depends on their physical and chemical changes at high temperatures. In the combustion process, inorganic flame retardants such as carbonates and borates will decompose to produce non-combustible gases, such as carbon dioxide and water vapor, which can dilute the oxygen concentration in the combustion zone and slow down the combustion reaction. For example, Ge et al. prepared a MOF flame retardant containing a phosphazene ring and studied its effect on the flame retardancy of epoxy resin[73] (Fig. 7). The carbon layer or glassy layer formed by these inorganic materials at high temperature can be used as thermal shielding to isolate heat transfer and reduce the temperature of the composite surface.

At the same time, some metal oxides and inorganic salt flame retardants can also interrupt the chain reaction of free radicals in the combustion process through catalysis, thereby further inhibiting the spread of flame. Peng et al. synthesized metal-based Schiff-based cyclic polyphosphazene microspheres based on polyoxometalates and applied them to the flame retardant modification of epoxy resin, which significantly improved its flame retardancy[74]. These studies have shown that inorganic flame retardants have a significant effect on improving the flame retardant properties of epoxy resin composites. Kamalipour et al. studied the decomposition kinetics of a phosphorus-containing flame retardant latent curing agent on a package of epoxy resin system, and found that it can effectively decompose at high temperatures to produce non-combustible gases, thereby inhibiting flame propagation[75]. Liu et al. developed a new type of epoxy resin system, which contains bismaleimide and DOPO-based flame retardants. The system not only has excellent flame retardant properties, but also maintains good toughness[76].

These studies further confirmed the important role of inorganic flame retardants in improving the flame retardancy of epoxy resin composites, and provided strong technical support for the development and application of high-performance composites. The various flame retardant mechanisms of inorganic flame retardants, including gas dilution, thermal shielding, and catalytic interruption of free radical chain reaction, make them an ideal choice to improve the fire safety of epoxy resin composites.

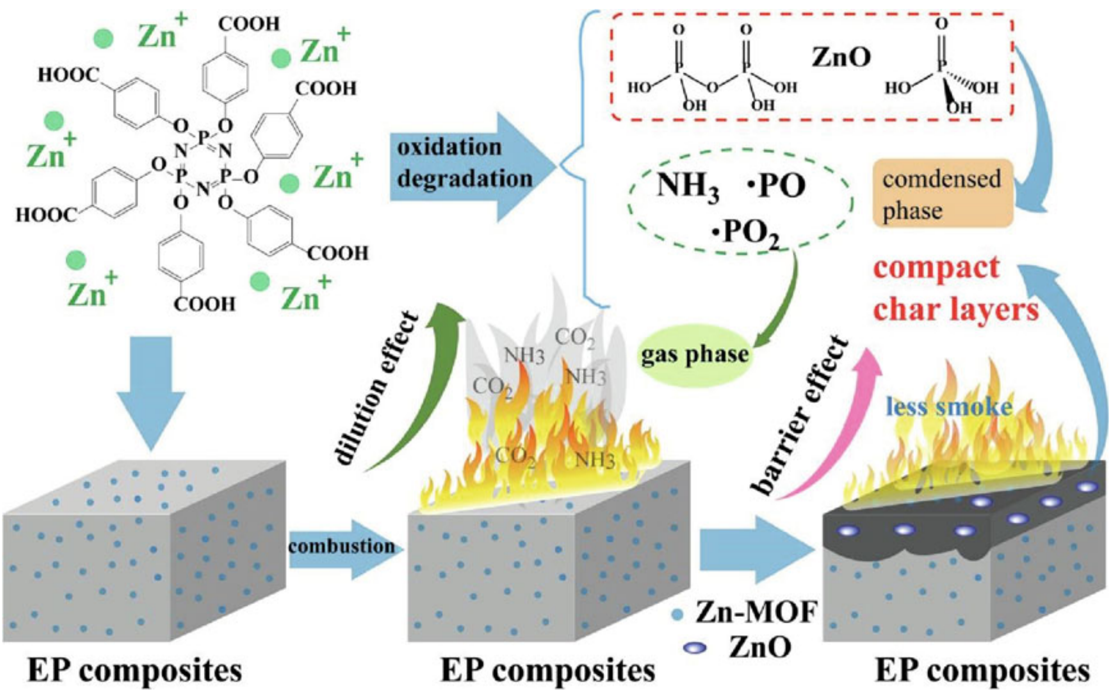

Figure 7. Schematic diagram of the synthetic route of HNT@PPZ[73]. (Copyright 2023, Elsevier.)

THE RELATIONSHIP BETWEEN THE TEST METHOD AND THE MECHANISM

To comprehensively evaluate the flame retardancy of epoxy resin and its composites, the commonly used test methods include UL-94 vertical combustion test (UL-94), limiting oxygen index test (LOI), and cone calorimeter test (CC). Different test methods can provide flame retardant performance data from different angles and are closely related to the flame retardant mechanism.

Flame retardant performance test method

UL-94 vertical burning test is the most commonly used flame retardant rating evaluation method, which is mainly used to evaluate the combustion behavior of materials under the action of combustion sources, including combustion duration, droplet situation, and self-extinguishing ability. According to the test results, the material can be classified as V-0 (highest grade), V-1 or V-2. The test mainly reflects the droplet behavior and surface carbonization ability of the material. For epoxy resins using char-forming flame retardants (such as phosphorus-nitrogen synergistic flame retardant systems), UL-94 tests can verify whether they can quickly form a stable carbon layer during combustion, thereby preventing flame propagation.

The limiting oxygen index (LOI) test is used to determine the minimum combustion-supporting oxygen concentration of the material in the air (usually expressed as %). The higher the LOI value is, the less likely the material is to burn in a normal air environment[77]. For flame retardants with gas phase flame retardant mechanism (such as phosphorus flame retardants or silicone flame retardants), the change of LOI can reflect its gas phase flame retardant effect, that is, by releasing phosphoric acid, siloxane or other gas phase active substances to inhibit free radical chain combustion reaction, thereby improving flame retardant performance.

Cone Calorimeter (CC) test is an important flame retardant performance evaluation tool, which can measure the key parameters such as heat release rate (HRR), total heat release (THR), smoke generation rate (SPR), and carbon layer structure of materials under specific thermal radiation conditions[78]. The low HRR value indicates that the material has good flame-retardant properties. For example, the addition of nanofillers (such as layered double hydroxides, LDH) can effectively reduce HRR[79], indicating that it can form an effective thermal insulation layer. Smoke generation is one of the important factors leading to casualties in fires. The epoxy resin with phosphorus-silicon synergistic flame retardant showed a lower SPR in the CC test, indicating that it can effectively reduce the formation of combustible gases and smoke during combustion. The residual carbon layer of the sample after CC test can reflect the charring ability of the flame retardant[80]. The high-quality carbon layer helps to isolate oxygen and heat and enhance the flame retardant effect of the material. For example, the composite flame retardant system containing graphene or carbon nanotubes can form a dense carbon layer after combustion, which improves the fire resistance of the material.

Combination with flame retardant mechanism

Different flame retardant mechanisms can be verified by the above test methods. For example, the condensed phase flame retardant mechanism (such as char-forming flame retardant) can be evaluated by the formation of char layer in UL-94, the increase of LOI, and the carbon residue rate in CC test. The gas-phase flame retardant mechanism (such as phosphorus-based or silicon-based flame retardants) can be demonstrated by LOI changes, HRR reduction, and SPR reduction. The synergistic flame retardant mechanism (such as the combination of nanofillers and traditional flame retardants) usually exhibits low HRR, high carbon residue, and low SPR in the CC test, indicating that it plays a flame retardant role in both the gas phase and the condensed phase[81]. The flame retardant test method can not only characterize the flame retardant effect of flame retardant on epoxy resin, but also reveal its mechanism in the combustion process. Reasonable selection of test methods and analysis of experimental data will help to further optimize the flame retardant system and improve the flame retardant and fireproof performance of epoxy resin.

CONCLUSIONS AND OUTLOOK

In this paper, the application progress of three kinds of new flame retardants, nano materials, organic materials, and inorganic materials, in epoxy resin composites is reviewed. Through the comparative analysis of the synthesis methods, structural design, and application prospects of these three types of flame retardants, we can see that all kinds of flame retardants have their unique advantages and limitations. Nanomaterials such as layered double hydroxides (LDHs), graphene, and carbon nanotubes offer excellent flame retardancy by forming a dense char layer, which acts as a physical barrier that prevents heat and oxygen transfer. Moreover, they can enhance the mechanical and thermal stability of the epoxy resin. However, the uniform dispersion of these nanomaterials within the polymer matrix remains a significant challenge, often resulting in agglomeration, which reduces their effectiveness. Organic Flame Retardants, such as Phosphorus-containing and nitrogen-based flame retardants, provide enhanced char formation and free radical quenching in the gas phase. They also offer high compatibility with epoxy matrices, leading to minimal impact on mechanical properties. Nonetheless, some organic flame retardants may generate volatile by-products during combustion, potentially compromising environmental safety. Inorganic Flame Retardants such as aluminum hydroxide (ATH) and magnesium hydroxide (MH) are cost-effective and highly thermally stable, making them attractive for large-scale applications. These flame retardants primarily act by releasing water molecules to dilute flammable gases and cool the polymer matrix. However, a higher loading percentage is usually required to achieve sufficient flame retardancy, which can adversely affect the mechanical and processing properties of the epoxy resin. In the future, researchers need to continue to optimize the structural design of flame retardants, improve their flame retardant effect, and reduce costs to meet the needs of different application fields. In addition, through in-depth study of the mechanism of action of flame retardants, it can provide a theoretical basis and practical guidance for further improving the flame retardancy of EP.

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