

New Progress in the Application of Flame-Retardant Modified Epoxy Resins and Fire-Retardant Coatings

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Abstract: Due to the enhancement of people's environmental awareness, flame-retardant epoxy resin (EP) tends to be non-toxic, efficient, and multi-functional, and its development is systematic. At present, many new flame retardants or intrinsic modification methods reported in studies can effectively improve the flame retardability and thermal stability of EP. However, many aspects still need to be further improved. In this review, the flame-retardant mechanism and method of flame-retardant epoxy resins are briefly analyzed. The research progress of the flame-retardant modification of epoxy resin by physical addition and chemical reaction is summarized and discussed. Furthermore, the research trend of flame-retardant epoxy resin in the field of fire-protective coatings is discussed, and future problems in this field are put forward. This work may provide some new insights for the design of multi-functional integrated epoxy resin fireproof coatings.

Keywords: epoxy resin; flame retardant; coating



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1. Introduction

Since the discovery of polymer materials, they have appeared in various fields of modern human life [1,2]. However, high flammability and poor thermal stability greatly limit their applications in some situations [3,4], as they will burn and release a lot of smoke and heat so long as they are exposed to enough energy [5]. According to reports, about 5000 people in Europe and 4000 people in the United States die in fires every year. The direct economic losses caused by these fire accidents are estimated at 0.3% of GDP [6]. Recently, fire safety authorities have stated that it is very necessary to apply suitable materials in different environments, which has led to stricter requirements on the flame retardancy of materials under certain conditions [7].

As an important thermosetting polymer material, epoxy resin (EP) has many advantages, such as high mechanical strength, excellent adhesion, chemical resistance, and electrical insulation, which makes it widely used in various industrial fields of construction, automotive, coatings, electronics, and aerospace [8–11]. Nevertheless, EP has a limiting oxygen index (LOI) of only about 19.8%. During the combustion process, large amounts of heat and harmful smoke will be released, which may cause huge casualties and property losses. At the same time, generated molten droplets can easily lead to the rapid spread of a fire, which is an important factor limiting the practical application of EP. For example, in the electrical and electronic industries, strict flame-retardant requirements are usually required, such as needing to reach the V-0 level in the vertical burning test. Therefore, there is an urgent need to develop high-performance flame-retardant materials, including high-efficiency flame retardants (FRs) and thermosetting flame-retardant materials.

Flame-retardant additives, especially halogen-based flame retardants, are considered to be the most effective fillers to improve the flame-retardant properties of EP. However, with the enhancement of human awareness of environmental protection, the release of toxic smoke and bromide pollution during the use of halogen flame retardants has become a more and more prominent concern [12,13]. Therefore, for the consideration of environmental protection, some halogen flame retardants are gradually being eliminated, and some halogen-free flame retardants and more environmentally friendly flame-retardant modification methods have emerged as the times require. In this review, two flame-retardant mechanisms are briefly introduced, and two flame-retardant modification methods (including physical addition and chemical reaction) for epoxy resin systems are summarized. After that, the future development direction of flame-retardant epoxy resin in the field of flame-retardant coating and the urgent problems are laid out.

2. Flame-Retardant Mechanism

The combustion of a polymer is a multistage process, including complex chemical and physical interactions [14]. The supply of heat, fuel, and oxygen are the three necessary factors required to maintain the combustion cycle [15]. Generally, the combustion process of a polymer is divided into four stages: heat, pyrolysis, ignition, and combustion [16]. Firstly, the polymer is warmed to a certain temperature by a heat source, and the backbone of the polymer begins to break and decompose, after which the following types of products may be formed [7]: (1) combustible gases, such as CO, methane, and ethane; (2) molten fluid produced by thermal decomposition of polymers; (3) incombustible gases such as CO_2 ; (4) fine solid particles composed of polymer fragments or soot; and (5) carbonaceous residues. Afterwards, when the concentration and temperature of released combustible gas reach certain values, they ignite spontaneously in the presence of air. Finally, great amounts of active free radicals such as HO• and O• generated by combustion participate in the chain reaction, accompanied by continuous heat release. Under the influence of heat transfer processes, new decomposition reactions are induced in the polymer, and more combustibles are produced. The combustion cycle is thus maintained [17] until all combustible materials are exhausted without external interruption.

The generation of extensive volumes of flammable gas is one of the direct reasons for increasing the combustibility of polymers; the other is the thermal fluid produced by thermal decomposition. Although not as flammable as gas, the flowing part can spread heat to adjacent parts. Therefore, reducing the release of flammable gases or preventing the spread of flames are the most essential ways to achieve flame retardancy. For the most part, on the basis of understanding polymer combustion, the combustion can be suppressed by breaking the combustion cycle with different methods (see Figure 1b)): (a) reducing heat transfer (the endothermic decomposition of some flame retardants causes a temperature decrease by heat consumption); (b) reducing the release of combustible gase (diluting combustible gases by adding flame retardants to produce inert, non-flammable gases); and (c) obstructing oxygen contact with flames (by forming a carbonaceous layer through the cross-linking reactions of flame retardants or the polymer matrix) [12].

Available studies have shown that there are two main flame-retardant mechanisms for the inhibition of polymer combustion:

 Condensed phase inhibition, which involves the change of polymer structure after combustion. As the combustion reaction progresses, the polymer gradually forms a low-thickness, high-porosity residual carbonaceous structure. The carbon residue layer has important functions, including protecting the integrity of the matrix structure, isolating the flame contact, and preventing the flame from spreading further. However, the generation of char residues is occasionally accompanied by a violent combustion process and produces a large amount of smoke;



Figure 1. (a) Fire-retardant methods and (b) schematic diagram of the flame-retardant mechanism.

Gas phase suppression, which involves the release of incombustible gases such as H_2O and CO_2 to dilute the concentration of flammable gases or to interfere with the chemical reactions of flame combustion. Inorganic hydroxides and halogen flame retardants are the most representative examples of using this mechanism. Such as the dilution effect of H_2O produced by the thermal decomposition of magnesium hydroxide [18]. And free radical inhibitors formed by volatilization of halogen flame retardants can convert highly active $H \bullet$ and $HO \bullet$ into low-activity $X \bullet$ to inhibit free radical reaction [19]. As shown in Reactions (1)–(4), this conversion first begins with the release of a halogen atom (1), which then reacts with the fuel to produce hydrogen halide (2). The hydrogen halide is believed to be the true combustion inhibitor by disrupting the chain reaction (3,4) [20]. Reactions (1)–(4), free radical inhibition reaction.

$$MX \to M \bullet + X \bullet \tag{1}$$

$$X \bullet + RH \to R \bullet + HX \tag{2}$$

$$H\bullet + HX \to H_2 + X\bullet \tag{3}$$

$$HO\bullet + HX \to H_2O + X\bullet \tag{4}$$

3. Different Flame-Retardant Modification Methods

Generally, there are two main methods to improve the flame retardancy of polymer materials: the physical addition of flame retardants and chemical reaction modification [21]. Among them, the addition of flame retardants will greatly improve the flame-retardant performance of polymer materials and extend the survival time in the flame by three times [3].

3.1. Physical Additive Flame-Retardant Method

For epoxy resin, the necessary flame-retardant modification can broaden its application potential in various fields [22]. The flame-retardant performance of epoxy resin is related to chemical structure and flame-retardant formulation. Halogen flame retardants, which are widely used, can improve the flame retardancy of polymers without reducing their physical properties. However, no matter what conditions are applied, the toxic substances produced in the firing process of composite materials containing halogen may cause serious environmental pollution [23]. Therefore, due to the awareness of environmental protection and health, halogen flame retardants have gradually been replaced by other more environmentally friendly and safer flame retardants [24]. As shown in Table 1, the common flame retardants used in epoxy resin systems include silicon-containing compounds, phosphorus/nitrogen compounds, inorganic hydroxides, and carbon-based

FRs **Common Example** Features References Siloxane (POSS, PDMS) Forms a protective char Layered silicate (Wollastonite, Decomposition endothermic Silicon-containing compounds [25-32] Montmorillonite, Kaolin) Releases non-flammable gases SiO₂ Green Phosphate (Polyphosphate) Phosphorous derivatives Promotes char formation Phosphorus, nitrogen (Phosphaphenanthrene, Releases non-flammable gases [33-39] compounds Phosphazene) Scavenge active free radicals Melamine (MLM) Strong synergy Phosphorus/nitrogen synergistic FRs Inert carbon residue Magnesium hydroxide (MH) Decomposition absorbs heat and Inorganic hydroxides [40-44]Aluminium hydroxide (ATH) releases H₂O Low cost, non-toxic Surface protection Carbon nanotubes (CNTs) Carbon-based materials Expandable graphite (EG) [45-51] Improves Tg Graphene, Oxidized graphite Promotes char formation

matrices and the intended use.

 Table 1. Different types of flame-retardant additives applied to the EP system.

materials. How to choose the appropriate flame retardants depends on the different resin

3.1.1. POSS

Silicon-based flame retardants, including siloxane [28], layered silicate [29], and SiO_{2} [30–32], have been at the forefront of flame-retardant additives due to their high versatility, compatibility, low toxicity, and environmentally protective qualities [25]. During combustion, silicon flame-retardant pyrolysis generates non-combustible substances such as SiO₂, which promotes the formation of a highly thermally stable char layer, inhibits further decomposition of the underlying polymer, and reduces the rate of heat release. Furthermore, silicon-based flame retardants are considered one of the most promising flame retardants because they do not produce toxic gases and fumes [26]. Among the various silicon-based flame retardants applied to EP, polyhedral oligomeric silsesquioxane (POSS) is one of the most studied structures in recent years. POSS is a well-defined compound consisting of a Si-O framework with the formula $(RsiO_{3/2})n (n = 6, 8, 10, ...)$ (Figure 2) [27]. This special composition structure can significantly improve its thermal performance and flame retardancy [52,53]. The combustion is retarded through both char formation in the condensed phase and trapping of dynamic radicals in the vapor phase if silicone flame retardants are functionalized by phosphorus or nitrogen. However, most reports pay more attention to the effect of POSS on the mechanical and thermal properties of epoxy resins, while less attention is paid to the fire performance of materials [54].



Figure 2. Polyhedral oligomeric sililoxane (POSS) [27].

An article reported [55] the effects of POSS with three different structures, octaphenyl POSS, glycidyl oxypropyl heptyl benzene POSS, and glycidyl oxypropyl heptaisobutyl POSS, on the flame-retardant properties of epoxy resin (Figure 3). The PHRR of the composite samples doped with different POSS decreased by 34%, 40%, and 25%, respectively. Among them, the cross-section of the carbon residue after burning the glycidyloxypropylheptylbenzene POSS/EP sample was a sponge-like structure with an outstanding heat insulation effect. This study demonstrates the potential of POSS as an efficient flame retardant for epoxy resins.



Figure 3. Octaphenyl-POSS (**left**), glycidyloxypropyl-heptaphenyl-POSS (**middle**), and glycidyloxypropyl-heptaisobutyl-POSS (**right**). (With permission from Ref. [55]; License number: 5617501151054, 2023, Elsevier).

However, the improvement of the flame-retardant properties of the epoxy resin system with a single use of POSS is limited; a more effective method, which has been widely reported, is to modify POSS by introducing other flame-retardant elements or compounding with other flame retardants. Due to the unique structure of polyhedral oligomeric silsesquioxane (POSS) and the synergism of Si and P in the structure, the method of introducing phosphorus element into POSS to form a novel flame retardant has attracted much attention [56,57]. Researchers also claimed that phosphorous derivatives of POSS [58,59] are a new trend in the development of flame-retardant candidates for polymer matrices.

For example, it was reported that the flame-retardant D-POSS for EP was prepared from aminopropylisobutyl POSS and diphenylphosphonyl chloride [60] (Figure 4a). The epoxy resin containing 4 wt% D-POSS reached an LOI value of 29.0% and passed UL94 V-1 grade, and PHRR, THR, and total smoke production were decreased by 35.3%, 30.3%, and 38.3%, respectively. Both the diphenylphosphine group and the POSS group in D-POSS had a strong synergistic effect in controlling PHRR, THR, and smoke production while promoting the carbonization of EP to form an expanded char layer. It is worth noting that some white silica was enriched on the surface of the residue (Figure 4c). White silica and expanded internal coke formed a double carbon layer that blocks heat transfer and improves the flame retardancy of EP composites. Similarly, Liu et al. [61] successfully synthesized a Si/P synergistic flame-retardant POSS-bisDOPO using DOPO, POM, and POSS as raw materials (Figure 5). The surfactant-like structure of POSS-bisDOPO has excellent self-assembly ability, which significantly improves the dispersion uniformity in EP. The EP, with the addition of 20 wt% POSS-bisDOPO, achieved an LOI value of 34.5%. In addition, the mechanical properties of EP were significantly improved due to the self-assembly of POSS-bisDOPO.

In addition to P and Si, Si and N also have an excellent synergistic effect. As shown in Figure 6 [62], two kinds of nitrogenous polyhedral oligomeric siloxanes (N-POSSs) were prepared by using side chain branches with amino groups in POSS, and the dispersibility, thermal stability, and flame-retardant properties of the two kinds of POSS/EP composites were studied. The results showed that N-POSSs containing Si and N formed a composite-stable, dense carbon layer rich in graphite, Si-C, and Si-N during the combustion process, which effectively suppressed the release of combustible organic volatiles and the generation

of smoke (As shown in Table 2, p-SPR, P-COP, and p-CO₂P). At the same time, the PHRR of the composite materials was decreased by 46.1% and 60.6%, respectively, compared with pure EP (Table 2), and the synergistic flame-retardant effect was remarkable.



Figure 4. (a) The synthesis of D-POSS; (b) HRR curve (A) and THR curve (B); and (c) the SEM images of residues: (A) Pure EP; (B) 4%D-POSS/EP external; and (C) 4% DPOSS/EP internal. (With permission from Ref. [60]; License number: 5617510624430, 2023, John Wiley and Sons).



Figure 5. (a) The synthesis of POSS-bisDOPO and (b) preparation of POSS-bisDOPO-modified epoxy resin. (With permission from Ref. [61]; License number: 1390727-1, 2023, Royal Society of Chemistry).



Figure 6. (Left) The synthetic process of AEAP-POSS and AP-POSS; (**Right**) digital photos of the cone calorimetry test samples (**A**–**C**) and char residues after the cone calorimeter tests (**A1,B1,C1**); SEM images of the char residue after cone calorimeter tests: EP (**A2,A3**), EP/AEAP-POSS (**B2,B3**), and EP/AP-POSS (**C2,C3**). (With permission from Ref. [62]; License number: 5617531324215, 2023, Elsevier).

Table 2. Cone calorimeter data of EP, EP/AEAP-POSS, and EP/AP-POSS composites (part).

Samples	TTI (S)	p-HRR (KW/m²)	THR (MJ/m ²)	p-SPR (m²/s)	p-COP (g/s)	p-CO ₂ P (g/s)	Residue (wt%)	LOI (%)
EP	27 ± 2	2554 ± 35	116.9 ± 8.3	0.44 ± 0.03	0.053 ± 0.003	1.37 ± 0.05	3.40 ± 0.12	20.4 ± 0.2
EP/AEAP-POSS	26 ± 1	1376 ± 26	103.3 ± 6.2	0.29 ± 0.01	0.029 ± 0.002	0.80 ± 0.04	6.15 ± 0.08	23.2 ± 0.1
EP/AP-POSS	25 ± 1	1005 ± 18	95.8 ± 4.1	0.21 ± 0.01	0.021 ± 0.001	0.56 ± 0.02	8.17 ± 0.04	24.5 ± 0.1

3.1.2. DOPO

Phosphorus-based flame retardants are the most important halogen-free flame retardants used to improve the flame-retardant properties of EP. Common phosphorusbased flame retardants include phosphorus-containing derivatives (phosphazene, phosphaphenanthrene) [33,34,36], phosphate esters [63], and polyphosphates [35,64,65]. For the consideration of environmental protection, phosphorus-based flame retardants have more advantages than halogen-based flame retardants. The main flame-retardant mechanism involved is to suppress flame combustion and reduce heat release, control melt flow, and promote char layer formation. The free radicals (PO₂•, PO•, and HPO•) generated by the decomposition of phosphorus-based flame retardants have a strong scavenging effect on H• and OH• in the gas phase, which effectively extinguishes the flame and reduces the reaction activity (See Figure 7) [66]. Furthermore, phosphoric acid and polyphosphoric acid produced by the decomposition of some phosphorus-containing compounds form a melt-adhesive layer that protects the polymer surface and prevents oxygen penetration. The combustion of nitrogen-based flame retardants not only promotes the formation of insulating layers but also releases inert gases to dilute the combustion atmosphere and often co-occurs with phosphorus-based flame retardants [67], which promotes the development of some phosphorus-nitrogen synergistic new flame retardants [37,39].

9,10-dihydro-9-oxaze-10-phosphoxene-10-oxide (DOPO) and its derivatives have been widely used in EP systems due to their advantages of thermal stability, high flame-retardant efficiency, and strong design ability [13,68,69]. The new multi-component phosphorus-based flame retardant can be prepared by combining nitrogen, silicon, boron, sulfur, and other elements with the phosphorus phenanthene group as the reaction site for molecular design [70,71].





As mentioned above, the multi-element synergistic flame retardant formed by P and Si elements has an excellent flame-retardant effect. Figure 8 shows the structural formulas of two flame retardants (DOPO-TMDS and DOPO-DMDP) containing phosphorus phenanthene/siloxane groups, which are applied to the EP system [72]. When DOPO-TMDS content was 20 wt%, the LOI of flame-retardant epoxy resin was as high as 33% and passed the vertical burning test V-0 rating, and PHRR and THR were greatly reduced. In contrast, 24 wt% DOPO-DMDP was required to achieve a LOI value of 32% and obtain UL94 V-0 grade. In addition, although the addition of DOPO-TMDS and DOPO-DMDP enhanced the mechanical strength of the EP, a decrease in Tg was observed due to the presence of the siloxane structure.



Figure 8. Structures of DOPO-TMDS and DOPO-DMDP. (With permission from Ref. [72]; License number: 5617560166971, 2023, Springer Nature).

Huo et al. [73,74] designed two kinds of highly efficient flame-retardant additives, DOPO-TMT and DMT, containing DOPO and maleimide groups for EP systems (Figure 9a,d). In DOPO-TMT, phosphenanthrene and triazine were flame-retardant groups, and in DMT, phosphenanthrene and triazine-trione were flame-retardant groups. When the phosphorus concentration was only 1.25 wt%, the EP/DOPO-TMT-1.25 system passed UL94 V-0 grade with a LOI of 37.5%. The PHRR and THR values of EP/DOPO-TMT and EP/DMT samples gradually decreased with the increase in phosphorus content. Compared with EP, the PHRR of EP/DOPO-TMT-1.25 was reduced by 54%, while that of EP/DMT-1.25 was reduced by 59%, which shows a higher flame retardancy. DOPO acted with nitrogen-containing groups simultaneously in the gas and condensed phase. In the condensed phase, both DOPO and nitrogen-containing groups contributed to the formation of expanded and dense carbon residue, which acts as a fire barrier (Figure 9c,f). In the gas phase, DOPO groups produced free radical inhibitors to quench reactive free radicals, and the nitrogen-containing groups



released inert gas to dilute the combustible gas by pyrolysis. This work provided strong evidence for the synergistic effect of phosphorus and nitrogen.

Figure 9. (a) Structure of DOPO-TMT; (b) HRR curve for EP and EP/DOPO-TMT; (c) combustion residue of EP/DOPO-TMT-1.25; (d) structure of DMT; (e) HRR curve for EP and EP/DMT; (f) combustion residue of EP/DMT-1.25. (a–c) [73] and (d–f). (With permission from Ref. [74]; License number: 5617561446517, 2023, Elsevier).

The combination of phosphorus-containing flame retardants and other flame-retardant elements (nitrogen, boron, silicon) not only further improves the flame-retardant properties of flame retardants but also reduces the overall load of flame retardant in the material and maximizes the effectiveness under the same conditions [75]. Multi-component synergistic systems will become one of the possible development trends of phosphorus-based flame retardants in the future.

3.1.3. Carbon-Based Materials

The family of carbon-based nanomaterials, including carbon nanotubes (CNTs) [45,76], graphene [46,47,77], and expandable graphite (EG) [49–51], have been widely used in the preparation of polymer composites. The addition of carbon materials can not only enhance the mechanical properties of the substrate but also give the substrate excellent thermal stability, thermal or electrical conductivity, and fire resistance [78]. According to the reports, the flame-retardant mechanism of carbon-based materials mainly comes from strengthening the carbon layer and catalyzing the formation of carbon. The carbon layer formed on the heated surface of the matrix material blocked the contact between heat and oxygen, reduced the diffusion of active free radicals, and improved flame retardancy [79].

Graphene is a two-dimensional nanomaterial formed by a hexagonal network of sp² hybrid carbon atoms with high mechanical strength and specific surface area [76]. Layered graphene can be dispersed in the polymer matrix, creating a "tortuous path" effect to slow down the heat diffusion rate and matrix decomposition rate [80]. However, graphene is prone to aggregation due to its special flake-like structure and the existence of π - π interactions and van der Waals force, and untreated graphene is difficult to disperse evenly in the polymer [81]. Therefore, in order to solve the problem of dispersion, many scholars

often treat graphite to obtain graphene oxide (GO) to improve the interface binding force between graphene and epoxy resin first [45]. Then, GO is modified by chemical grafting or electrostatic adsorption of nanoparticles [82,83] to improve the dispersion and bring excellent flame retardancy to the graphene/epoxy resin system. For example, Li et al. [84] grafted 2-(diphenylphosphine) ethyl triethoxysilane (DPPES) onto the surface of graphene oxide nanosheets (GON) by condensation reaction. The addition of DPPES-GON (up to 10 wt%) to neat epoxy significantly increased its thermal stability and improved the LOI by 80%.

Based on their unique structure and properties, CNTs are widely used in nanoelectronic devices, composite materials, electrical and thermal conductivity, nano-flame retardants, and other fields [85]. CNTs have the potential to improve the mechanical properties and fire resistance of epoxy resin matrices at the same time, but the difficulty of dispersion limits the load capacity of CNTs. Too low a load will lead to poor fire resistance, while too high a load will affect the mechanical properties of the composite [86]. Therefore, in order to balance the load contradiction and obtain CNTs/epoxy composites with superior mechanical properties and flame-retardant properties, reasonable modification of CNTs seems to be a feasible scheme. Wang et al. [86] performed concentrated acid oxidation and ball milling on pristine CNTs, which significantly increased the content of carbon-centered free radicals. The obtained carbon-centered free-radical-rich CNTs were used to try to improve the fire safety of a high-performance CNT/epoxy composite without sacrificing its mechanical properties. The test found that the overhanging bonds present in carbon-centered free-radical-rich CNTs had strong free radical scavenging capacity (as shown in Figure 10). This ability increased the loading of CNTs to 3 wt% with an LOI of 28.4% (LOI for pure EP was 21.9%) while enhancing mechanical properties.



Figure 10. LOI performances of the 2coCNT/epoxy and 2TcoCNT/epoxy composites (**a**); relationship between the relative free radical content of the filler and the LOI performance of the composite (**b**); free radical scavenging effect of the coCNTs during thermal decomposition of composites (**c**) [86].

Moreover, functionalized grafting or inorganic filler loading of CNTs are also the modification approaches that have recently attracted much attention from researchers. It has been reported [87,88] that grafting functionalized siloxane (PDMA) onto CNTs can enhance the interfacial adhesion between CNTs and the polymer matrix, improve their dispersion in epoxy resins, and contribute to enhancing the flame-retardant properties of composites. Dopo-functionalized multiwalled carbon nanotubes (MWCNT) were ob-

tained by grafting 10-(2,5-dihydroxyphenyl)-9,10-dihydro-9-oxygen-10-phospho-10-oxide (ODOPB) onto the outer surface of acylated multiwalled carbon nanotubes (MWCNT), as shown in Figure 11 [89]. MWCNT-ODOPB was co-introduced into the epoxy matrix with aluminum diethyl phosphate as a flame-retardant filler. When MWCNT-ODOPB content was only 1 wt%, the composite system achieved a LOI value of 39.5% and passed the UL94 V-0 grade. It is mainly due to the char formation of MWCNT-ODOPB and the synergistic effect of diethylaluminum phosphate. In a simpler method [90], phosphorus-nitrogen flame retardants were coated on CNTs and combined with epoxy resin to form composite materials. The synergistic effect of phosphorus-nitrogen flame retardants and nanomaterials endowed composites with excellent flame-retardant properties.





Typically, the fire performance of the epoxy resin was effectively improved by the organic combination of inorganic nanoclay and carbon nanotubes [91]. Lee et al. [92] studied the effect of adding fluoromontmorillonite-containing MMT/MWCNT additives on EP. The mechanism of flame retardants was analyzed from three aspects, and conclusions were drawn: ① Fluorinated MMT/MWCNT enhanced the dispersion in epoxy resin. ② The addition of MWCNT reduced the degradation rate of epoxy resin and increased carbon residue yield (increased from 9.1% to 15.4%). Meanwhile, due to the formation of gel epoxy resin during combustion and the flame retardation of MWCNTs, the fire was hindered and had difficulty spreading, as shown in Figure 12c. ③ The exfoliated MMT acted as a heat storage medium to inhibit the heat transfer inside the epoxy resin, as shown in Figure 12d. Under the joint action of the three aspects, the flame-retardant performance of the epoxy resin was significantly improved, and the LOI value was increased from 21% to 31%.

As another well-known carbon-based material, expandable graphite (EG) is a typical expansion flame retardant with an inherent self-expanding graphite flake [93]. When heated, it can expand and form a worm-like carbon layer that acts as a physical barrier to heat transfer, providing the polymer with fire-protection properties [50]. In addition, although EG contributes to the formation of carbon, the carbon structure is not tightly enough [49]. Therefore, EG will often be used in conjunction with other materials [23]. Yang et al. [94] reported the effect of DOPO or 6-phenoxy-cyclotriphosphonitrile (HPCP) and EG as flame retardants on the flame retardancy of epoxy resins. They found that the residual chars of EP/EG/DOPO and EP/EG/HPCP composites exhibited more compact and tough structures composed of worm-like graphite and a carbonized resin matrix.



Figure 12. The mechanism of flame retardant additives: (**a**) Oxygen free radicals initiate high temperature thermal oxidation of polymers; (**b**) Oxygen radicals was hindered by the formation of MWCNT/carbon char protective film; (**c**) Formation of internal network structure of MWCNT/EP composites; (**d**) Formation of internal network structure of MMT/EP composites. (With permission from Ref. [92]; License number: 5617570717974, 2023, Elsevier).

3.2. Reactive Flame-Retardant Method

Although adding a flame retardant to improve the flame-retardant properties of polymer materials is a relatively mature method, the disadvantages of the additive system are obvious, including reduced mechanical properties of the resin and poor durability in long-term use. And what is worse is that as the material degrades, the flame retardant migrates, and there will be seepage, which will lead to the loss of flame retardancy and environmental pollution. Conversely, chemical reaction flame-retardant modification is achieved by functional modification of the epoxy molecular chain or curing agent. The flame-retardant elements are connected in the resin cross-linking network in the form of chemical bonds so that the flame-retardant elements have difficulty migrating and seeping, and the flame-retardant ability is more durable.

Given the above, phosphorus flame retardant is an important halogen-free flame retardant, which has a flame-retardant effect in both condensed and gaseous phases [95]. As early as 20 years ago, researchers proposed the idea of introducing phosphorus-containing groups in the main or side chains of epoxy resins to improve the flammability of the resin itself (as shown in Figure 13). By introducing a low amount of flame-retardant elements (such as phosphorus, nitrogen, silicon, etc.) into the epoxy resin chain, the LOI value, UL94 level, and thermal stability are improved, and the PHRR and THR are reduced without affecting the mechanical and physical properties. Huo [66], Dagdag [33], and Zhi [16] made detailed reviews on this aspect.

Currently, 90% of epoxy resins are bisphenol A (BPA) resins, and 67% of BPA resins are derived from petrochemical and non-renewable raw materials [96,97]. Moreover, BPA has a series of disadvantages, such as flammability, and the toxicity caused by material degradation not only destroys the ecological environment but also endangers organisms. For this reason, with the requirements of regulations and environmental protection, bio-based epoxy resin materials derived from sources such as vegetable oil [98,99], lignin [100,101], itaconic acid [102], and cardanol [103,104] have attracted attention because of the great availability of raw materials, and they have been applied in many fields such as toughening, flame retardation, and high-temperature resistance.

How to design and prepare a sustainable, biodegradable flame-retardant epoxy resin, which is expected to replace resource-limited petrochemical products, especially bisphenol A type epoxy resin (DGEBA), is one of the potential directions for the future development of constitutive flame-retardant epoxy resin. Ma et al. [105] synthesized a novel epoxy resin

(MVE) from vanillin and melamine (See Figure 14). The epoxy equivalent of MVE is about 217 g/eq. After being cured by 4,4-diaminodiphenylmethane (DDM), MVE showed better mechanical properties than DGEBA resin, and the carbon residue yield increased to 41.77%. MVE has excellent intrinsic flame retardancy and achieved a LOI value of 39.5%; THR and smoke generation rate (SPR) were reduced by 67.44% and 64.69%, respectively, which was much better than DGEBA. In addition, under suitable conditions (THF:H₂O = 6:4, 50 °C), the cured product of MVE/DDM can be completely degraded within 6 h.



Figure 13. Development of reactive phosphorous-containing flame retardants: representative phosphorous-containing epoxy resins and curing agents [66].



Figure 14. Synthesis of intermediates of vanillin derivatives. (With permission from Ref. [105]; License number: 5617580564610, 2023, Elsevier).

Diphenol acid (DPA), as a plant derivative, has been shown to be one of the sustainable alternatives to bisphenol A. A flame-retardant bio-based epoxy resin (TEBA) was synthesized from DOPO, diethanolamine, and DPA in three steps (Figure 15) [106]. Compared with the original resin, the TEBA passed UL94 V-0 grade with an LOI of 42.3%, and the PHRR, THR, and total smoke production (TSP) were decreased by 67%, 27%, and 35%, respectively. As a consequence, the presence of phosphorous and nitrogen flame-retardant elements in the molecular chain of the resin endowed TEBA-DDM with remarkable fire resistance.



Figure 15. (a) The synthesis of TEBA; (b) HRR and THR curves of the TBEA-DDM and DGEBA-DDM epoxy thermosets; (c) digital photos of epoxy thermosets char residues after the cone calorimeter test. (With permission from Ref. [106]; License number: 5617580950671, 2023, Elsevier).

4. Epoxy Fireproof Coating

Fireproof coatings are one of the important branches in the field of coatings, which are used to protect materials such as metals, polymers, textiles, and wooden structures [107]. EP is one of the most important binders in common coatings used in human production and life [108]. Generally, EP cross-links under the action of an amine curing agent to form a coating with high strength, high resistance to impact [109], and high chemical resistance, but the EP coating system also has defects such as easy combustion and poor toughness. Therefore, in order to improve upon the above problems, the existing solutions mainly include two aspects: on the one hand, starting from the molecular structure, the molecular structure of the monomer or curing agent can be optimized, and functional molecular chains at the end of the chain, such as a toughened polyurethane chain and flame-retardant silicone chain, can be inserted. On the other hand, directly filled organic or inorganic fillers can improve the mechanical, anti-corrosion, and flame-retardant properties of the EP coating.

After sorting out the reports on epoxy resin flame-retardant coatings in recent years (Table 3), it can be found that most of the research focuses on the preparation of new flame-retardant fillers, among which the modification methods include chemical reaction, organic–inorganic/inorganic–inorganic hybrids, assembly, coating, etc.

Table 3. Flame retardancy of epoxy coatings containing new flame retardants.

EPs and Flame Retardant	Composition of FRs	wt%	LOI (%)	PHRR (kW/m ²)	Residue Char * (%)	Reference
EP/FNP-Co	P, N, Co	0 2 4	24.2 27.6 30.2	988.07 930.02 791.97	19.89 26.50 27.71 (700 °C)	[110]
EP/BP@Si/CNTs	Polydopamine, KH560, Layered hexagonal BN, CNTs	0 1.5 2.0 2.5	- - -	- - -	$\begin{array}{c} 20.90 \pm 1.9 \\ 27.15 \pm 1.4 \\ 31.94 \pm 3.1 \\ 28.84 \pm 2.7 \end{array}$	[111]
EP/PZS@ZIF-67	Polyphosphazene, ZIF-67	0 1 3 5	25.5 30.1 31.2 31.9	1156.16 957.56 748.09 565.59	14.60 14.90 18.35 23.27	[112]

EPs and Flame Retardant	Composition of FRs	wt%	LOI (%)	PHRR (kW/m ²)	Residue Char * (%)	Reference
	Titanium dioxide nanotubes (TNTs),	0	-	1406	-	
EP/(CH/PT)-TNTs	Chitosan (CH), Synthetic	0.5	-	1009	-	[113]
	phosphatized chitin (PT)	2	-	719	RR (m²) Residue Char * (%) 06 - 09 - 9 - 20.6 28.8 32.2 30.5 4.2 5.71 4.9 7.15 0.7 11.71 5.1 13.49 20.1 26.9 28.8 27.6 20.5 30.3	
	Zine aluminum lawarad daubla	0	-	-	20.6	
	hydroxides (Zn-Al/LDH), Reduced 1.0	1.0	-	-	28.8	[114]
EP/Zn-AI/LDH@RGO		1.5	-	-	32.2	
		-	30.5			
		0	21.8	1304.2	5.71	[115]
ER /Sam@AlDO	Fibrous type sepiolite, AlPO ₄	5	25.2	1244.9	7.15	
Er/Sep@AlrO4		10	27.4	1130.7	11.71	
		20	30.1	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		
		0	-	-	20.1	[116]
EP/GO@M-CNTs	Polydopamine, KH550, CNTs, Graphene oxide (GO)	1.0	-	-	26.9	
		1.5	-	-	28.8	
		2.0	-	-	27.6	
	Polyethyleneimine (PEI),	0	-	-	20.5	[117]
Er/ dr@ZHS	Zinc hydroxystannate (ZHS), BN	3.0	-	-	30.3	

Table 3. Cont.

* Data were derived from TGA test curves at 800 °C unless otherwise stated.

However, with the deepening of research on fireproof materials, people now have higher and higher expectations for the service life of coatings, so the demand for multi-functional organic coatings has become more and more urgent [118]. When it is difficult for a single-performance coating to meet the application requirements in some harsh environments, flame-retardant coatings based on EP gradually developed into high-performance coatings with multiple functions such as flame retardancy and anti-corrosion or wear resistance qualities in order to extend the service life. Furthermore, the organic combination and synergy of the components may be the key to the successful preparation of multi-functional integrated fireproof coatings.

As shown in Figure 16, two kinds of silicon-sulfur multi-functional carboxyl curing agents (S-I and S-II) were synthesized from cashew phenol as raw materials by mercaptoene coupling method and applied to EP [119]. The curing agent is mixed with conventional epoxy resin instead of a traditional curing agent and coated on the steel plate to form a coating. The coatings cured by S-I and S-II still maintain excellent corrosion resistance after 1000 h of exposure to a salt spray test. Compared with the S-I coating, the S-II-cured coating exhibits high impedance values and low corrosion rates and has a higher weight loss temperature and carbon residue yield (As shown in Table 4). This is because the presence of additional functional groups in S-II increased the cross-linking density of the resin and improved the thermal stability and other coating properties.

It has been reported that the introduction of bifunctional phosphate-containing triazole derivatives (D-ATA) into the epoxy resin system through curing reactions can simultaneously improve the flame retardancy and corrosion resistance of the resin (Figure 17) [120]. In this system, the structure of triazole phosphate not only contributes to flame retardation but also effectively inhibits electrochemical corrosion. When D-ATA content was only 5 wt%, the flame-retardant epoxy resin achieved an LOI value of 33.2%, passed the UL94 V-0 grade, and residual char yield reached 16.6%. Moreover, the anti-corrosion efficiency of EP/5 wt% D-ATA was increased by 95.3% compared with pure EP. At the same time, the mechanical properties of composite epoxy thermoset materials were also improved due to the existence of hydrogen bonds and π - π interaction in D-ATA.

Porous coordination polymers (PCPs), commonly known as metal–organic frameworks (MOFs), are a new class of organic–inorganic porous structures in which metal cations serve as nodes and organic molecules serve as bridges [121]. Because of their controllable structure and easy surface functionalization, MOFs are often used to prepare MOFs/polymer nanocomposites. Additionally, MOFs have satisfactory compatibility with polymer substrates due to the presence of organic–inorganic hybrid structures [122]. The existing research reports indicate that the addition of MOFs to epoxy resins can affect various properties of epoxy resins, such as anti-corrosion [123,124], flame retardation [125–127], thermomechanical [128], and dielectric properties. Accordingly, MOFs/EP system has great potential in the preparation of multi-functional integrated coatings such as fire protection and anti-corrosion.



Figure 16. The synthesis of multi-functional carboxyl curing agent. (With permission from Ref. [119]; License number: 5617630790172, 2023, Springer Nature).

	Tl	nermal Propert	ies			Corrosion	n Properties
Coatings	T _{5%} (°C)	T _{onset} (°C)	T _{offset} (°C)	Char Yield (%)	Impedance	Icorr (A)	Corrosion Rate (mm/yr)
S-I-0.6	240	305	399	5.74	$1.71 imes 10^9$	$4.5 imes 10^{-6}$	$7.40 imes10^{-3}$
S-I-0.8	243	313	429	24.8	$1.43 imes10^{10}$	$2.74 imes10^{-7}$	$4.50 imes10^{-4}$
S-I-1.0	267	309	403	48.2	$2.02 imes 10^{10}$	$1.28 imes10^{-7}$	$2.10 imes10^{-4}$
S-II-0.6	297	351	443	29.2	$6.39 imes10^9$	$3.2 imes10^{-6}$	$5.26 imes10^{-4}$
S-II-0.8	300	363	450	47.3	$9.27 imes10^{10}$	$9.7 imes10^{-8}$	$1.60 imes10^{-4}$
S-II-1.0	335	365	453	63.1	$2.91 imes 10^{11}$	$7.47 imes 10^{-8}$	$1.45 imes 10^{-4}$

Table 4. TGA values and electrochemical parameters of coatings cured with S-I and S-II.

For example, it has been reported that an anti-corrosion coating (ZnG@ZIF-8/EP) was successfully prepared by adding MOF-based anti-corrosion materials loaded with corrosion inhibitors (ZnG@ZIF-8) to EP [129]. ZnG@ZIF-8 is uniformly dispersed in the coating system and exhibits better corrosion resistance than ZIF-8/EP, EP, and ZnG+ZIF-8/EP coatings. The mechanism study showed that the corrosion rate was delayed due to the defects, and the pores in the EP coating were fully populated by ZnG@ZIF-8. Organic ligands in the MOF structure not only help to improve compatibility but also provide flame-retardant elements or groups, including nitrogen-containing groups and aromatic structures [130]. The ligand of ZIF is composed of imidazole compounds rich in nitrogen atoms. Furthermore, it has recently been reported that nitrogen-rich MOF, when used as a flame retardant for EP, had a remarkable catalytic carbon formation ability to improve fire safety performance [131].



Figure 17. Preparation of corrosive flame-retardant multi-functional epoxy resin coating. (With permission from Ref. [120]; License number: 5617631477525, 2023, Elsevier).

The multi-functional integrated flame-retardant coating is mostly used in special conditions; in addition to the necessary fire prevention ability, it also usually has other properties such as anti-fouling, antibacterial, anti-corrosion, and wear-resistant. For example, the fireproof coating applied to a tunnel surface needs both anti-fouling and water resistance [132]. This is because the environment inside the tunnel is closed, and the oil smoke generated by the car is not easy to dissipate and adsorb on the tunnel wall surface, so the fireproof coating on the surface should have the ability to resist the adhesion of oil smoke and withstand high-pressure water cleaning. For this reason, when designing the coating formulation, nano-silica, titanium dioxide, and organosilane were introduced into the epoxy resin expansion flame-retardant system to enhance the fire protection, anti-fouling, and waterproof properties of the coating.

5. Summary and Perspectives

As one of the most important polymer materials since it was discovered by human beings, epoxy resin is widely used in various fields due to its excellent performance. However, the high flammability caused by its structure is an urgent problem for researchers to explore and solve. This review first describes the combustion process of polymer and its flame-retardant mechanism. The research progress of flame-retardant epoxy resin in recent years is summarized from two modification methods: the physical additive flame-retardant method (including silicon-, phosphorus- nitrogen- and carbon-based flame retardants) and the reactive flame-retardant method, and their advantages and disadvantages and flameretardant properties are briefly summarized. Finally, the new flame retardants used for epoxy resin flame-retardant coatings are summarized, and the development trend of epoxy flame-retardant coatings with multi-function integration of flame retardant/anti-corrosion is proposed. Although the flame-retardant chemical system has gradually matured after decades of development, the following issues still need to be further studied in the future:

 The flame-retardant life is short. With the degradation of the resin, the doped fillers will continue to overflow, losing the flame-retardant effect and easily causing environmental pollution. Therefore, green and efficient reactive flame retardants need to be further explored;

- 2. The performance is not long-lasting, which makes it difficult to meet the application requirements of special environments, especially in the application of coating preparation. Generally, harsh environments (such as aviation, aerospace, plateau, and deep-sea) will accelerate the aging of materials, so there is an urgent need to develop a series of multi-functional epoxy flame-retardant materials that have longterm durability, low-temperature mechanical properties, antibacterial and corrosion resistance, etc.;
- 3. The flame-retardant effect of multi-element coordination is much greater than that of a single element, but the high cost limits the development and application of multi-element flame retardants. Therefore, active flame retardants with cheap raw materials, simple preparation methods, and low overall costs need to be further explored. Ultimately, it will be an important research direction in the future to prepare reactive flame-retardant resins from abundant bio-based raw materials or to regulate the flame retardancy of resins through molecular structure design.

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