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Advanced Flame-Retardant Methods for Polymeric Materials

*Bo-Wen Liu, Hai-Bo Zhao, and Yu-Zhong Wang**

Most organic polymeric materials have high flammability, for which the large amounts of smoke, toxic gases, heat, and melt drips produced during their burning cause immeasurable damages to human life and property every year. Despite some desirable results having been achieved by conventional flame-retardant methods, their application is encountering more and more difficulties with the ever-increasing high flame-retardant requirements such as high flame-retardant efficiency, great persistence, low release of heat, smoke, and toxic gases, and more importantly not deteriorating or even enhancing the overall properties of polymers. Under such condition, some advanced flame-retardant methods have been developed in the past years based on "all-in-one" intumescence, nanotechnology, in situ reinforcement, intrinsic char formation, plasma treatment, biomimetic coatings, etc., which have provided potential solutions to the dilemma of conventional flame-retardant methods. This review briefly outlines the development, application, and problems of conventional flame-retardant methods, including bulk-additive, bulk-copolymerization, and surface treatment, and focuses on the raise, development, and potential application of advanced flame-retardant methods. The future development of flame-retardant methods is further discussed.

1. Introduction

Fire lights the world and human civilization; however, even today, fire disasters are still causing immeasurable damages to human life and property every year.[1] In 2020, over 250 000 fire disasters occurred in China, resulting in 1183 deaths, 775 injuries, and direct property losses of more than 4 billion yuan.[2] Under such serious condition, all industries have put forward strict flame-retardant requirements for the materials used.[3] Polymeric materials, as an inseparable fundamental materials for civilian equipment, industrial facilities, as well as medical applications,[4] are mostly highly flammable due to their organic chemical structure.[3] Upon heating, as illustrated in **Figure 1**a, polymeric materials will undergo thermal decomposition, "a process of extensive chemical species change caused by heat",[3] resulting in the formation of combustible gaseous fuel vapor, which will burn on the top of polymeric materials in the presence of heat and oxygen. The combustion of gaseous fuel vapors generates a large amount of heat, part of which feeds back to the polymeric materials, leading to further decomposition of polymeric materials and continuous generation of combustible gaseous fuel vapor. On this basis, flame retardancy can be realized in either or both of the gas phase and the condensed phase. In the gas phase, flame retardation is mainly achieved by capturing combustion free radicals, diluting combustible or combustion-supporting gases.[5] In the condensed phase, flame retardation is mainly achieved through heat absorption/heat dissipation, dripping promotion, and barrier protection effects.[6] Many flame-retardant methods have been proposed according to the above mechanism, and have achieved desirable results.

The methods for improving the flame retardancy of polymeric materials are usually based on flame-retardant modifications either in the bulk polymer matrix or on the polymer surfaces. Adding flame retardants into the polymer matrix by physic blending (Figure 1b),[7] incorporating flame-retardant monomeric units into the polymer chains (Figure 1c),[8] and constructing flame-retardant layers on the polymer surfaces (Figure 1d)[1] are the fundamental flame-retardant methods for polymeric materials. The flame-retardant modification of polymeric materials can be traced back to ancient Greece, when alum solution was first coated on the surface of wooden blockhouse (mainly consisted of cellulose, a natural polymeric material) to improve its flame-retardant performance. In the following centuries, many practical flame-retardant methods have been developed which in different degrees solved the flame-retardant issues of polymers. With the rapid development of modern society, higher and higher flame-retardant requirements have been put forward, making conventional flame-retardant methods insufficient for some practical applications. Under such circumstances, some advanced flame-retardant methods have been developed in the past years, aiming to address the issues of conventional flame-retardant methods or provide new strategy for the design of flame-retardant polymeric materials.

This review briefly outlines the development, application, and dilemma of conventional flame-retardant methods that are most frequently used, and focuses on the raise, development, and potential application of advanced flame-retardant methods. The future of flame-retardant methods is discussed on the basis of both the

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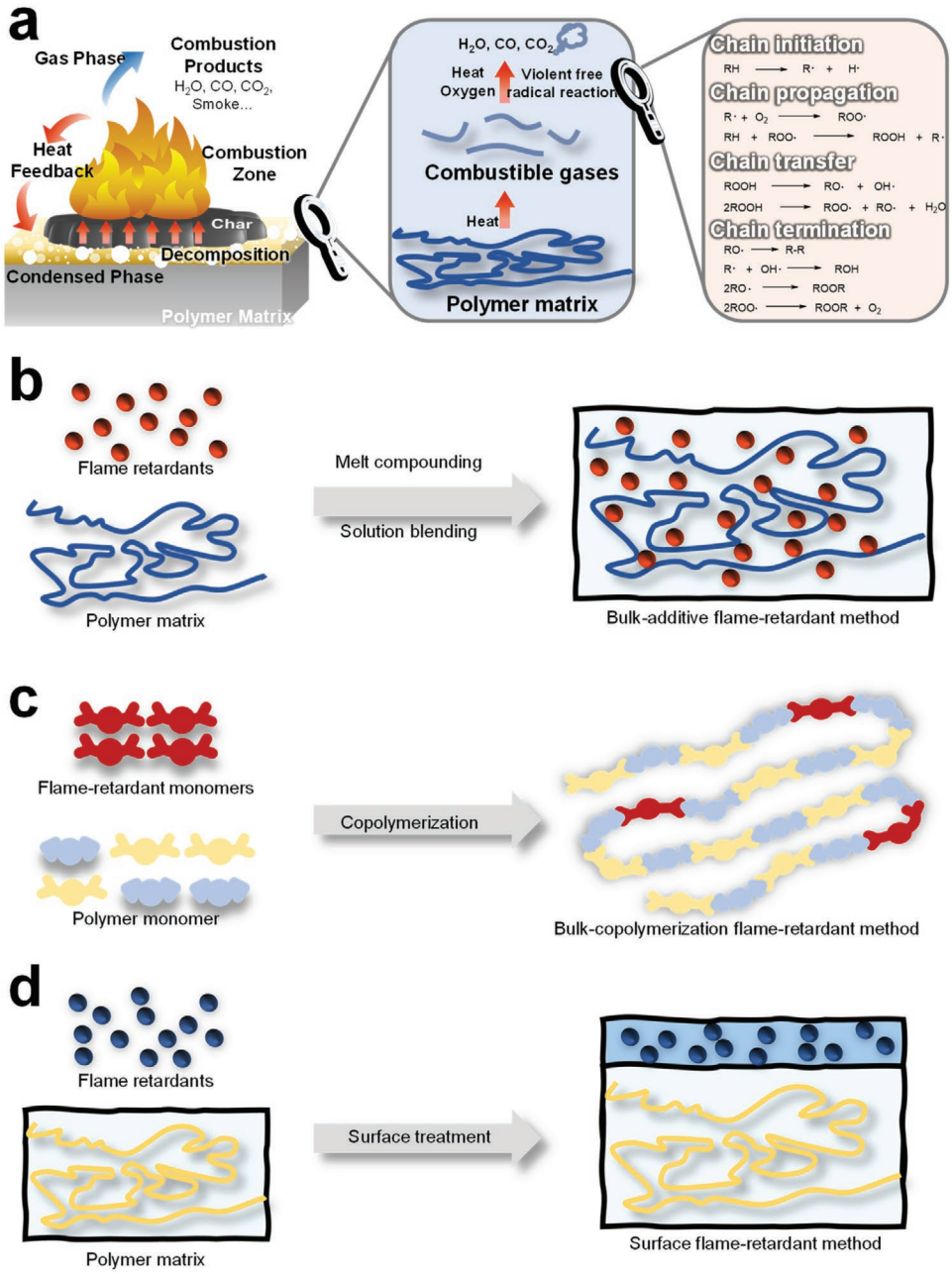


Figure 1. a) Burning process of polymeric materials. b–d) A schematic illustration of the bulk-additive (b), bulk-copolymerization (c), and surface treatment (d) flame-retardant methods.

scientific fundaments and industrial applicability. The influence of government laws and environmental issues on the development of flame-retardant methods have also been discussed.

2. Bulk-Additive Flame-Retardant Methods

Physically blending flame retardants into the polymer matrix is one of the earliest flame-retardant methods. This method does not require the change of the synthetic process of polymer and is simple to operate, thus is highly favored in industrial applications. After the fast development in the past decades, various kinds of flame retardants have been developed based on different flame-retardant elements and mechanism, and some advanced methods were also proposed. In this section, the authors will briefly discuss the conventional additive flame-retardant methods with typical representatives, and will focus on the development of advanced additive flame-retardant methods.

2.1. Conventional Bulk-Additive Flame-Retardant Methods

2.1.1. Inorganic Flame Retardants

Inorganic flame-retardant fillers are widely used in various kinds of polymeric materials due to their low cost, low

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toxicity, low corrosivity and low smoke release, and account for 40–50% in mass of flame retardants sold globally.[3,9] Among them, metal hydroxides (such as aluminum hydroxide (ATH), magnesium hydroxide (MH)),[10] metal hydroxy carbonates[10a,11] are predominately used. The flame-retardant actions of a series of mineral fillers such as ATH, MH, magnesium carbonate, etc., were compared by Hull et al.[12] Upon heating, these metal compounds will undergo endothermic decomposition with the release of noncombustible gases (water vapor and/or carbon dioxide), for which the heat-sink effect, the generated protective layer and the dilution effect together contribute to the flame-retardant performance. Unfortunately, the above fillers usually exhibit low flame-retardant efficiency, thus high loading is needed for decent flame retardancy, which leads to the deterioration of mechanical properties of the final products. Metal oxides are mainly used as synergists to commercial flame retardants. For instance, the synergism between antimony trioxide (Sb_2O_3) and halogen-containing flame retardants has been proved in various polymers.[13] The synergism was observed in both the condensed phase and the gas phase, but mainly in the gas phase.[13] Zinc oxide (ZnO) shows the effect of promoting char formation, and is generally used in combination with commercial intumescent flame retardants.[14]

Phosphorus-containing inorganic flame retardants have also found wide application. Red phosphorus (RP), the red allotropic of elemental phosphorus, is a classic inorganic phosphorus-containing flame retardant with relatively low toxicity, which shows high flame-retardant efficiency in both the gas phase and the condensed phase.[15] In the gas phase, the generated PO· radical quenches the combustion free radicals and efficiently stops the fire; in the condensed phase, red phosphorus is oxidized to form phosphoric acid, which promotes the char formation of the polymer matrix and inhibits the heat transfer and release of combustible volatiles.[16] However, owing to the many drawbacks of RP, such as water absorption (during which toxic phosphine is released), easy oxidation, potential flammability, bad compatibility with most polymers, and poor thermal stability, RP is usually used after microencapsulation.[7,17] Metal phosphate/ phosphinates, with high phosphorus content, good thermal stability and low affinity to moisture,[18] are efficient flame retardants for thermoplastic polymers, and are the most commercially successful flame retardants for polyesters and polyamides (the OP series flame retardants of Clariant, Germany).[19] A series of aluminum salts such as aluminum hypophosphite (AP), aluminum isobutylphosphinate (APBu), aluminum phenylphosphinate (BPA-Al), aluminum hydroxymethylphosphinate (AHMP), etc., have been comprehensively investigated.[18,20]

2.1.2. Organic Flame Retardants

Halogen-containing flame retardants (HFRs) are typical flame retardants that take effect mainly in the gas phase by capturing the combustion free radicals, and show high universality to almost all kinds of polymeric materials. The ease of the release of halogen radicals determines the effectiveness of HFRs.[7] Since the thermal stability of iodine compounds is too poor to satisfy the processing of polymeric materials and the fluorine compounds are too thermally stable to release radicals,[3] chlorine- and bromine-containing flame retardants were mainly applied. Numerous HFRs such as decabromodiphenyl oxide, dechlorane plus, hexabromocyclododecane, 1,2-bis(2,4,6-tribromophenoxy)ethane, pentabromoethyl benzene, tris(2,3-chloropropyl)isocyanurate, tetrabromobisphenol A-bis(2,3-dibromopropane ether), etc., have been designed and practically applied in various kinds of polymeric materials and products for the past decades. However, due to their environmental issues and toxicity,[21] the use of HRFs has been gradually banned world widely since the beginning of the 21st century.[22] From then on, the research focus has been put on non-halogen flame retardants.

Organophosphorus compounds, as a large class of flame retardants represented by phosphines, phosphine oxides, phosphonates, phosphonium compounds, phosphorus heterocyclic compounds, phosphites, phosphate, etc., exhibited high flame-retardant efficiency in either or both of the gas phase and condensed phase, and have been widely applied in almost all kinds of polymeric materials.[7,15,23] 9,10-dihydro-9,10-oxa-10-phosphaphenanthrene-10-oxide (DOPO) has been attracting increasing attention from researchers due to its great thermal stability, oxidation resistance and hydrolysis resistance,[24] and has been used as starting materials for the synthesis of various organophosphorus compounds that are mainly used as flame retardants.[25] DOPO-based flame retardants are mainly used in epoxy resins,[26] and exhibit high flame-retardant efficiency in both the gas phase by releasing PO· free radicals to interrupt the burning process and the condensed phase by dehydrating the polymer matrix to char layers.[24] Furthermore, nitrogen-[27] and silicon-[3,28] containing compounds can also be used as flame-retardant additives, but their flame-retardant efficiency is relatively low. Phosphorus-based flame retardants are currently the research topic, and multi-element synergistic flame retardants is one of the important development directions of future flame retardants.

2.2. Organic–Inorganic Hybrid Flame-Retardant Methods

Conventionally, to obtain the flame-retardant effect of both the barrier effect of inorganic particles and the radical-trapping and dehydration effect of organic component, these two kinds of flame retardants needed to be added into the polymer matrix simultaneously. This, unfortunately, brings some drawbacks such as the processing difficulty and the deterioration of mechanical properties of polymers. To solve these drawbacks, organic–inorganic hybrid (which possesses the combined advantages of both the inorganic and organic components) has been attracting increasing attention due to their relatively high efficiency and multifunctionality. In this section, recent development of this technology will be discussed with some typical representatives.

2.2.1. Silicon-Based Hybrids

SiO_2 is widely used as an inorganic flame-retardant additive for polymers due to its high strength, low cost, and great thermal

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stability. However, the flame-retardant efficiency of SiO_2 is low, and more importantly, its processability and compatibility with polymer matrix are always poor. Constructing organophosphorus structures on SiO_2 to prepare organic–inorganic hybrid is a good choice to further improve the flame retardancy and processibility. Based on this, Wang and co-workers[29] synthesized a SiO_2-based and phosphorus-containing organic–inorganic hybrid (SiO_2@DPP, **Figure 2**a), and used it as flame retardant for polycarbonate (PC). As a result, the PC containing 0.8 wt% of SiO_2@DPP achieved a limiting oxygen index (LOI, the limiting amount of oxygen (vol/vol%) that is needed to either maintain burning of the material for 3 min or consume a length of 5 cm of a sample.) value of 29.3%, passed the UL-94 (a test to measure the ignitability and flame spread of a vertically hung plastic sample, and the classification (e.g., V-0, V-1, and V-2 rating) can be made based on the test results) V-0 rating, and exhibited a 41.6% lower peak heat release rate (pHRR) and 15.4% lower peak smoke production rate (pSPR) in the cone calorimetry test (CCT, an oxygen-consuming test providing similar burning scenario to real fire). DOPO was also employed to synthesize a SiO_2-based hybrid flame retardant (DM), which was used to prepare flame-retardant polycarbonate/acrylonitrile butadiene styrene copolymer (PC/ABS) composites.[30] The results showed that, with 2 wt% of DM and 6 wt% of triphenyl phosphate (TPP) incorporated, the PC/ABS composite achieved a LOI value of 28.0% and passed the UL-94 V-0 rating.

Polyhedral oligomeric silsesquioxanes (POSS, Figure 2a) itself is an inorganic–organic hybrid with silica-like nanocage structure surrounded by at most eight organic groups like alkyl, alkylene, acrylate, hydroxyl, epoxied unit, etc.,[32] whose

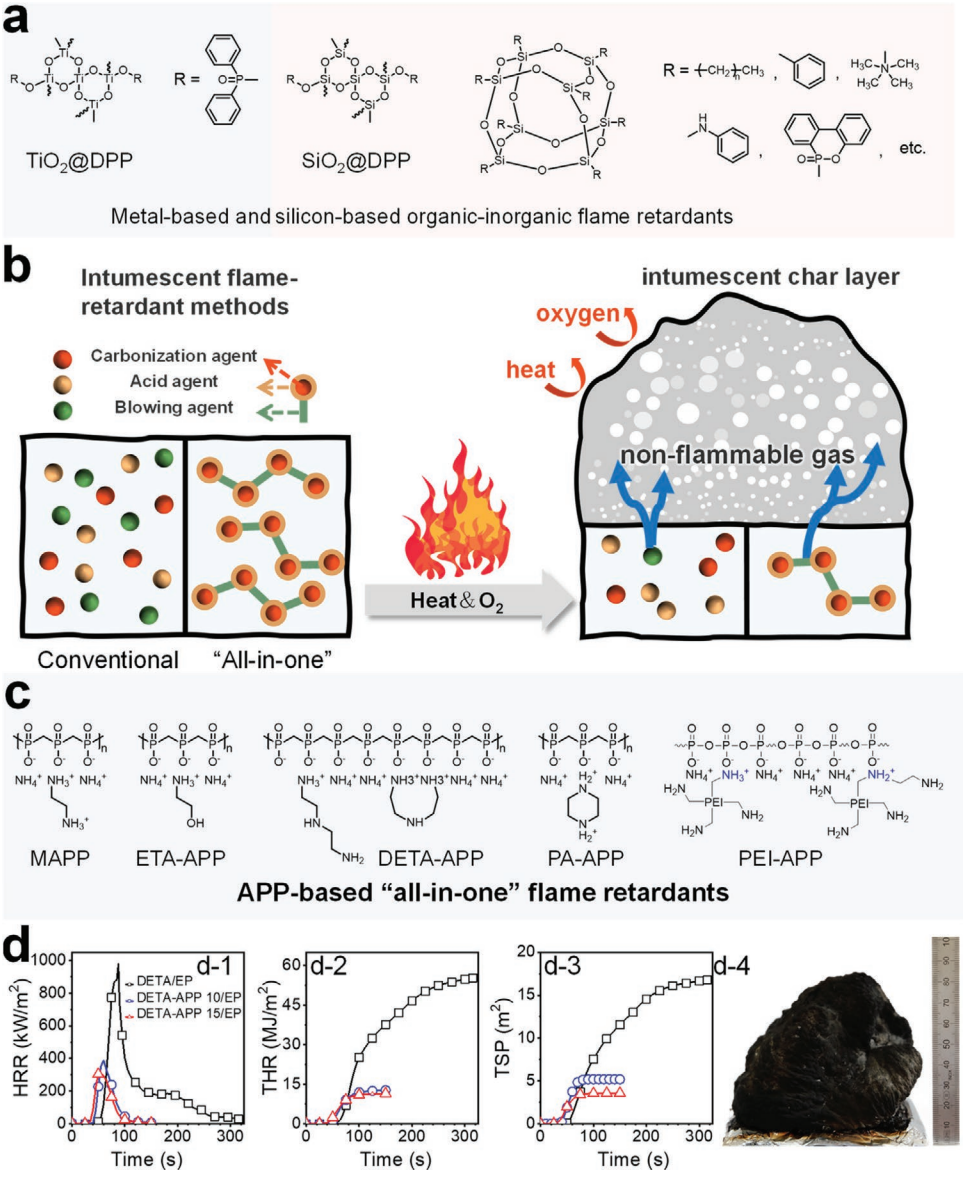


Figure 2. a) Typical organic–inorganic flame retardants. b) A schematic illustration of the intumescent flame-retardant methods. c) Typical APP-based "all-in-one" intumescent flame retardants. d) Typical inhibition effect on heat and smoke release and intumescent char layer of the DETA-APP system. d) Reproduced with permission.[31] Copyright 2015, American Chemical Society.

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unique nanostructure have attracted wide attention for the preparation of polymer/ POSS nanocomposites. Upon heating or during burning of polymer/POSS nanocomposites, POSS serves as precursor to the formation of thermally stable ceramic materials,[32a] which protect the underlying polymer matrix from further burning thus largely reduce the heat release. Various kinds of POSS with different chain length and structures have been comprehensively investigated in polymers like polyolefins,[33] polystyrene,[34] polyesters,[35] polycarbonate,[36] epoxy resin,[37] etc., and high flame retardancy was realized, indicating the university of POSS in different polymer matrix. Camino and co-workers[38] prepared metal functionalized POSS (Al-POSS and Zn-POSS) as flame retardant for PP. They found that the incorporation of 10 wt% of T_8-POSS did not reduce but increase the pHRR of PP by 20.1%, while the incorporation of 10 wt% of Al-POSS led to 52.9% decrease of pHRR compared with T_8-POSS.

2.2.2. Metal-Based Hybrids

Metal hydroxides and metal salts have been widely applied as inorganic flame retardants in various polymers, however, their low flame-retardant efficiency and poor compatibility with polymer matrix led to processing problems and deterioration of mechanical properties, thus modification is needed to improve the overall performance. An ATH hybrid (AOPH-NR) based on dibenzylphosphinic acid was synthesized and used as flame retardant for epoxy resin (EP).[39] At a loading amount of 4.25 wt%, the resultant EP achieved a LOI value of 28.0% and exhibited a 23.0% lower pHRR. DOPO was also employed to prepare ATH hybrid (DOPA-ATH),[40] which showed improved flame-retardant efficiency in ethylene vinyl acetate copolymer (EVA) than pristine ATH. Recently, Wang and co-workers[41] reported a novel Al salt-based organic–inorganic hybrid flame retardant (BM@Al-BuPPi) with core-shell structure, the resultant high-temperature nylon (HTN) composite exhibited a UL-94 V-0 rating and high LOI value of 42.5% at a flame retardant content of 20 wt%. Other metal compounds are also favored to prepare metal hybrid flame retardants. Wang and co-workers[42] prepared two novel Ti-containing organic–inorganic hybrids, the nanorods OPTS and the nanosphere TiO_2@DPP (Figure 2a), and used them to prepare flame-retardant PC. At a content of 0.10 wt%, both OPTS and TiO_2@DPP helped PC achieve the UL-94 V-0 rating and LOI value higher than 29.0%, and more importantly the resultant PC exhibited higher tensile strength and elongation at break.

Metal–organic frameworks (MOFs), which were first reported by Yaghi et al.[43] in 1995, are themselves organic–inorganic hybrid materials with a 3-D ordered porous material composed of inorganic clusters bridged by organic ligands. MOFs are usually useful in the inhibiting the heat and smoke release. Hu and co-workers[44] added two iron-based and cobalt-based MOFs (Fe-MOF and Co-MOF) into polystyrene (PS) as flame retardants, leading to a decrease of 14% and 28% of pHRR at the MOFs content of 2 wt%. The flame-retardant mechanism of MOFs has been comprehensively investigated, which was mainly summarized in three aspects:[45] 1) the gas dilution effect derived from non-flammable gases such NH_3 released by MOFs; 2) the absorption of gases and smoke; and 3) the formation of protective char layer, owing to the generation of metal oxide covering the polymer surface.

2.2.3. Phosphorus-Based Hybrids

As shown above, various phosphorus compounds have been widely utilized as the organic components of organic–inorganic hybrid flame retardants, and some great effects have been achieved. Recently, phosphorene, an emerging phosphorus-containing inorganic 2D nanomaterial first reported in 2014,[46] is attracting increasing attentions as a potential candidate for preparing hybrid flame retardants. The application of phosphorene as flame retardant was first reported by Mei and co-workers[47] to prepare flame-retardant waterborne polyurethane (WPU). To further improve the flame-retardant efficiency and compatibility of phosphorene with polymer matrix, melamine–formaldehyde was employed to prepare phosphorene-based organic–inorganic hybrid (BP@MF). At a content of 1.2 wt%, the resultant EP nanocomposite successfully passed the UL-94 V-0 rating and exhibited a LOI value of 31.1%, and the pHRR of which also decreased by 43.3% compared with pure EP.

2.3. "All-In-One" Intumescent Flame-Retardant Methods

Since Camino et al.[48] first successfully applied intumescent flame retardants to bulk polymers (mainly thermoplastics) in 1980s, intumescent flame-retardant methods have been comprehensively investigated for the past decades.[49] A typical intumescent flame retardant (IFR) system usually consists of three parts: acid source (acids, such as ammonium salts and phosphates), carbonization agent (hydroxyl-containing compounds, such as polyols) and blowing agent (compounds that emits gas when heated, such as melamine and urea). The IFR system usually works in the condensed phase during burning, forming a foamed porous char layer on the polymer surface to protect the underlying material from further burning, and slow down the heat transfer and release of combustible volatiles (Figure 2b). The corresponding intumescent process of a typical IFR system consisted of ammonium polyphosphate (APP) and pentaerythritol (PER) has been comprehensively investigated by Bourbigot et al.[50] Usually, an ideal intumescent flame-retardant effect can be obtained when the ratio of acid source, carbonization agent and blowing agent is ≈1:0.5:0.3. In order to meet this requirement, conventional IFRs are mainly achieved by adding three sources separately into the polymer matrix, which inevitably bring serious negative effects such as inhomogeneity of mixing ratio of the "three sources", bad processability, the deterioration of mechanical properties, the migration of flame retardants, low flame-retardant efficiency, poor water resistance, etc.

In order to solve the disadvantages of conventional intumescent flame-retardant methods, researchers have long been committed to the design and synthesis of novel "all-in-one monocomponent" IFR molecules, and have achieved certain results.[51] APP has always been the ideal choice for the preparation of monocomponent IFR, because it inherently meets

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the requirements of the acid source and blowing agent. In 2013, Wang's group found that fatty amines include aliphatic diamines (typical molecules such as ethylenediamine[52]), triamines (diethylenetriamine[31]), alcohol amines (ethanolamine[53]), heterocyclic amines such as piperazine,[54] and polymeric amines (such as polyethyleneimine[55]), etc. (Figure 2c), can directly form partially substituted polyphosphoric acid-organic ammonium salt in the water environment through a simple cation exchange reaction with APP, resulting in the trinity monocomponent IFRs. The organic amine component can promote carbonization through the rearrangement and cross-linking of unsaturated bonds formed at high temperature, and then realize the high-efficiency intumescent flame-retardant system. Among these organic-amines-modified APPs, piperazine-modified APP (PAz-APP),[54] has the highest flame-retardant efficiency in PP, for which a high LOI value of 31.2% and UL-94 V-0 rating were obtained at a PAz-APP content of 22 wt% (the content needed for a similar flame-retardant performance is ≈30 wt% for conventional IFR systems). The author further proposed the corresponding flame-retardant mechanism: when PAz-APP is heated to a certain temperature, the ammonium salt will form a P–N–C structure under high temperature and the catalysis of P-OH, which helps to form a stable carbon layer; when a certain temperature is reached, the C-N bond is broken and aromatized to form intumescent char layers covering the polymer surface, inhibiting the exchange of heat and oxygen. Furthermore, three typical organic-amines-modified APPs (PAz-APP,[56] polyethyleneimine-modified APP (PEI-APP),[55] and diethylenetriamine-modified APP (DETA-APP)[31]) were used as novel intumescent flame-retardant curing agents for EP. The curing kinetic parameters results demonstrated that, owing to the low content of primary or secondary amines that can participate in the curing reaction, the activation energy of the curing reaction is higher and the curing efficiency is low, particularly, additional curing accelerator is needed for PEI-APP. As for the flame-retardant performance, these three modified APPs all exhibited high flame-retardant efficiency and helped the corresponding EPs pass the UL-94 V-0 rating at a low content. Comparing among these three modified APPs, the PEI-APP system has the lowest flame-retardant efficiency, for which a content of 15 wt% was needed for the UL-94 V-0 rating and a LOI value of 29.5%; while for a similar flame-retardant performance, the content needed for DETA-APP and PAz-APP was 10 and 7.5 wt%, respectively. Furthermore, 68.3% decrease of pHRR, 79.3% decrease of total heat release (THR), and 79.0% decrease of total smoke production (TSP) were realized by these modified APPs (Figure 2d).

2.4. Nanocomposites-Based Flame-Retardant Methods

Nanotechnology, as one of the key technologies of the 21st century, has found wide application in flame-retardant polymers in the past two decades.[57] Polymer nanocomposites usually exhibit high flame-retardant efficiency at a low content (usually < 5 wt%), positive impact on mechanical properties, and potential for industrial application.[58] Their flame-retardant effect is mainly ascribed to two aspects: first, the barrier formation that effectively reduce the fire risk such as HRR and flame spread, however usually does not affect the fire load (THR) and ignitability to small flame such as UL-94 and LOI; second, the increased melt viscosity that prevents melt dripping during burning.[57,59] Herein, the advantages and limits of flame-retardant polymer nanocomposites based on the layered silicates and carbon-based materials are discussed.

2.4.1. Polymer/Layered Silicates Nanocomposites (PLSN)

Layered silicates-based minerals have long been used as additive fillers to prepare polymer/layered silicates nanocomposites (PLSN),[60] however their application as flame retardants only started from the later 1990s by Gilman et al.[61] With the combination of the advantages of both the organic polymer and the inorganic fillers, PLSN usually exhibit enhanced thermal stability, mechanical properties, barrier properties, as well as flame retardancy.[60a,62] Layered silicates that frequently used as flame retardants are montmorillonite (MMT),[63] mica,[64] fluoromica,[65] hectorite,[66] fluorohectorite,[67] saponite,[68] bentonite,[69] zoelite,[49g,70] etc.[12] Their main flame-retardant effect is the inhibition of heat release represented by decreased pHRR, which was ascribed to the formation of multilayered carbonaceous-silicate char layer on the surface of PLSN.[60a]

Schartel and co-workers[59a] comprehensively investigated the fire behavior of PLSNs. They found that PLSNs mostly exhibit condensed-phase flame-retardant mechanism: the layered silicates accumulate on the polymer surface acting as protective barrier for pyrolysis gases, and the increased melt viscosity prevents the melt dripping. Thus, PLSNs mainly show flame-retardant effect in forced flaming conditions such as the reduction of flame spread and fire propagation in CCT, and show limited effect in ignitability. Under such condition, layered silicates are mostly used in combination with other flame retardants for promising flame retardancy. As proved by various works, the synergism between layered silicates and conventional flame retardants is highly related to the type of layered silicates, flame retardants, and polymer matrix. For instance, synergism was achieved between organically modified sepiolite (OSEP) and APP in PP,[71] among organophilic montmorillonite (OMMT), decabromodiphenyl oxide (DB) and antimony oxide (AO) in PA 6,[72] between modified bentonite and ATH in EP,[73] between MMT and APP/PER/MPP in PP,[74] and among MMT, MH, and RP in methyl vinyl silicone rubber;[75] while antagonism was observed between modified bentonite and APP in EP,[76] between OMMT and melamine cyanurate (MCA) in PA 6,[72] and between modified bentonite and phosphorus-containing flame retardants in EP.[73] Morgan et al.[77] found that the polymer viscosity also played some role in reducing the HRR of these nanocomposites, for which the PS/MMT nanocomposite showed 30% lower HRR with higher molecular weight PS.

2.4.2. Polymer/Layered Double Hydrates Nanocomposites

Layered double hydroxides (LDHs) are a kind of metal hydroxides with structures based on $Mg(OH)_2$-like layers where some divalent cations are replaced by trivalent ions resulting in positive charged sheets, and the positive charge is

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balanced by intercalation of anions in the hydrated interlayers.[78] Due to their unique chemical composition and layered structure, LDHs have been widely used to prepare flame-retardant polymer nanocomposites,[79] for which the content needed for promising flame retardancy is much lower than that of metal hydrates like MH and ATH. The flame-retardant effect of LDHs were mainly ascribed to the heat absorption during the thermal degradation of LDHs and the barrier effect due to the formation of the ceramic-like structure, thus the kinds of metal cations, the interlayer anions, the particle size, and the dispersity all will influence the flame-retardant effect of LDHs.[78b] Wilkie and co-workers[80] investigated the influence of different divalent cations (Co^{2+}, Ni^{2+}, and Zn^{2+}) on the flame-retardant effect of LDHs with Al^{3+} as trivalent cation in PMMA, and found that at a content of 10 wt%, the pHRR-inhibition effect followed this order: $CoAl_2$ (41%)> $ZnAl_2$ (26%) > $NiAl_2$ (16%). They[81] also compared the effect of different trivalent cations, and found that the Ca_3Al LDH outperformed the Ca_3Fe LDH in poly(methyl methacrylate) (PMMA). Except for the above finding, there is still no convincing mechanism of how the divalent and trivalent cations influence the flame-retardant performance of LDHs. Due to the small gallery distance (usually < 1 nm) between each pair of LDHs layers and their hydrophilic surface, it is important to modify LDHs with organic anions for better dispersity and flame-retardant performance.[82] Recently, Wang and co-workers[83] Reported an organically modified LDH (LDH-DBS@$Ni(OH)_2$) through in situ self-assembly of $Ni(OH)_2$ on nanosheets of DBS intercalated LDH (LDH-DBS), which at a content of 3 wt%, endowed the EP nanocomposite with UL-94 V-0 rating, 60.6% lower pHRR, and 66.5% lower TSP.

2.4.3. Carbon-Based Polymer Nanocomposites

The emerge of carbon-based nanomaterials brings a new approach for preparing flame-retardant polymeric materials in the context of nanotechnology. Except for the application of expandable graphite (EG) as flame retardant for different polymers in the past decades, the arise of new carbon-based nanoparticles such as carbon nanotubes (CNTs) and graphene have provided a new way for preparing flame-retardant polymer nanocomposites.

Carbon nanotubes (CNTs, **Figure 3**b), with unique characteristics such as high aspect ratio, nanoscale size, and high mechanical and electric properties,[84] are capable of being used as flame retardants mainly through a condensed-phase mechanism. During burning, the so-called 3D network is formed when the CNTs content reaches a threshold value, leading to the formation of protective continuous char layer covering the surface of the polymer matrix, insulating the exchange of heat and reducing the release of combustible volatiles.[85] The application of CNTs as flame retardants for polymers was reported at the beginning of this century when Beyer[86] investigated the influence of multi-walled carbon nanotubes (MWNTs) on the flame-retardant performance of EVA/organoclay nanocomposite. Till now, CNTs have showed the effect to reduce the pHRR of a series of polymers like PE,[87] PP,[88] PS,[87] EVA,[87] PLA,[89] PMMA,[84b,90] PA 6,[91] PC,[92] EP,[93] etc. Takashi and co-workers[84b,88,90,93,94] have done great works on CNTs-based flame-retardant polymer nanocomposites, and found that the incorporation of SWNTs and MWNTs all largely inhibit the degradation of PMMA, thus lead to significant decrease of peak mass loss rate (pMLR) (Figure 3d).[84b] They further investigated the influence of dispersity of CNTs on the flame-retardant efficiency.[90a] At a fix CNTs content of 0.5 wt%, the dispersity of CNTs was controlled by changing the CNTs concentration in DMF, and as a result, about 70% reduction was observed in pMLR at the highest dispersion level. Unfortunately, the dispersity of CNTs and the flame-retardant efficiency in small flame test like UL-94 and LOI are unsatisfactory, thus CNTs are usually modified through the following approaches: 1) surface modification by coupling agent for better dispersion between CNTs and the polymer matrix;[95] 2) covalent bonding of organic flame retardants for better char-forming ability;[96] 3) hybridization of CNTs by inorganic particles for higher flame retardancy.[97] Wang and co-workers[98] took advantages of the catalytic effect of Fe, and prepared the Fe-CNTs nanoparticles in large scale. The incorporation of 6 wt% of Fe-CNTs led to 30.7% and 39.1% decrease of pHRR and THR of its EP nanocomposite, and more importantly, a LOI value of 35.0% and UL-94 V-1 rating were achieved.

Graphene (Figure 3c) has ultrahigh specific surface area, Young's modulus and fracture strength, high electronic conductivity, and good thermal conductivity.[85,99] Graphene-based flame retardants mainly take effect through the following two aspects: 1) the so-called "tortuous path" (Figure 3a) effect derived from the unique 2D platelet morphology, which efficiently alters the diffusion path of combustible pyrolysis products;[100] 2) graphene can promote the formation of compact, uniform and dense protective char layer.[101] The overall performance of graphene nanosheets was compared with other carbon fillers by Mülhaupt and co-workers,[102] who found that the graphene-based PP/TRGO (thermally reduced graphene oxide) composite exhibited simultaneously improved electrical conductivity, stiffness, as well as flame retardancy with a 76% lower pHRR. The oxidation states of graphene/GO is a key parameter influencing their flame-retardant efficiency. As reported by Jeong and co-workers,[103] the excessive oxidation is detrimental to the flame-retardant effect of GO due to the reduced intumescent ability, and a similar phenomenon was also observed in the following work.[104] Similar to CNTs, modification of graphene is usually needed for better overall performance, and various flame-retardant groups such as DOPO,[105] phenylphosphonate,[106] polyphosphamide (PPA),[107] 2-(diphenylphosphino) ethyltriethoxy silane (DPPES),[108] hyperbranched flame retardants,[109] and poly(piperazine spirocyclic pentaerythritol bisphosphonate) (PPSPB)[110] have been utilized to prepared grafted functionalized graphene-based flame retardants. Hu and co-workers[79d,107,111] have done a series of works on flame-retardant polymer nanocomposites based on functionalized graphene with or without the cooperation of other flame retardants, and the higher flame-retardant performance was obtained than the use of pristine graphene.

Other carbon-based materials including carbon black (CB)[112] and carbon nitride[113] have also been employed as flame retardants in recent years, and are attracting increasing attentions. Of all the above-mentioned carbon materials, the morphology

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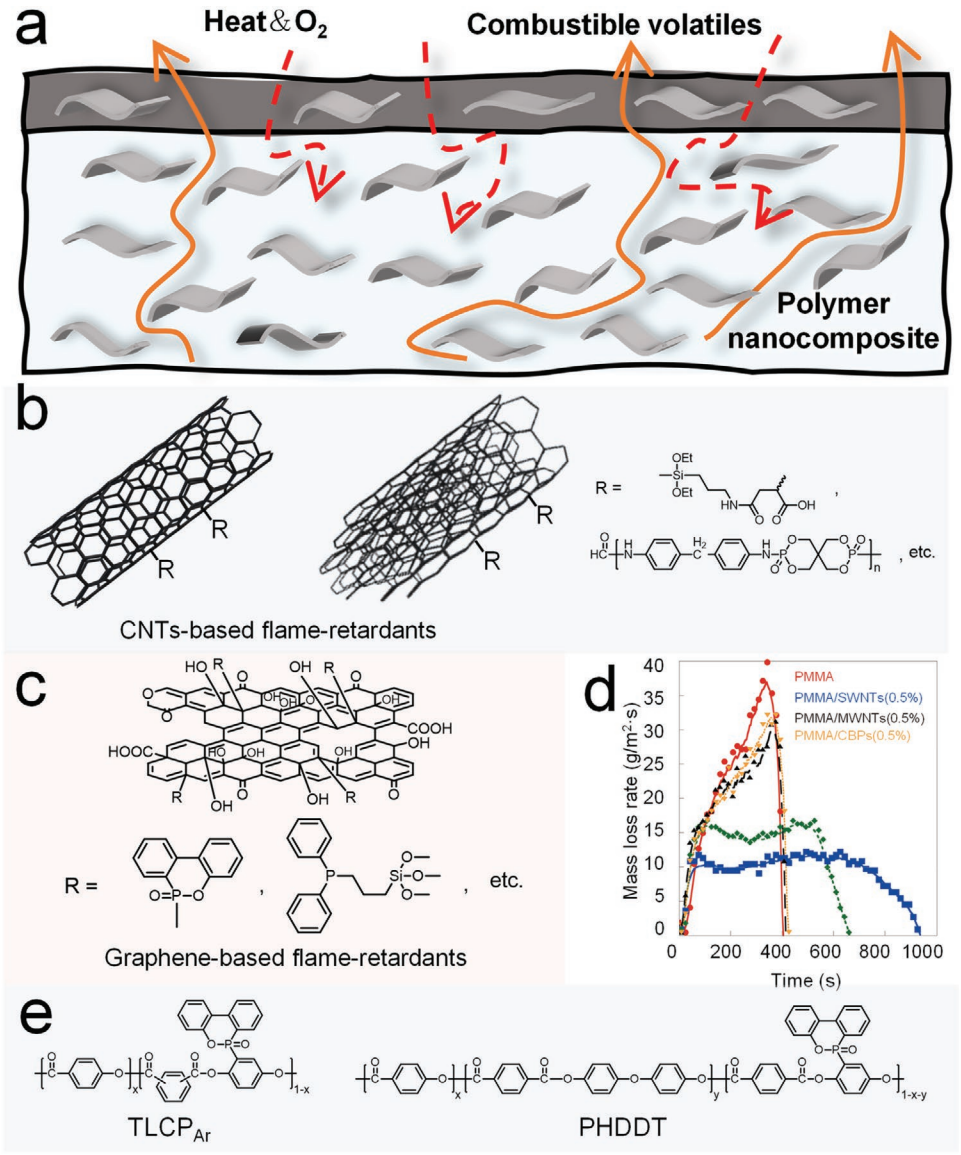


Figure 3. a) A schematic illustration of the so-called "tortuous path" of 2D nanoplate–polymer nanocomposites. b,c) Typical carbon-based flame retardants based on CNTs (b) and graphene (c). d) The inhibition effect on decomposition of polymer nanocomposites. e) Typical structures of the in situ reinforcing flame-retardant TLCP. d) Reproduced with permission.[84b] Copyright 2005, Springer Nature.

has great influence on their flame-retardant performance. Schartel and co-workers[114] investigated the influence of carbon materials with different particle sizes and shapes (such as TRGO and multilayer graphene (MLG250) with layered structure, CB with spherical structure, MWNTs with tubular structure, and EG with platelet-like structure) on the flame retardancy of PP. They found that the incorporation of carbon materials all largely improved the thermal stability and melt viscosity of the polymer nanocomposites, and the well-exfoliated layered morphology is favorable to spherical and tubular ones in terms of closed residue structure formation, and reduction in pHRR. A drawback of polymer nanocomposites is their unsatisfactory flame-retardant efficiency, mainly in small flame like UL-94 and LOI. As a results, the polymer nanocomposites are insufficient for most applications, thus must be used in combination with other flame retardants.[58a,94,115] Furthermore, the practical application of CNT and graphene is limited by their relatively high cost compared with other commercial flame retardants.

2.5. In Situ Reinforcing Flame-Retardant Methods

Generally, the incorporation of conventional flame retardants usually leads to the deterioration of mechanical properties of polymeric materials, and flame-retardant polymeric materials with simultaneously enhanced mechanical properties are highly desired. In situ microfibrillation of thermotropic liquid crystalline polymer (TLCP) in polymer matrix has been proved to be able to improve the mechanical strength and modulus of

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polymers.[116] Taking advantage of this characteristic of TLCP, researchers believed that the incorporation of intrinsically flame-retardant TLCP into polymer matrix may lead to flame-retardant polymeric materials with reinforced mechanical properties.

Based on the above concept, Wang et al.[117] proposed the in situ reinforcing flame-retardant method. They first prepared a series of fully aromatic TLCP ($TLCP_{Ar}$, Figure 3e) containing DOPO through the melt polycondensation, which all exhibited intrinsic flame retardancy with LOI values higher than 60.0%.[118] Then, they blended $TLCP_{Ar}$ into the PET matrix to prepare in situ reinforced flame-retardant PET composites.[117] The results showed that, due to the in situ microfibrillation of $TLCP_{Ar}$, the tensile strength of the PET composites increased greatly with the increase of $TLCP_{Ar}$ content, and the elongation at break was basically the same as that of pure PET. At the same time the PET composites exhibited enhanced flame-retardant properties. Adding 2 wt% of $TLCP_{Ar}$ can increase the LOI value of the PET composite material from 21.3% of pure PET to 26.4%; when the $TLCP_{Ar}$ content reached 15 wt%, the LOI value can be further increased to 32.4%. More importantly, the melt dripping behavior was suppressed. Following this work, Wang and co-workers further investigated the influence of $TLCP_{Ar}$ on the flame-retardant and mechanical properties of PET as engineering plastics. They found that,[119] at a $TLCP_{Ar}$ content of 8 wt%, the PET composite passed the UL-94 V-0 rating with 25% higher tensile strength; when the $TLCP_{Ar}$ content reached 15 wt%, the LOI value was increased by 62.4% compared with that of pure PET, and the tensile strength was increased by 51%. Further studies showed that the incorporation of $TLCP_{Ar}$ in some degree promoted the thermal oxidative decomposition of PET.[120] The flame-retardant mechanism investigation showed that,[121] on the one hand, $TLCP_{Ar}$ provides phosphorus-containing functional groups that were further converted to phosphonic acid groups; on the other hand, the fully aromatized molecular structure of $TLCP_{Ar}$ serves as carbon source of char layer, which finally achieves the condensed-phase flame-retardant effect. In the following years, intrinsically flame-retardant TLCP with different structures such as PHDDT (Figure 3e),[122] TLCP-AE,[123] P-TLCP-FS,[124] etc., were designed and synthesized, and were blended with PET, PC, PC/ABS, and PBT. As expected, all of these polymer/TLCP composites exhibited improved flame retardancy and in situ reinforced mechanical properties. The in situ reinforced flame-retardant methods are of the very few flame-retardant methods that could simultaneously improve the mechanical properties, and represent an important future development direction of flame-retardant polymeric materials.

2.6. Controlled Carbonization-Based Flame-Retardant Methods

Upon heating, polymeric materials will undergo thermal decomposition, resulting in the formation of combustible gaseous fuel vapor, which will burn on the top of polymeric materials in the presence of heat and oxygen. Based on this, it is believed that if the decomposition process of polymers could be changed to the in situ controlled carbonization process, the flame retardancy of polymers may be improved.

Tang and co-workers[125] have been exploring the methods for increasing the carbon yield of polymers during burning since 2005, and discovered the synergism between solid acid (such as OMMT and HZSM-5) and nickel compound in improving the flame retardancy of polyolefins (**Figure 4**a). With 10 wt% OMMT and 5 wt% HZSM-5 incorporated, the PP/OMMT/Ni-cat nanocomposite exhibited an 80% lower pHRR compared with pure PP, and the residual char was largely increased from 0 wt% of pure PP, 5.7 wt% of PP/OMMT and 7.0 wt% of PP/Ni-cat to 37.5 wt% of PP/OMMT/Ni-cat. The OMMT nanosheets in the PP nanocomposite prevented the release of pyrolysis volatiles by forming a tortuous path, and the pyrolytic products further interacted with the catalyst to form char that mainly consisted of CNTs. Tang and co-workers[126] further investigated the influence of the combined catalyst halogenated compound/Ni_2O_3 on the flame retardancy of polyolefins (Figure 4b-e). With 0.9 wt% CuCl and 5 wt% Ni_2O_3 incorporated, the pHRR of PP decreased by 64.3% and the residual char was increased to 46.4 wt%. The chlorine-grafted CNTs/Ni_2O_3 (CNT-Cl/Ni_2O_3) catalysts[127] drastically improved the flame retardancy of PP, the pHRR of which decreased by 73.1% and the residual char was increased to 54.3 wt% with 3 wt% CNT-Cl and 5 wt% Ni_2O_3 incorporated. The combined SiO_2/Ni_2O_3[128] catalyst largely enhanced the flame retardancy of poly(lactic acid) (PLA), whose pHRR decreased by 45% compared with that of pure PLA. The CB/Ni_2O_3[125b] catalyst also exhibited high efficiency on improving the flame retardancy of PLA, for which a 51.3% lower pHRR and a residual char of 50 wt% were achieved with 5 wt% CB and 5 wt% Ni_2O_3 incorporated. They also found that the quality of char layer is more important to improve the flame retardancy of polymers than the quantity of char layer. Thus, a stiffener skeleton strategy together with catalytic carbonization to improve the flame retardancy of PC in the presence of CB/Ni_2O_3. With 1 wt% CB and 2 wt % Ni_2O_3 added, the resultant PC achieved a LOI value of 31.4%, a UL-94 V-0 rating, and a 50% lower pHRR. These works by Tang and co-workers[83,129] provide a strategy for preparing flame-retardant polymer composites through controlled carbonization, which has been attracting increasing research attention of scientists in recent years.

2.7. Biomaterials-Based Flame-Retardant Methods

With the growing awareness of environmental issues regarding the increasing use of fossil feedstock, the development of flame retardants based on renewable resources has been attracting increasing attention in recent years.[130] Some bio-based compounds, with special chemical composition and structure, possess the ability to form thermally stable char layers when exposed to fire. This unique trait makes them capable of being used as flame retardants. Herein, the development and application of some typical bio-based flame retardants will be discussed.

2.7.1. Carbon-Based Biomaterials

Carbon-based biomaterials such as cellulose, starch, chitosan and lignin (Figure 4f), have been proved to be able to

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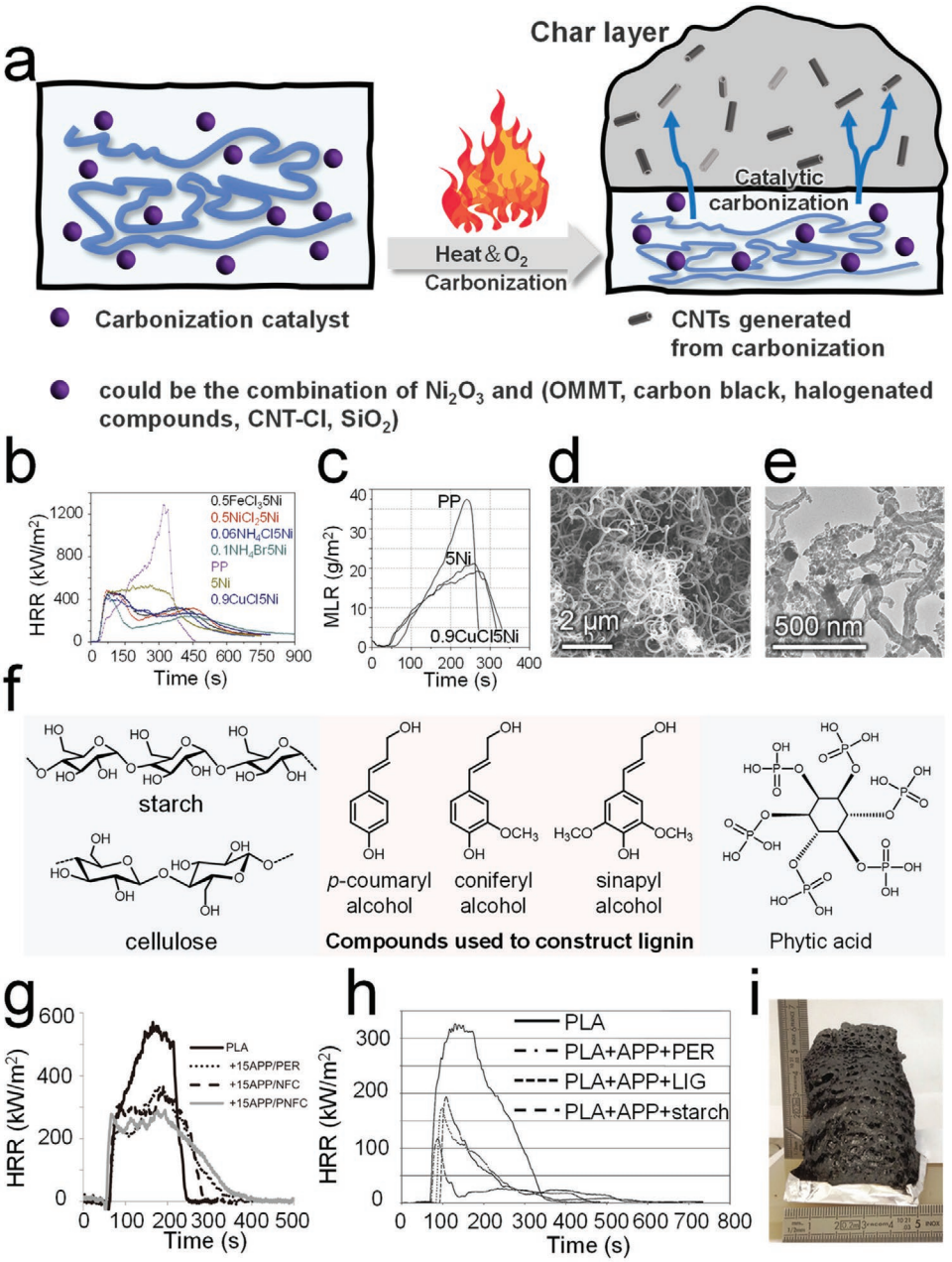


Figure 4. a) A schematic illustration of the controlled carbonization-based flame-retardant methods. b,c) Typical HRR (b) and MLR (c) curves of carbonization-based flame-retardant PP. d,e) Typical morphologies of the CNTs generated from controlled carbonization. b–e) Reproduced with permission.[126] Copyright 2009, Elsevier. f) Representative bio-based materials. g,h) Typical HRR curves of the bio-based intumescent flame-retardant PLA. g) Reproduced with permission.[131] Copyright 2013, Elsevier. h) Reproduced with permission.[132] Copyright 2008, Wiley VCH. i) The intumescent char layer generated by DNA at a heat flux of 35 kW m^{-2}. Reproduced with permission.[133] Copyright 2014, Elsevier.

produce charred structure during decomposition in some conditions.[4,130,134] Taking advantage of this characteristic, these carbon-based biomaterials can be used as carbon source in intumescent flame-retardant systems, which can interact with other constituents of the intumescent system such APP to form expanded char layer on the polymer surface.[132,135] Casetta and co-workers[132] investigated the performance of starch and lignin in the APP-based intumescent flame-retardant PLA, and proved their potential as carbon source. Compared with the commercial APP/PER system, the APP/starch and APP/lignin exhibited lower LOI but improved the UL-94 rating from V-2 to V-0. With 12 wt% APP and 28 wt% starch incorporated, the PLA composite exhibited a LOI value of 32.0%, a UL-94 V-0 rating, and a 50% lower pHRR (Figure 4h). Nanofibrillated cellulose (NFC) and POSS-modified NFC (PNFC) were investigated as potential alternative to PER in the flame-retardant PLA/APP system.[131] The resultant PLA/APP composites containing NFC and PNFC as

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carbon source all exhibited lower pHRR than that containing PER as carbon source (Figure 4g). At the same time, higher molar mass of the PLA composite was obtained by the PNFC system, leading to the higher storage modulus than the PER system. A microencapsulated APP (MCAPP) was prepared from cellulose acetate butyrate to enhance the performance of APP.[136] The results showed that, compared with APP, MCAPP improved the LOI of the EVA composite from to 28.5% to 31%, improved the UL-94 rating from V-2 to V-0, and further reduced the pHRR by 51%. More importantly, MCAPP endowed the EVA composite with better mechanical properties and water resistance, which still possessed a LOI value of 27.5% and a V-0 rating after water treatment at 70 °C for 3 days. Kandola and co-workers[137] prepared an intumescent flame retardant named BSDH by integrating β-cyclodextrin, triazin ring, and nanohydroxyapatite into a hybrid system. BSDH exhibited synergistic effect with APP, for which the PLA/APP/BSDH sample containing 7.5 wt% APP and 2.5 wt% BSDH showed 38.7% lower pHRR and 30.8% lower THR than the PLA/APP sample containing 10 wt% APP.

2.7.2. Phosphorus-Based Biomaterials

Phosphorus is not only important to flame-retardant science, but also very important to lives, for which phospholipid is the main component of cell membrane, and the phosphorus element was first discovered from human urine. As a typical phosphorus-containing biomaterial, phytic acid (PA, Figure 4f) is the main storage form of phosphorus in plant seeds, cereal grains, and beans. Its chemical structure that containing six phosphate groups (with high phosphorus content of 28 wt%) makes it attractive for being used as flame retardants. PA was reacted with polyethylenimine (PEI) to prepare a novel polyelectrolyte complex (PEC),[138] which was used as flame retardant in PP. At a PEC content of 20 wt%, the LOI value was improved from 18.0% of pure PP to 25.1% of PP/20PEC, and evident char layers were formed during burning. Recently, Wang and co-workers[139] reported a fully bio-based aerogel with PA as flame-retardant and cross-linking components, which exhibit enhanced flame retardancy, high mechanical properties, as well as good thermal insulation performance. Metal phytate is another choice of PA-based bulk-additive flame retardant, which will restrict the migration of PA when being used alone.[130,140] The use of phosphorus–nitrogen (P–N) compounds as flame retardants has been extensively investigated, the great flame-retardant performance of which was mainly ascribed to the P–N synergism. As a representative, deoxyribonucleic acid (DNA) is a P–N compound that exists in all organisms that carry genetic information. Its unique chemical structure of nucleotide, i.e., a nitrogen-containing nucleobase (cytosine, guanine, adenine, and thymine), a five-carbon sugar (deoxyribose), and a phosphate group, makes DNA a naturally monocomponent IFR (Figure 4i).[133] Upon heating, the phosphate group generates phosphoric acid, which serves as acid source; the deoxyribose unit acts as carbonization agent and decomposes through the self-cross-linking process to form aromatic structures, and the nucleobase acts as blowing agent to release ammonia.

3. Bulk-Copolymerization Flame-Retardant Methods

3.1. Conventional Bulk-Copolymerization Flame-Retardant Methods

Although the bulk-additive flame-retardant methods have shown promising results for improving the flame retardancy of almost all kinds of polymeric materials, some imperfections such as migration and blooming of small-molecular additives, deterioration of the polymers' inherent properties, and potential persistence, bio-accumulation and toxicity (PBT) issues still exist and are urgent to be addressed. Bulk-copolymerization flame-retardant methods by chemically incorporating flame-retardant structure into the molecular chain of polymeric materials is a perfect choice to address the above issues. However, due to the more complex preparation process including the design and synthesis of flame-retardant comonomers, the copolymerization between comonomers and polymer monomers, the tedious adjustment process of the copolymerization parameters, as well as the high cost, the bulk-copolymerization flame-retardant methods have only been realized in a quite few polymeric materials like polyesters, polyamides, polyurethanes, epoxy resins, unsaturated polyesters, and polystyrenes. In this section, the authors will discuss the conventional bulk-copolymerization flame-retardant methods used in the past decades.

3.1.1. Halogen-Based Bulk-Copolymerization Flame-Retardant Methods

Tetrabromobisphenol A (TBBA) is a typical reactive bromine-based flame-retardant monomer that has long been commercially used as reactive intermediate in the production of EP for electric and electronic applications. TBBA is known to release bromine free radicals that trap the combustion free radicals to form non-flammable hydrogen bromide gas, leading to high flame-retardant efficiency.[141] TBBA was also used by Liaw and Chang[142] to partially or completely replace bisphenol A (BPA) to prepare flame-retardant PC. The results showed that the incorporation of TBBA into the molecular chain of PC largely enhanced the thermal stability and flame retardancy of PC. The $T_{10\%}$ was increased from 446 °C of BPA-PC to 477 °C of TBBA-PC, and the LOI value was significantly increased from 25.5% of BPA-PC to 93.0% of TBBA-PC.

3.1.2. Phosphorus-Based Bulk-Copolymerization Flame-Retardant Methods

In recent years, phosphorus-containing bulk-copolymerization flame-retardant methods have developed rapidly, thanks to the advantages of reactive phosphorus-containing flame retardants such as eco friendliness, high flame-retardant efficiency, various kinds, high reactivity, as well as ease of modification. The mostly used reactive phosphorus-containing flame retardants include phosphate, DOPO, phosphine oxide, cyclophosphazene, and phosphoramide, which will be discussed in the following sections.

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CEPPA (2-carboxyethylphenylphosphinic acid) is a highly efficient reactive flame retardant for polyester and polyamide, and its corresponding flame-retardant PET copolyester has been commercialized by a Germany company Hoechst (Trevira CS). At a low content of ≈3 mol%, CEPPA improved the LOI value from 22.0% of pure PET to 33.6% of CEPPA-PET,[143] while higher CEPPA content will lead to a decrease of the T_m and T_g of the copolyester, deteriorating the crystallinity.[144] DDP (9,10-dihydro-10[2,3-di(hydroxycarbonyl)propyl]-10-phosphaphenanthrene-10-oxide) is a DOPO derivative widely used as reactive flame retardant for polyester and polyamide,[145] however, the phosphorus-containing side groups of DDP destroys the regularity of the polyester molecular chain, leading to the decrease of the crystallinity and tensile strength of the copolyester.[146] Döring and his co-workers[147] prepared a DOPO-based amine-containing reactive flame retardant, which was used as hardener for EP and carbon fiber (CF)-reinforced EP. The resultant EP/CF composite exhibited a LOI value of 48.0%, a UL-94 V-1 rating, and at the same time, the mechanical properties of the composite was maintained. Other phosphorus-containing monomers, such as cyclophosphazene[148] and phosphine oxide,[149] were also widely used as reactive flame-retardant monomers.

3.1.3. Silicon-Based Bulk-Copolymerization Flame-Retardant Methods

Silicon is another element frequently used to prepare reactive flame retardants for PC, EP, and PU. Kambour et al.[150] studied the influence of silicone on the LOI value of a series of dimethylsiloxane (DMS)-based block copolymers. They found that the synergistic effect on LOI varied with the hard block type in the following order: BPA-PC and BPF-PC > PS and poly(2,6-diphenyl-1,4-phenylene oxide) > BPC-PC > PMMA and phenolphthalein-based PC. Nodera and Kanai[28b] prepared an intrinsically flame-retardant PC-polydimethylsiloxane (PDMS) block copolymer with different DMS block sizes of 15–350 units. The results showed that high LOI values were obtained when 1.0 wt% of PDMS with DMS units of 40–130 was incorporated. Qian and co-workers[151] synthesized a series of phosphaphenanthrene- and silicone-containing compounds (DDSi-*n*), and prepared the corresponding intrinsically flame-retardant DGEBA/DDM resins. The incorporation of DDSi-*n* largely enhanced the anti-ignition and self-extinguishing performance of the resultant DDSi-*n*/EP, the heat release of which was significantly inhibited. A silicone-containing reactive flame retardant MGSO was synthesized and used to prepare the intrinsically flame-retardant RPUF with MGSO as a part of the soft segment.[152] The MPA and the imide groups suppressed the "back-bite" of silicone and promoted the formation of a silica-rich char layer on the surface of RPUF. The LOI value was increased from 18.8% of pure RPUF to 23.9% of MGSO-based RPUF, and the pHRR of the MGSO-based also decreased by more than 50%.

3.2. Intrinsic Char-Forming Flame-Retardant Methods

Conventional bulk-copolymerization flame-retardant methods mostly rely on the use of phosphorus. For thermoplastics like polyester and polyamide that widely used as fabrics, phosphorus-containing copolymers mainly achieve flame retardancy by promoting the melt dripping of the matrix to remove heat from the flame zone. However, melt dripping is highly dangerous since it may cause immediate empyrosis, secondary damage, and further fire spread.[19] The contradiction between flame retardancy and melt dripping has become the main issue that urgent to be solved for thermoplastics polymers. Facing this dilemma, researchers have done a lot of works for the past decades, and put forward an innovative flame-retardant and anti-dripping method based on the thermally induced reactions such as "ionic aggregation", "cross-linking", and "rearrangement".[153]

3.2.1. Ionic Aggregation

Ionomers are polymers consisted of both electrically neutral repeat units and ionized repeat unites covalently bonded to the polymer backbone as pendent group.[154] Ionomers have been widely used as additives due to the unique physical and rheological properties, for which the incorporation of a small amount of ionomers efficiently increase the melt viscosity and strength of polymers due to the formation of ionic aggregation.[155] This special ionic aggregation leads to the formation of thermally reversible physical cross-linking networks, which restricts the movement of the polymer chain and may be positive for inhibiting the melt dripping.

Taking advantage of this special ionic aggregation phenomenon, Wang and co-workers[156] first synthesized a phosphorus-containing ionic monomer named SHPPP, and prepared its corresponding poly(ethylene terephthalate) (PET) copolyester PPETIs. PPETIs show typical multiple melting endothermic peaks in the DSC test, which proves the existence of the ionic aggregation, affecting the crystallization process and crystal phase stability of PPETIs. The thermogravimetric analysis (TGA) results showed that the ionic aggregation can improve the thermal stability of PPETIs copolyesters in air atmosphere and promoted the char-forming ability. Unlike conventional phosphorus-containing copolyesters, the amount of residual char at 700 °C of the PPETIs copolyesters is significantly higher than that of pure PET. Benefitting from the ionic aggregation of SHPPP, PPETI10 exhibited a LOI value of 27.3%, and most importantly, evident anti-dripping phenomenon was observed and compact char layer was formed during the LOI test.

However, the mono-reactive group at the end of SHPPP restricts the molecular weight of the copolyester, and the content of ionic groups in the copolyester, leading to poor ionic aggregation effect. To overcome this drawback, a bifunctional ionic monomer named DHPPO-Na (**Figure 5**b) was designed and synthesized, and the corresponding PET copolyester PETIs were prepared.[157] Due to the ionic aggregation of DHPPO-Na, the crystallinity of the obtained PETIs copolyester first increased and then decreased with the increase of DHPPO-Na content. As expected, a much higher ionic aggregation phenomenon than that of SHPPP was observed, for which the complex viscosity of PETIs first decreased then sharply increased with the increase of temperature, which was attributing to the strong ionic aggregation reaction. The TGA results showed that, the residual char

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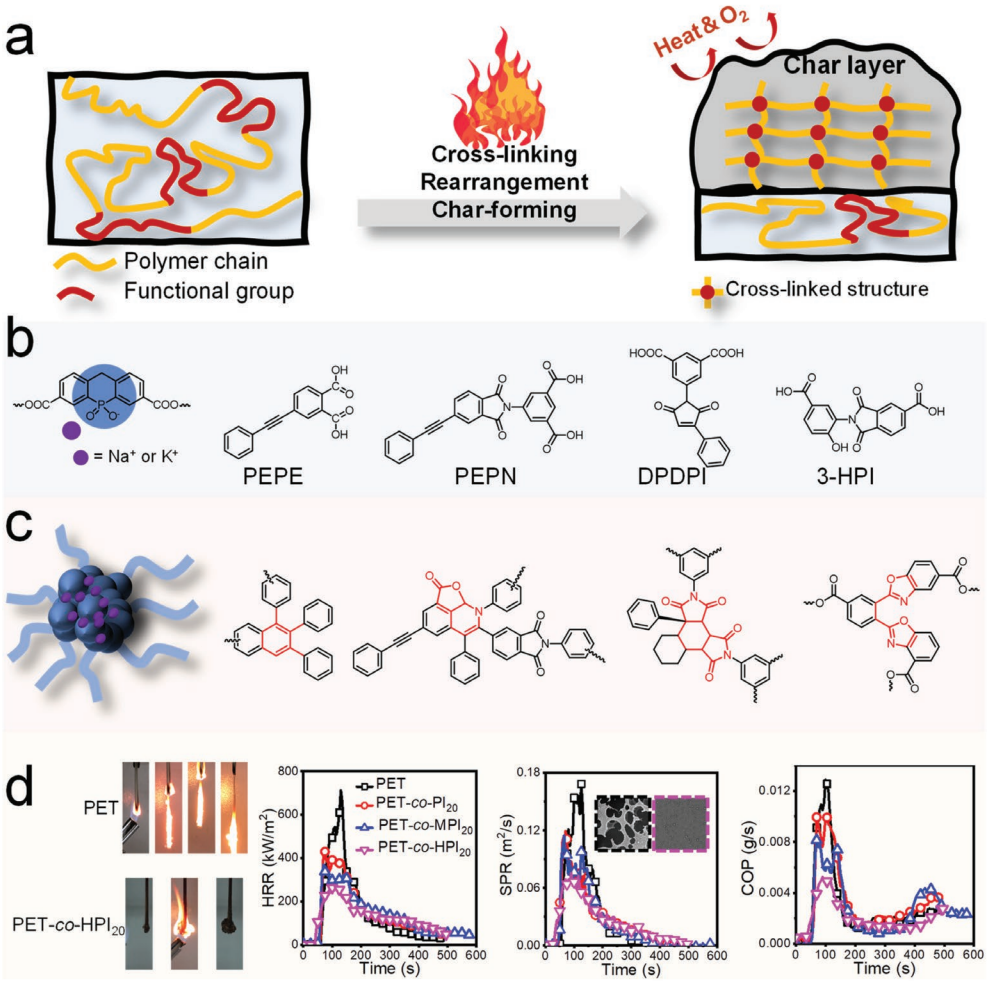


Figure 5. a) A schematic illustration of the intrinsically char-forming flame-retardant methods. b) Representative functional groups. c) Typical cross-linked structure generated by thermal ionic aggregation, self-cross-linking, and rearrangement. d) Typical flame-retardant and anti-dripping performance. d) Reproduced with permission.[165] Copyright 2019, Wiley VCH.

at 700 °C of PETIs significantly increased compared with pure PET. Furthermore, a high LOI value of 31.0% was achieved for PETI10 and no melt drips were generated during the test, and the pHRR of PETI10 drastically decreased by 71% compared with that of pure PET.

In order to further study the contribution of ionic aggregation to the flame retardant and anti-dripping performance of copolyesters, three comonomers DHPPO-Na, DHPPO-K, and a phosphorus heterocyclic compound without ionic group DCPPO-Ph were designed and synthesized, and the corresponding PET copolyesters PETI-Na, PETI-K, and PETPs were prepared.[158] Despite the similar chemical structure between PETI-K and PETPs, they exhibited significantly different rheological performance. The rheological test results proved that the increase in the melt viscosity of the copolyester is entirely caused by the ionic aggregation of the ionomer: similar to PETI-Na, the complex viscosity of PETI-K increases with increasing temperature; while the complex viscosity of PETPs gradually decreases with the increase of temperature. Due to the occurrence of ion aggregation, PETI-K has a higher melt viscosity and char-forming ability than PETPs, thus has better flame retardancy and anti-dripping performance. The CCT results showed that, the ionic monomer DHPPO-Na effectively reduces the release of combustible volatiles into the gas phase, while DCPPO-Ph exhibited no effect on inhibiting the heat release. The different flame-retardant mechanism was further investigated by XPS and Py-GC/MS: For PETPs copolyesters without ionic groups, the phosphorus element is mainly released into the gas phase; for PETI-K copolyesters containing ionic groups, the phosphorus element is mostly retained in the solid phase through ionic aggregation, which promotes the formation of a stable chary layer and reduces the release of smoke and heat.

Although some great flame-retardant and anti-dripping results were achieved by incorporating ionomers into the molecular chain of PET, the resultant PET copolyesters unfortunately fail to pass the UL-94 test during which melt drips still could be observed. This is because that the thermally reversible ionic aggregation is insufficient for completely anti-dripping that requires much higher melt viscosity and strength.

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3.2.2. Self-Cross-Linking

Unlike reversible physical cross-linking based on ionic aggregation, irreversible chemical cross-linking based on cross-linked covalent bond is much more stable, making it the perfect choice to address the melt dripping problem. However, irreversible chemical cross-linking will destroy the processability and spinnability of PET copolyesters. Thus, to obtained anti-dripping PET copolyesters, the cross-linking structures should not be in the polymer chain during processing and daily use, but should appear when exposed to fire. Facing this challenge, Wang and co-workers[159] proposed an innovative concept of "self-cross-linkable copolyesters", which will stay stable during polymerization and processing, but will cross-link rapidly at high temperature or when exposed to fire (Figure 5a). The key to realize such self-cross-linkable copolyesters is the appropriate cross-linkable monomer, which should: 1) be reactive to be copolymerized into the PET chain, 2) be inactive at the temperature of copolymerization and processing (250–300 °C), and 3) be able to cross-link rapidly at higher temperature.

Based on the above concept, Wang and co-workers first chose the phenylacetylene structure, which can be cured at high temperature (>300 °C) to form highly cross-linking networks, as the key structure to prepare the self-cross-linkable PET copolyesters. They first design and synthesized the phenylacetylene -containing monomer PEPE (Figure 5b), and prepared the corresponding PET copolyester P(ET-*co*-P).[159] As expected, P(ET-*co*-P) exhibited the cross-linking behavior as proved by the TG-DSC and dynamic rheology results. The TG-DSC thermogram of P(ET-*co*-P) showed an evident exothermal cross-linking peak at 340 °C between the melting peak (220 °C) and the decomposition peak (440 °C). The complex viscosity of P(ET-*co*-P) first decreased, then increased sharply at higher temperature, similar to that of ionomer-based PET copolyesters. As a result, flame-retardant and anti-dripping performance were achieved, for which the pHRR of P(ET-*co*-P)$_{20}$ was only 32% to that of pure PET, and P(ET-*co*-P)$_{80}$ achieved a high LOI value of 30.0%. Most importantly, P(ET-*co*-P)$_{80}$ passed the UL-94 V-0 rating without dripping, and compact and intumescent char layers were generated during the UL-94 test. The real anti-dripping PET copolyester was achieved, and it should be noticed that such PET copolyester was consisted of only carbon, oxygen, and hydrogen elements, without the use of any flame-retardant elements.

In order to improve the cross-linking efficiency of the phenylacetylene group and reduce the monomer content, Wang and co-workers[160] designed and synthesized a flame-retardant monomer containing phenylimide phenylacetylene structure (PEPN, Figure 5b) in the side chain, and prepared the corresponding copolyester P(ET-*co*-PN). Phenylimide can undergo an "imide-isoimide" rearrangement at high temperature to form an isoimide structure containing unsaturated C=N group, which further decomposed to form a benzonitrile structure. They found that, the phenylacetylene group can not only undergo self-cross-linking reaction at high temperature or during burning, but also capture the benzonitrile structure produced by the decomposition of phenylimide, leading to the synergistic cross-linking effect. Based the cross-linking efficiency and the char-forming ability of P(ET-*co*-PN) was significantly enhanced compared with that of P(ET-*co*-P). At a low monomer content of 13 mol%, P(ET-*co*-PN)$_{15}$ successfully passed the UL-94 V-0 rating without dripping, and achieved a high LOI value of 33.5%. More importantly, the π-π stacking between the phenylacetylene groups largely increased the tensile strength of P(ET-*co*-PN)$_{15}$ by 45.0% compared with pure PET.

Azobenzene can undergo the π–π^* electronic transition due to the "N=N" structure, and form a conjugated system with the benzene ring, resulting in the high thermal stability of azobenzene. Wang and co-workers[161] prepared PET copolyesters PEATs containing azobenzene in the main chain. The results showed that, the azobenzene structure can also undergo high-temperature self-cross-linking reactions, and the generated nitrogen-containing stable cross-linking structure will participate in the char-forming process; at the same time, azobenzene will decompose to produce nitrogen gases to dilute the concentration of oxygen and combustible volatiles in the gas phase. Based the flame-retardant effect in both the condensed phase and the gas phase, great flame retardancy was achieved by PEATs. At an azobenzene content of 15 mol%, PEAT15 exhibited a high LOI value of 29.0%, a 57.1% lower pHRR and 34.7% lower TSP compared with those of pure PET. Unfortunately, PEAT15 failed to pass the UL-94 V-0 rating, and the melt dripping phenomenon could not be totally inhibited.

PET copolyesters containing phenylmaleimide group (Figure 5b) (PET-*co*-DPDPI$_x$)[162] will undergo a 2π+π cycloaddition cross-linking reaction during burning, leading to high melt viscosity of the copolyester. At the same time, this 2π+π cycloaddition reaction can also promote the char formation of the copolyester, and largely improve the flame-retardant and anti-dripping performance of PET-*co*-DPDPI$_x$. At a DPDPI content of 10 mol%, PET-*co*-DPDPI$_{10}$ passed the UL-94 V-0 rating without dripping, achieved a high LOI value of 30.4%, and exhibited 47.8% lower pHRR and 64.2% lower TSP compared with pure PET. The Schiff base structure was also employed by Wang and co-workers[163] to prepare PET copolyesters. At a Schiff base content of 9.1 mol%, the corresponding BA$_{10}$PET passed the UL-94 V-0 rating without dripping, achieved a high LOI value of 31.0%, and showed significant decrease of pHRR and TSR.

The chemical self-cross-linking copolyester achieved desirable flame-retardant and anti-dripping performance, at the same time, great mechanical properties and the spinnability of the resultant copolyester were obtained, providing new ideas and new thinking for preparing high-performance flame-retardant polymeric materials. Very recently, this method has been proved to be highly efficient in other semi-aromatic polyesters such as PTT.[164]

3.2.3. Thermal Rearrangement

Similar to chemical cross-linking, thermal rearrangement of some aromatic structures such as "Ar-CH_2-Ar", "Ar-O-Ar", "Ar-O-Ar-O-Ar", and"Ar-O-Ar-CO-Ar-O-Ar", can promote the formation of char layer with conjugated aromatic structures, which is beneficial for improving the flame retardancy and anti-dripping performance. If these structures were incorporated into the molecular chain of PET, the flame-retardant and

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anti-dripping performance may be achieved. Based on this, Wang and co-workers[166] first designed and synthesized an arylene-ether containing monomer named PBPBD, and prepared the corresponding PET copolyester BD*x*PET. The results showed that the thermal stability and char-forming ability were largely enhanced with the incorporation of PBPBS. At a PBPBD content of 20 mol%, BD20PET exhibited a high LOI value of 32.0%, and no melt drips were generated during the test.

In order to study the effect of the rearrangement reaction on the flame retardancy and anti-dripping performance of the copolyesters, they further designed two monomers based on bisphenol F and bisphenol A (BHBPF and BHBPA,), and introduced them into the PET molecular chain through melt polycondensation. In the preparation of the corresponding FxPET and AxPET copolyesters. Interestingly, the small structural difference between FxPET and AxPET copolyesters led to evidently different pyrolysis processes and flame-retardant properties. The Py-GC/MS results showed that the "Ar-CH_2-Ar" group in BHBPF will rearrange to form a phenanthrene ring structure at high temperature, while such reaction was not observed for the "Ar-C$(CH_3)_2$-Ar" group in BHBPA. The rearrangement of BHBPF promotes the char formation of FxPET during the burning, leading to better flame retardancy of FxPET than AxPET. They further designed and synthesized monomers containing "Ar-CO-Ar", "Ar-O-Ar", "Ar-O-Ar-O-Ar" and "Ar-O-Ar-CO-Ar-O-Ar" groups, prepared the corresponding PET copolyesters (PKT, POT, PEET, and PEKET) as a model compound to study its rearrangement process and flame-retardant mechanism.[167] The flame retardancy and anti-dripping performance of these copolyesters are significantly improved compared to pure PET, particularly, the copolyesters containing "Ar-O-Ar-O-Ar" and "Ar-O-Ar-CO-Ar-O-Ar" groups exhibited high LOI values of 34.1% and 31.6%, respectively. More importantly, the incorporation of the "Ar-O-Ar-O-Ar" group helped the corresponding copolyester pass the UL-94 V-0 rating without dripping.

Recently, a thermally induced "end-group-capturing" flame-retardant method was proposed by Wang and co-workers.[165] They designed and synthesized a flame-retardant monomer containing *ortho*-hydroxyphenylimide (3-HPI, Figure 5b) structure, and prepared the corresponding copolyester PET-*co*-HPI_n. At high temperatures, the HPI structure rapidly rearranges into the benzoxazole structure, and the benzoxazole structure will capture the terminal carboxyl segment generated by the thermal decomposition of PET, thereby inhibiting the thermal decomposition of PET, reducing the release of combustible small molecules. Furthermore, the formed benzoxazole and its cross-linked structure in the solid phase can increase the melt viscosity and strength of the copolyester, promoting the formation of char layer, inhibiting the heat transfer and release of combustible volatiles, and finally realizing the flame-retardant and anti-dripping performance (Figure 5d). The parameters affecting the "end-group-capturing" flame-retardant efficiency,[168] and the application of this method in other polyesters like PTT and PBT were further studied.[169]

Emrick and co-workers have also done many works based on the concept of thermal rearrangement. Taking advantage of the rearrangement of deoxybenzoin to diphenylacetylene at 300–500 °C,[170] they synthesized deoxybenzoin (BHDB)-containing polyarylates, and investigated the influence of deoxybenzoin on the thermal stability and flame retardancy of the polyarylates.[171] They found that the thermal rearrangement of BHDB promoted the aromatization and enhanced the char-forming ability, for which the char yield in the TGA test increased from 25.8 wt% of the BPA-polyarylate to 42.2 wt% of the BHDB-polyarylate. More importantly, pyrolysis combustion flow calorimetry (PCFC, also known as microscale combustion calorimetry (MCC), a non-flaming method for evaluating the combustibility of milligram samples) results showed that the heat release capacity (HRC) decreased from 456.3 to 61.5 J g^{-1} K^{-1}, and the THR decreased from 17.7 to 7.5 kJ g^{-1}. To improve the solubility of the BHDB copolymer, they synthesized novel BHDB-containing polyphosphonates,[172] and synthesized the bis-allyl-substituted BHDB monomer (BA-BHDB),[173] which all exhibited enhanced solubility and desirable flame retardancy. The application of BHDB was further extended to the preparation of flame-retardant EP,[174] PU,[175] polysulfones and polysulfoxides,[176] as well as branched polymer-type flame retardants.[177] Emrick and co-workers[178] also found that the triazole-to-indole thermal rearrangement contributed to the flame retardancy of polymers, for which the triazole-containing polyarylate exhibited HRC of 23 J g^{-1} K^{-1}, THR of 4.6 kJ g^{-1}, and char yield of 56 wt% (**Table 1**).

4. Surface Flame-Retardant Methods

Despite many advances, the bulk flame-retardant technologies have more or less caused other problems such as matrix compatibility, deterioration of mechanical properties, etc. In this regard, the surface flame-retardant treatment has gradually attracted a lot of attention, which can concentrate the flame-retardant effect on the interface between materials and combustion.[1,188] Especially for high surface area substrates (foams, textiles, etc.), active flame-retardant ingredients can cover the surface of the 3D framework to extinguish fires in the initial stage. Consequently, the surface flame-retardant treatment can endow the polymer matrix with flame retardancy, while the effect on the overall performance is relatively small. In the following part, we outline the history and development of surface flame-retardant treatment from the perspective of conventional coatings and advanced methods. Meanwhile, this section focuses on the advancement, defects, and key influencing factors of various surface treatment technologies. Opportunities and challenges for new designs and further trends are proposed and discussed in detail.

4.1. Conventional Surface Flame-Retardant Treatments

4.1.1. Back Coating

The earliest surface flame-retardant treatment is the back coating, which usually places the resin dispersed with flame-retardant ingredients on the side of the substrate that may be exposed to fire. This method is particularly suitable for lower-surface-area materials, such as polymer films, plates, etc. As early as the 1st century BC, Vitruvius recorded in his "The

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Table 1. Flame-retardant performance for representative bulk- additive and copolymerization flame-retardant methods.

	Substrate	Flame Retardant	Content	Results	Ref.
Organic–inorganic hybrid flame-retardant methods	PC/ABS	DOPO-grafted hybrid mesoporous silica (DM) + triphenyl phosphate (TPP)	2 wt% DM + 6 wt% TPP	UL-94 V-0; LOI: 28.0%; CCT: pHRR –21%	[30]
	PC	SiO_2@DPP (diphenylphosphoric acid)	0.8 wt%	UL-94 V-0; LOI: 29.3%; CCT: pHRR –42%	[29]
	EP	DOPO-POSS	2.5 wt%	UL-94 V-1; LOI: 30.2%	[179]
	EP	ATH hybrid based on dibenzylphosphinic acid (AOPH-NR)	4.25 wt%	LOI: 28.0%, CCT: pHRR –23%	[39]
	EVA	DOPO-ATH	60 wt%	UL-94 V-0; LOI: 33.4%	[40]
	PC	TiO_2@DPP (diphenylphosphoric acid)	0.10 wt%	UL-04 V-0; LOI: 29.3%; CCT: pHRR –34%	[42a]
	PC	OPTS (a hybrid nanorod)	0.10 wt%	UL-04 V-0; LOI: 29.7%; CCT: pHRR –47%	[42b]
	HTN	BM@Al-BuPPi (an organic–inorganic hybrid)	20 wt%	UL-94 V-0; LOI 42.5%; CCT: pHRR –57% (15 wt%)	[41]
	PS	Fe-MOF or Co-MOF	2 wt%	Fe-MOF: CCT: pHRR –14% Co-MOF: CCT: pHRR –28%	[44]
	EP	BP@MF (black-phosphorus-modified melamine-formaldehyde)	1.2 wt%	UL-94 V-0; LOI: 25.9%; CCT: pHRR –43%	[180]
	EP	RuL_3@BP (black phosphorus)	3 wt%	UL-94 V-0; LOI: 26.7%; CCT: pHRR –62%	[181]
"All-in-one" intumescent flame-retardant methods	PP	MAPP (ethylenediamine-modified APP)	40 wt%	UL-94 V-0; LOI: 32.5%; CCT: pHRR –81%, THR –32%	[52]
	EP	DETA-APP (diethylenetriamine-modified APP)	15 wt%	UL-94 V-0; LOI: 30.5%; CCT: pHRR –68%, THR –79%, TSP –79%	[31]
	PP	ETA-APP (ethanolamine-modified APP)	35 wt%	UL-94 V-0; LOI: 35.0%; CCT: pHRR –88%, THR –75%, TSP –77%	[53]
	PP	PAz-APP (piperazine-modified APP)	22–25 wt%	22 wt%: UL-94 V-0; LOI: 31.2% 25 wt%: CCT: pHRR –81%, TSP –17%	[54]
	EP	PEI-APP (polyethylenimine-modified APP)	15 wt%	UL-94 V-0; LOI: 29.5%; CCT: pHRR –74%, THR –76%, TSR –71%, TSP –70%	[55]
Nanocomposites-based flame-retardant methods	EVA	MWCNT+OMMT	2.5 phr + 2.5 phr	CCT: pHRR –36%	[86a]
	PP	MWNT	1 vol%	CCT: pHRR –73%	[88a]
	PP	TRGO or MLG 250	5.0 wt%	TRGO: CCT: pHRR –74% MLG 250: CCT: pHRR –68%	[102]
	PP	CB	5.0 wt%	CCT: pHRR –73%, THR –7%	[112]
	TPU	C-$CuCo_2O_4$ (graphitic carbon nitride modified $CuCo_2O_4$)	2.0 wt%	MCC: pHRR –37%	[113]
	PBT	*m*-CNT+AlP (aluminum phosphinate)	0.5 wt% *m*-CNT + 9.5 wt% AlP	UL-94 V-0; LOI: 37.5%; CCT: pHRR –66%, THR –36%	[182]
	SEBS	BDP (bisphenol A bis(diphenyl phosphate)) + MWNTs	5.0 wt% BDP + 3.0 wt% MWNTs	UL-94 V-0; LOI: 25.5%; CCT: pHRR –66%	[183]
	EP	DOPO-rGO	10 wt%	LOI: 26.0%	[105]
	PP	FRs-FGO	20 wt%	CCT: pHRR –67%, THR –24%	[107]
	EVA	CRG (chemically reduced GO)-PPSPB (poly(piperazine spirocyclic pentaerythritol bisphosphonate))	1 wt%	CCT: pHRR –56%, THR –22%	[110]

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Table 1. Continued.

	Substrate	Flame Retardant	Content	Results	Ref.
	PBS or PLA	CO_3O_4/graphene	1 wt%	PBS: CCT: pHRR –31% PLA: CCT: pHRR –40%	[111d]
Controlled carbonization-based flame-retardant methods	PP	OMMT+Ni-cat	10 wt% OMMT + 5 wt% Ni-cat	CCT: pHRR –80%; TGA: CR^{700}: 37.5 wt%	[125a]
	PLA	CB+Ni_2O_3	5 wt% CB + 5 wt% Ni_2O_3	CCT: pHRR –51%; TGA:CR^{700}: 50 wt%	[125b]
	PP	halogenated compounds + Ni_2O_3	0.9 wt% CuCl + 5 wt% Ni_2O_3	CCT: pHRR –64%; TGA: CR^{700}: 46.4 wt%	[126]
	PP	CNT-Cl + Ni_2O_3	3 wt% CNT-Cl + 5 wt% Ni_2O_3	CCT: pHRR –73%; TGA: CR^{700}: 54.3 wt%	[127]
	PLA	SiO_2 + Ni_2O_3	5 wt% SiO_2 + 5 wt% Ni_2O_3	CCT: pHRR –44%; TGA: CR^{700}: 18.2 wt%	[128]
Biomaterials-based flame-retardant methods	PLA	APP + starch	12 wt% APP + 28 wt% starch	UL-94 V-0; LOI: 32.0%	[132]
	PLA	Phosphorylated microcrystalline cellulose (MCC-P)	20 wt%	UL-94 V-0; CCT: pHRR –15%	[184]
	PLA	POSS-modified nanofibrillated cellulose (PNFC)	15 wt%	CCT: pHRR –45%, THR –20 wt%	[131]
	EA	Chitosan phosphate acrylate (GPCS)	20 wt%	LOI: 26.0%; CCT: pHRR –56%, THR –50%	[185]
	PLA	Microencapsulated APP (MCAPP) + Lignin	23 wt%	UL-94 V-2; LOI: 21.0%; CCT: pHRR –59%	[186]
	PP	PEC	20 wt%	LOI: 25.1%; CCT: pHRR –28%, THR –19%	[138]
	PLA	Metallic phytate	30 wt% Al-Phyt	CCT: pHRR -53%, THR -29%	[140]
	LDPE	DNA	5 wt%	UL-94 H: reduced burn distance	[187]
Intrinsic char-forming flame-retardant methods	PET	SHPPP	10 mol%	LOI: 26.0%	[156]
	PET	DHPPO-Na	10 mol%	LOI: 31.0%; CCT: pHRR -71%	[157]
	PET	PEPE	20–80 mol%	20 mol%: CCT: pHRR-68%, THR -39% 40 mol%: LOI: 28.0% 80 mol%: UL-94 V-0 without dripping	[159]
	PET	PEPN	15 mol%	UL-94 V-0 without dripping; LOI: 33.5%	[160]
	PET	azobenzene-4,40-dicarboxylic acid	15 mol%	LOI 29.0%; CCT: pHRR -57%, THR -15%, TSP -35%	[161]
	PET	DPDPI	10 mol%	UL-94 V-0 without dripping; LOI: 30.4%; CCT: pHRR -48%, THR -7%	[162]
	PET	BA	10 mol%	UL-94 V-0 without dripping; LOI 31.0%; CCT: pHRR -32%, THR -11%, TSR -36%	[163]
	PTT	PEPN	20 mol%	UL-94 V-0 without dripping; LOI: 32.0%; CCT: pHRR -68%, THR -17%, TSR -20%	[164]
	PET	PBPBD	20 mol%	LOI: 32.0%; CCT: pHRR -46%, TSP -31%	[166]
	PET	3-HPI	20 mol%	UL-94 V-0 without dripping; LOI: 33.0%; CCT: pHRR -62%, pSPR -53%, pCOP -59%	[165]
	PET	4-HPI	15 mol%	UL-94 V-0 without dripping; LOI: 30.0%; CCT: pHRR -59%, THR -12%, pSPR -43%, pCOP -65%	[168]

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Table 1. Continued.

Substrate	Flame Retardant	Content	Results	Ref.
Polyarylate	BHDB	–	PCFC: HRC -86.5%, THR -57.6%; TGA: char +63.6%	[171]
Polyphosphonate	BHDB	–	PCFC: HRC -77.8%; TGA: char +126.1%	[172a]
Polyarylate	Triazole	–	PCFC: HRC -95.0%, THR -74.0%; TGA: char +115.4%	[178a]

Ten Books on Architecture" that a layer of hair-reinforced clay was applied to a wooden castle to prevent arsonists from fire attacking.[189] In modern society, the earliest back coatings use halogenated compounds as the active ingredients, most of which preferably function in the gas phase by acting as a radical scavenger.[190] However, similar to bulk flame-retardant methods, the halogen-based coating systems gradually comes under scrutiny, due to toxicity and bioaccumulation. Currently, phosphorus-containing ingredients dominate and show great potential as high-efficiency flame-retardant additives for coating. Among them, intumescent coatings widely used since the 1970s are typical representatives, of which active ingredients are similar to bulk intumescent flame retardants, including phosphorus-containing acids (such as APP), carbon sources (such as polyols), gas sources (such as melamine), and binder resins.[49d] Once upon a fire, the acid source decomposes and interacts with the carbon sources to form a stable viscous cross-linked carbonaceous material, which is inflated by the incombustible gas released by the foaming agent to form an insulating carbon foam to protect the underlying polymer.[191] Researchers have continued to develop and optimize intumescent systems, in terms of the chemical formulations (component ratio, reactivity, and catalysis) and the formed carbon foam (high-temperature thermal stability, conductivity, and mechanical stability).[192] In addition, other halogen-free flame retardants, such as phosphate, inorganic metal compound, etc., are well known for flame-retardant back coatings. Although back coating has been widely used in the commercial field, it is gradually not the mainstream of academic research. Some obvious shortcomings limit their developments: on the one hand, the appearance of the substrate (transparency, color, etc.) is always severely affected; on the other hand, the issues of adhesion and durability are difficult to solve.

4.1.2. Dip/Pad-Dry Treatment

As a classic conventional surface flame-retardant method, dip/pad-dry treatments have been widely developed for high-surface-area materials, especially fabrics. For the dip-dry treatment, the substrates are fully soaked in flame-retardant precursor solution and then dried at a certain temperature, while the pad-dry method uses a roller-like machine to help the flame-retardant precursors better enter the substrate. The stable cross-linked action between flame-retardant moieties and the substrate is the key, which directly determines the durability of flame retardancy. Consequently, flame-retardant ingredients should have the ability to self-polymerize or copolymerize with resin monomers to achieve a stable coating on the surface of the substrate. Decades ago, the first large-scale application of the pad-dry treatment is to polymerize a mixture of tetrakis(hydroxymethyl) phosphonium chloride and amines on cotton fabric.[193] A larger amount of halogen-containing compounds, such as decabromodiphenyl ether, hexabromocyclododecane, tris-(2,3-dibromopropyl) phosphonate, etc., have been developed for the high-efficiency flame-retardant treatments.[194] Notes that, to further improve the water resistance of the coating, formaldehyde is always introduced to the cross-linking system of the coating befitting from its high reactivity with -OH of cotton. However, serious adverse health effects from halogen compounds and formaldehyde have largely limited their applications.

Recent works commit to the development of formaldehyde-free and halogen-free flame-retardant systems for dip/pad-dry treatment. At present, phosphorus and nitrogen synergistic systems, such as cyclotriphosphazene derivatives, are highly efficient for fabrics instead of halogen flame retardants.[195] Based on the spontaneous cross-linking reaction of branched PEI and hexachlorocyclotriphosphazene, Grunlan and co-workers[196] reported a dip-dry coating, which can make the LOI of cotton fabric up to 33.8%. Generally, P/N-containing functional monomers are introduced into the cross-linked coating to improve water resistance through condensation reactions such as acid–alcohol, acid–ammonia, etc., which can occur during dipping, padding, or drying processes at high temperatures. Although many works confirmed the water resistance (surviving after 10–50 washing cycles) of these surface treatments, some imperfections remain.[197] Firstly, high temperatures (>100 °C) and acidic conditions are often required to promote the reaction in the process of building covalent bonds, which will damage the mechanical properties of substrates (especially for cellulose-based fabrics). Secondly, in the absence of formaldehyde, the covalent bonds formed by the polycondensation of these flame retardants and adhesives (or bridging agents) with substrates are still sensitive to water, resulting in a rapid decline in flame retardancy after multiple washing. Due to the urgent need for flame-retardant cotton fabrics and the prospects for commercial applications, the dip/pad-dry treatment method still attracts many researchers. Future works can expand more construction methods of covalently cross-linked networks under mild conditions, achieving eco-friendly and durable flame retardancy.

4.2. Plasma/Ultraviolet-Aided Treatment

As mentioned above, the key to improving the durability of the flame-retardant surface treatment is to enhance the interaction

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between the substrate and the functional coating, which can be probably achieved by the following two types of surface modification. In the first case, the active groups of the substrate can be increased through the special pre-treatment, such as plasma-aided treatment. In the second case, additional treatments, such as ultraviolet (UV) irradiation, are used to promote the cross-linking interaction between the substrate and the coating.

4.2.1. Plasma-Aided Treatment

Plasma is a gas medium composed of electrons, ions, and neutral particles in the ground or excited state, which can promote the surface functionalization reaction. In 1990, plasma technology was first used for surface flame-retardant treatment, in which, with the help of plasma, hexamethyldisiloxane and phosphate-based monomers were polymerized on the surface of polyacrylonitrile fibers to achieve a certain flame retardancy.[198] A follow-up report by Bourbigot confirmed that the argon ions and free radicals generated by the plasma can promote the surface flame-retardant treatment of polyamide 6.[199] In 2002, Schartel et al.[200] further conducted a study based on the use of plasma polymerization to control the flame retardancy of the polymer surface, and clarified the possibilities and limitations of this technology. Until today, plasma-aided flame-retardant surface treatment has developed rapidly. The most common use of plasma is to initiate the polymerization and grafting reaction of the flame-retardant coating system (**Figure 6**a). For example, Worawan and co-workers[201] grafted a synthetic phosphate onto cotton fabric through argon radio frequency plasma at room temperature. When the weight gain of the flame-retardant coating reached 65 wt%, the LOI of the treated cotton fabric increased from 19.0% to 28.0%. In addition, researchers use plasma to enhance the bonding force between the flame-retardant component and the substrate by activating the substrate, etching the surface, and introducing oxygen-containing polar functional groups. Alongi and co-workers[202] found that the absorption of MMT particles on the PET fabric after plasma activation was greatly increased, thus making the fabric exhibit higher flame-retardant performance. Lam et al.[203] used atmospheric pressure plasma technology to pretreat the cotton fabric, and then treated the fabric with flame retardants and ZnO/nano-ZnO solution. The results indicated that plasma etching can produce rough and wrinkled surfaces, leading to more deposition of the active ingredients on the fiber surface. Compared with conventional surface flame-retardant treatment, plasma treatment has no need for liquid solvents, which may be more environmentally friendly.

Further, in plasma treatment, a large number of chemically active functional groups can be produced on the surface of the substrate, which is conducive to the construction of the covalent force between the substrate and the coating. Therefore, many researchers have focused their attention on plasma-assisted flame-retardant surface treatment with water resistance. Grützmacher and co-workers[204] prepared flame-retardant and hydrophobic silk fabrics through a two-step low-pressure plasma process. In the first step, argon plasma was used to induce the graft polymerization of phosphorus-containing monomers. In the second step, the silk fabric was treated with SF_6 plasma to obtain hydrophobicity. The results showed that plasma treatment helped the coating gain higher flame retardancy and hydrophobicity. Even after boiling for 4 h, the LOI value of the treated silk fabric only dropped from 30.5% to 29.0%. Another example with more washing tests can be found in Zhou's results, which used O_2 plasma to activate polyester fabric grafted with maleic acid, and then successfully grafted with pentaerythritol urea phosphate.[205] The obtained sample has a high LOI of 29.3%, as well as good thermal stability, self-extinguishing, and droplet suppression capabilities. After 20 washing cycles, the sample still passed the vertical flame test with a few droplets, and the LOI value could be maintained at 26.8%.

Although plasma-assisted flame-retardant surface treatment has progressed a lot, the following problems should be solved

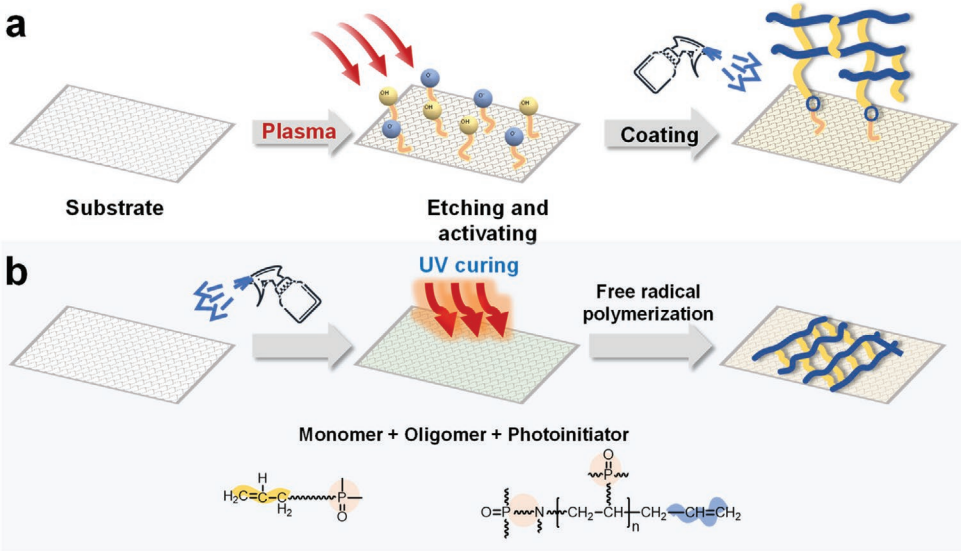


Figure 6. a,b) Schematic representations of plasma-treatment (a) and UV-curing systems (b).

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as much as possible. The mechanism of plasma surface modification is difficult to clearly understand due to its complexity and uncontrollable chemical changes on the modified surface. Consequently, it is difficult to design and control the specific chemical properties and activity of the modified surface according to the expected results of the plasma treatment. Other defects, such as limited excitation functional groups, short-lived activity, and weak universality, still need to be overcome. Nevertheless, as the technology matures, the atmospheric pressure plasma is expected to be used as an eco-friendly alternative to the construction of durable flame-retardant coatings.

4.2.2. Ultraviolet-Aided Treatment

Ultraviolet (UV) curing technology that utilizes the polymerization, crosslinking, and grafting of photosensitive monomers in the UV-initiated system is increasingly used in flame-retardant surface coating applications. Compared with conventional thermal cross-linking processes, UV cross-linking treatment has the advantages of a mild condition and less impact on the performance of the substrate. In the first UV-aided flame-retardant treatment, cyclotriphosphazenes containing various amounts of 2-hydroxyethylmethacrylate were synthesized and further coated on the surface of wood blocks at the assistant of UV irradiation.[206] The coated woodblock maintained its original appearance and exhibited intumescent flame-retardant properties. Similar to the method of this work, subsequent researchers usually use ultraviolet light to initiate cross-linking of monomers or oligomers containing flame-retardant elements (such as phosphorus, nitrogen, silicon, boron, etc.) on the surface of the substrate, achieving the construction of UV-aided flame-retardant coatings. For example, Hu and co-workers[207] synthesized a series of P–N-containing vinyl-based monomers that were polymerized and grafted onto the surfaces of fabrics by UV curing technology in air atmosphere. The resultant UV-cured coating can endow nylon 66 and cotton fabrics with high flame retardancy, including increasing LOI, decreasing pHRR, and fire extinguishing performances. In addition, UV curing technology can be used to stabilize nanoparticles and polymers that have a weak affinity with the substrate surface, thereby building a more stable flame-retardant physical barrier.[208] Gashti et al.[209] adhered MWNTs on the surface of cotton fabric using vinyl phosphonic acid monomer as the crosslinking agent through UV curing, which improved the thermal stability and flame retardancy of cotton fabrics.

Meanwhile, UV curing technology has been used in the construction of durable coatings, due to the promotion of stable covalent bonds between the coating and the substrates (fabrics, woods, etc.).[210] As shown in Figure 6b, the monomers or oligomers should have both P–N flame-retardant groups and unsaturated bonds, which can be further chemically crosslinked with the active groups (–OH, $-NH_2$, etc.) of the substrates under the action of the initiator and UV. Nguyen et al.[210b] synthesized a new type of phosphorus-containing acrylate, and then initiated grafting onto cotton fabric under a broadband UV light source. After 10 cycles of gentle washing at 40 °C, the weight gain rate of the coating remained unchanged, and the fabric could still pass the vertical flammability test. The grafting ratio of the coating induced by UV is the key to the flame-retardant durability of the treated fabric. Based on this point, on one hand, more unsaturated bonds are introduced into the flame-retardant monomer/oligomer to increase the crosslinking reaction sites.[211] On the other hand, the researchers try to graft a group that is more reactive to UV-induced free radical reactions as a "bridge" on the surface of the substrate, and then crosslink with flame retardants under UV light. Yu and co-workers[212] firstly deposited thiol-containing reactive groups on the surface of the cotton fabric, and then used the thiol–alkenyl click method initiated by UV light to covalently graft the synthesized unsaturated phosphates. After 30 cycles of washing, the treated fabric could pass the vertical flammability test, and the LOI value was reduced from 27.2% to 25.1%.

Notes that, in the UV curing technology, the solvent of the flame-retardant immersion liquid is usually an organic solvent such as acetone, which probably limits its application. In addition, the adjustment method of UV-aided flame-retardant treatment temporarily stays at the shallow level of adjusting UV light intensity, irradiation time, and irradiation distance. There are few reports on specific control methods and in-depth mechanisms of UV-induced flame-retardant grafting efficiency on the substrate. However, due to the advantages of fast curing speed, low energy consumption, less pollution, high chemical stability, and wide application conditions, UV curing technology are still highly attractive for flame-retardant surface treatment. In the future, the application of UV curing technology used in the curing process of dip-dry, Sol–gel, and layer-by-layer assembly flame-retardant surface treatment will be an important development trend.

4.3. Sol–Gel Flame-Retardant Treatments

Since the 1950s, sol–gel technology has been widely used in the surface functional modification of materials due to the designability of composition and morphology.[216] The sol–gel process always includes a two-step hydrolysis/condensation reaction of metal alkoxides-based precursors as shown in **Figure 7**a,b. First, the metal alkoxide precursor is dispersed and slightly hydrolyzed in a solvent to form a stable suspension of colloidal particles, that is, a sol. And the sol can be deposited on the surface of the substrate by spraying, brushing, or dipping. Second, the metal alkoxide in the sol is further hydrolyzed and condensed to form a gel, which is then dried to obtain a functional coating. Recently, benefitting from the advantage of soft treatment conditions (low temperature, facile process, ambient pressure, etc.), sol–gel technology has attracted extensively interesting attention in the field of flame retardancy.

4.3.1. Metal Alkoxide Sol–Gel Treatment

Early sol–gel surface flame-retardant systems directly used metal alkoxides to build the gel network.[188a] The first flame-retardant sol–gel coating was reported in 2007, which used tetraethylorthosilicate (TEOS) precursors on regenerated cellulose fibers.[217] The process of TEOS hydrolysis and polycondensation is influenced by many factors, including pH value, the

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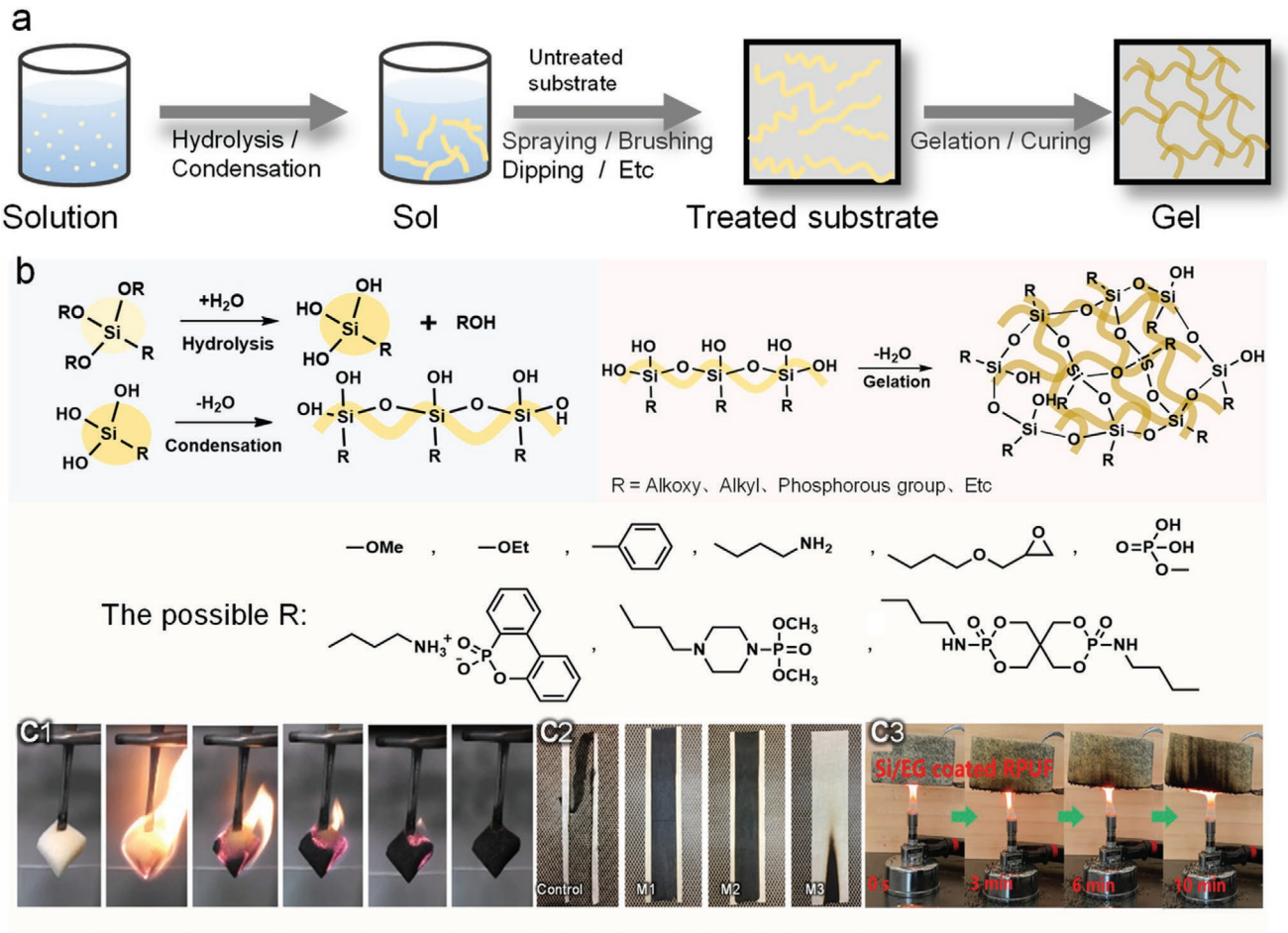


Figure 7. Sol–gel flame-retardant surface treatment a) Main steps for preparing sol–gel coatings. b) Schematic representation of the sol–gel process. c) Typical flame-retardant performances of treated substrates: c1) Time-lapse photos for burning of silica-treated polyurethane foam. c2) Digital pictures for the control and coated cotton fabrics after vertical flame tests. c3) Continuous burning test for Si/EG coated polyurethane foam. c1) Reproduced with permission.[213] Copyright 2019, American Chemical Society. c2) Reproduced with permission.[214] Copyright 2017, Elsevier. c3) Reproduced with permission.[215] Copyright 2020, Elsevier.

ratio of components, and so on. For example, Alongi et al.[218] used the sol–gel method to treat polyester, cotton, and their blended fabrics, and studied the key factors in detail. When a proper ratio of TEOS/H_2O was 3:1, TTI of the fabric was significantly increased (up to 98%), and HRR and pHRR values are significantly reduced (up to 34%) compared to the pure fabric. The corresponding mechanism study confirmed that the coating promoted the formation of a silica-based insulating barrier on the surface of the fabric, thereby improving its thermal oxidation stability and flame retardancy.[219] Further research explored the influence of different siloxane precursors, in which aromatic-containing structures were beneficial for the improvement of thermal stability and flame retardancy of the fabric.[219] Up to now, siloxane precursor-based precursors have been the most popular in the sol–gel flame-retardant treatments.

Other metal alkoxides from Ti, Al, Zr, etc. have been also developed for the sol–gel precursors in order to obtain more special properties.[220] A comparative study showed that the silica-based coating imparted the best flame retardancy to cotton fabric (56% increase of time to ignition (TTI) and 20% decrease of pHRR), while the alumina/titania-based coatings with the similar structure had much better abrasion resistance.[221] These findings provide a strategy for the design of Si–Ti or Si–Al hybrid alkoxides-based coating to simultaneously achieve high flame retardancy and abrasion resistance.[222] It is possible to use mixed metal alkoxides to build multifunctional flame-retardant coatings.

Although most sol–gel flame-retardant coatings are applied to fabrics, some researchers have turned their interest to other polymer substrates, such as polymer foams and woods. For example, Li et al.[223] deposited silica aerogel on the surface of rigid polyurethane foam from TEOS precursors via a sol–gel and freezing-dry process. The resultant coating with a nanoporous structure formed by the sol–gel process could give the foam better thermal insulation and high flame retardancy (LOI of 32.5%, 40.4% decrease of pHRR, and 45.6% decrease of PRSR). A similar method is further used for flexible polyurethane foam to extinguish the foam (Figure 7c1), inhibit dripping, and reduce heat release.[213] As for woods, a typical sample is that vinyl-functionalized zirconium oxoclusters are copolymerized with vinyltrimethoxysilane on wood for fire protection.[224] Compared with fabrics, sol–gel technology can apply

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more coatings on foam or wood to obtain a more significant flame-retardant effect with less impact on material properties.

Indeed, most metal alkoxide sol–gel treatments show limited flame-retardant efficiency and usually require a large number of loadings on the protected substrate to achieve satisfactory flame retardancy. Due to the lack of flame-retardant elements (such as P, N, etc.), the metal oxide insulation barrier formed at high temperatures has a certain effect on reducing heat release, but is useless in extinguishing the fire. However, the massive deposition of metal alkoxide sol–gel coatings will severely deteriorate the mechanical properties of flexible fabrics and films.

4.3.2. Phosphorus-Doped Sol–Gel Treatment

Fortunately, benefitting from the inclusiveness of the hydrolysis and condensation step of sol–gel, the flame-retardant efficiency of sol–gel coatings can be largely enhanced by utilizing the synergistic effect between silicon and flame-retardant elements (Figure 7b). Of all them, the phosphorus-doped sol–gel treatment is the first to be developed with high flame-retardant efficiency.[188a] This can be achieved by the following three approaches: 1) directly doping of phosphorus-containing small molecules, such as phosphorus aid, phosphate, etc.; 2) copolymerizing with functional alkoxysilane precursors that connect with phosphorus-based groups via physical or chemical bonds; 3) copolymerizing with functional alkoxysilane precursors that have both phosphorus and nitrogen elements. In this first case, phosphorus-containing small molecules are directly introduced into the sol–gel system, accompanied by the hydrolysis and condensation of metal alkoxides. The first report on phosphorus-doped sol–gel treatment is the use of phosphoric acid or ethyl dichlorophosphate to dope TEOS precursors.[225] The treated fabric showed an improvement in self-extinguishing properties that was difficult to achieve by the pure metal alkoxide sol–gel treatment. Other similar results have been reported by using different phosphorus-based molecules, such as aluminum phosphinate, phytic acid, triphenylphosphate, etc.[188d,226] However, the doping content of these phosphorus-based molecules is largely limited by sol–gel conditions, and the poor interaction between small molecules and the cross-linked silica network will result in poor durability.

In the second case, the phosphorus group is first connected to the alkoxysilane precursor through a physical or chemical bond, and then construct the sol–gel coating. Therefore, the functional P-containing alkoxysilane precursor is the key, which has been extensively developed in recent years. Wang and co-workers[227] used DOPO-based acid to modify poly(γ-aminopropyl silsesquioxane) to obtain the functional precursor with electrostatic bonds. The obtained sol–gel coating exhibited high flame-retardant efficiency on PET fabrics, that was, when the coating load was 8 wt%, the treated fabric showed an increase in LOI (up to 32.0%), a decrease in heat release, and complete suppression of melt dripping. And a dominating vapor-phase flame-retardant activity was found due to the presence of DOPO. Compared with electrostatic bonds, the alkoxysilane precursor modified with phosphorus groups by covalent bonds will have better stability, and the corresponding flame-retardant mechanism may be changed. 3-glycidyloxypropyl triethoxysilane (GPTES), as one of the most used silica precursors, was chemically modified by a phosphorous-containing acid through epoxy ring-opening reaction.[228] The resultant functional alkoxysilane was copolymerized with TEOS to treat cotton fabrics. The coating played a role in the condensed phase, which promoted the formation of dense P-Si-C hybrid residues at high temperatures, thereby improving flame retardancy (increase in TTI and decrease in HRR and CO/CO_2 ratio).

As for the third case, P–N synergism is expected to be used in sol–gel coating systems. The P and N groups can be modified into one siloxane precursor, or modified in different precursors, further to construct the sol–gel coatings. Generally, the former method can better exert the P–N synergy and attract more people's attention. For example, phytic acid and (3-piperazinylpropyl)methyldimethoxysilane was used to synthesize a P–N functional silicane precursor with electrostatic bonds.[229] The treated PET fabric showed improved self-extinguishing performance, reduced heat release, and inhibited melt dripping, under the coaction of P and N that effectively reduced the combustible products during burning. In addition, the P–N synergistic coating can be constructed by additionally introducing P–N flame retardants into the sol–gel system. More recently, Rao et al.[230] used sodium alginate to stabilize APP and further co-gelled with TEOS, thus constructing a sol–gel coating on cotton fabrics. In this coating, alginate was used as a carbonizing agent, APP was used as an acid source and foaming source, and TEOS was used as a silicon source to construct a hybrid intumescent system containing P/N/Si. Consequently, under an ultralow loading of 10 wt%, the coating allowed the fabric to pass the vertical burning test with a high LOI value of 31.0%, and significantly reduced THR (–63%) and TSR (–70%). Meanwhile, the highly transparent coating had little effect on the appearance and mechanical properties of the fabric.

Furthermore, since siloxane may undergo a co-hydrolysis reaction with hydroxyl groups on the surface of the fabric, the phosphorus-doped sol–gel treatment can be used to fabricate water-resistant flame-retardant coatings. Bis(trimethoxysilylpropyl) spirocyclic pentaerythritol diphosphate was designed and used in sol–gel technology to prepare flame-retardant cotton fabrics.[231] These P–N-type flame retardants containing two silane groups can form C–O–Si covalent bonds through the hydrolytic condensation of $Si–O–CH_3$ at both ends with the hydroxyl groups of cotton cellulose. Consequently, the LOI value of the treated cotton fabric reached 29.5% and remained at 26.2% after 20 washing cycles. Similar to the UV curing technology, the introduction of active bridging agents on the surface of the fabric is also suitable for increasing the interaction between the substrate and the sol–gel coating. Xing and co-workers[232] used butane tetracarboxylic acid to pretreat the silk fabric, and then introduced the flame-retardant sol–gel coating composed of TEOS, boron and urea to impregnate the treated silk fabric. It was worth noting that after 10 washing cycles, the LOI value of the treated fabric was maintained at 30.8% in comparison with the original 31.0%.

4.3.3. Particle-Hybrid Sol–Gel Treatment

The inclusiveness of the sol–gel method also provides a way for the introduction of various inorganic components such as nanoparticles and metal minerals, of which the active groups on the surface can participate in the sol–gel reaction. This particle-hybrid sol–gel treatment can bring two benefits: improving

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fire safety and bringing new multifunctional capacity. In particular, the inorganic particles in the sol–gel coating are helpful in reducing the release of smoke and toxic gases, which is the main problem that the phosphorus-doped sol–gel treatment is difficult to solve. For example, zinc borate, zinc acetate dehydrate, or zinc oxide was incorporated into the classic metal alkoxide sol–gel system, which effectively reduced the release of smoke and CO for the cotton fabric.[233] In another work, expandable graphite (EG) and silicone resin were together coated on the rigid polyurethane foam surface through a sol–gel process.[215] The introduction of EG greatly improved the quality of the protective carbon layer formed during the burning process, further to inhibit the generation and release of smoke.

On the other hand, the particle-hybrid sol–gel treatment has been developed to simultaneously endow the substrates with flame retardancy and multifunctionality (hydrophobicity, antibacterial, oil absorption, UV resistance, etc.).[234] Usually, the flame-retardant and functional layers are sequentially coated on the surface of the substrate through the sol–gel process. Hu and co-workers[235] deposited alkyl ammonium silsesquioxane/phytic on the cotton fabric, and then coated the second layer of dimethylsiloxane and TiO_2 particles. Benefitting from the introduction of TiO_2 in the sol–gel coating, the flame-retardant cotton fabric also showed superhydrophobicity and self-clean ability. Further, researchers have developed more convenient one-pot sol–gel methods to prepare functional flame-retardant coatings. Typically, a nanocoating consisting of APP, MMT, and vinyltrimethoxysilane (VTMS) was directly applied to achieve both flame retardancy and hydrophobicity for cotton fabric.[214] In this system, APP and MMT particles not only were used as flame retardants (Figure 7c2), but also provided high roughness for hydrophobicity. In addition, APP particles can be hydrophobically modified first, and then introduced into the sol–gel coating to achieve the construction of super-hydrophobic and flame-retardant functional coatings.[236] In the future, the sol–gel coating with multifunctionality and flame retardancy will show great application prospects to meet the multiple requirements of complex environments.

4.4. Layer-By-Layer-Assembly Flame-Retardant Treatments

Of all surface flame-retardant treatments, layer-by-layer (LbL) assembly technique is the most active one, due to the advantages of simplicity, diversity, and designability.[237] The first example of layer-by-layer assembly appeared in 1966, but it was not until 2009 that Grunlan opened a new chapter in the use of flame-retardant treatments.[238] Generally speaking, as shown in **Figure 8**a, LbL technology is basically composed of

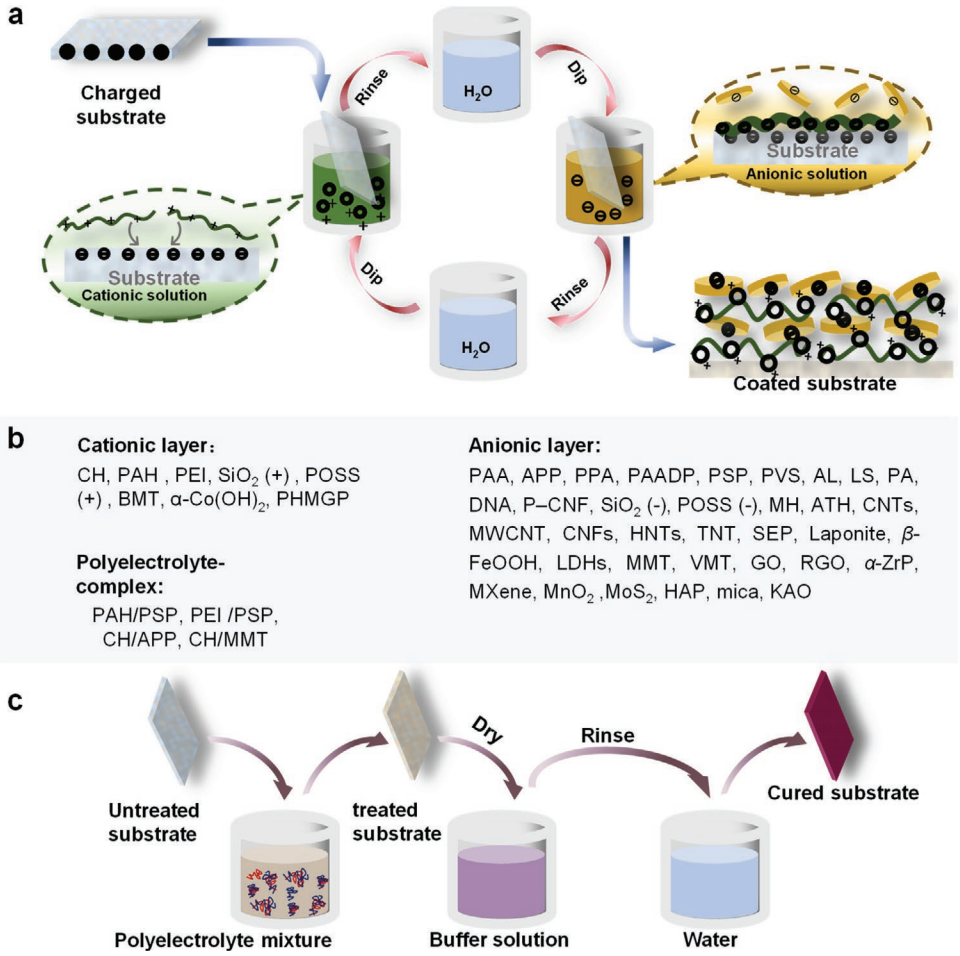


Figure 8. a) Schematic representation procedure of layer-by-layer assembly coatings. b) Main components used for layer-by-layer assembly and polyelectrolyte complex coatings. c) A schematic representation procedure of polyelectrolyte complex coatings.

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alternate adsorption and accumulation of oppositely charged substances on the substrates, mainly based on electrostatic force, hydrogen bonding, donor-acceptor interactions, etc. Despite the thin thickness ranged from 100 nm to 1 μm, the LbL coating can achieve a relatively high flame-retardant protective effect. In the following part, we focus on the representative systems with various active ingredients. And the corresponding advantages, defects, and key factors are also discussed.

4.4.1. Inorganic LbL Coating

The early LbL flame-retardant coatings were constructed from inorganic nanoparticles as flame-retardant components and polymers as binders. Grunlan and co-workers[238b,239] reported the first flame-retardant example by using cationic branched PEI and anionic clay (MMT or LAP). When applied to cotton fabrics, the coating improved the thermal stability due to the physical barrier effect of clay at high temperatures. After that, various inorganic nanoparticles, including SiO_2. TiO_2, POSS, ZnO, CNTs, GO, LDH, etc., have been used for the construction of LbL flame-retardant coatings.[240] However, it should be noted that the cationic polymers only play a role in assembling inorganic particles, but do not contribute to flame retardancy, thus leading to low flame-retardant efficiency.

One possible way to solve the above problem is to replace all organic layers with inorganic layers. For example, positively and negatively charged colloidal silica nanoparticles with different diameters were coated onto the surface of PET fabric through LbL assembly.[241] It was found that this fully inorganic coating increased TTI by 45%, decreased pHRR by 45%, and eliminated melt dripping. The size and uniformity of nanoparticles as well as the thickness of the coating have a critical impact on flame retardancy. The currently developed fully inorganic LbL flame-retardant coatings include positively and negatively charged Al_2O_3, POSS, ZrP, and their hybrids, etc.[242] It is no doubt that for these coating, the thermal barrier effects of nanoparticles are enhanced in comparison with the above polymer/inorganic nanoparticle coatings. However, there are three limitations: 1) poor distribution of nanoparticles; 2) many layers to be desired; 3) weak self-extinguishing ability.

In response to these new problems, Alongi et al. first used horizontal spraying to achieve the homogeneous deposition of silica LbL coating on fabrics.[243] Compared with conventional dipping and vertical spraying, the horizontal spraying approach showed much better flame retardance. But this method is not suitable for foam materials, of which internal skeleton cannot be coated by horizontal spraying. As for the second problem, a trilayer (TL) system with a rapid growth pattern was developed by adding an anionic poly(acrylic acid) (PAA) monolayer between anionic clay and cationic branched-PEI monolayers.[244] This TL approach used 40% less monolayers to achieve an order of magnitude thicker coating in comparison with the conventional bilayer method. However, for the third problem, it is difficult to achieve self-extinguishing by only relying on nanoparticles alone, and other flame-retardant elements are needed (**Table 2**).

4.4.2. Organic LbL Coating

Compared with inorganic nanoparticles, organic flame-retardant compounds used in LbL coatings show the advantages of high fire extinguishing efficiency and better substrate compatibility. According to the flame-retardant mechanism, organic LbL coatings can be divided into intumescent and non-intumescent systems. Non-intumescent organic LbL coatings mainly exhibit flame retardancy through strong carbonization ability in the condensed phase or release of incombustible gases.[270] For the former effect, polysaccharide-based materials, such as chitosan (CH), starch, etc., are usually used because of their high carbonization ability.[270a] However, similar to inorganic nanoparticles, these char layers formed at high temperatures can effectively reduce heat release, but cannot extinguish fires. On this basis, vapor phase dilution effect is further introduced to enhance flame-retardant efficiency.[270b,271] The LbL coating consisting of CH and poly(vinylsulfonic acid sodium salt) (PVS) can completely prevent the flame from spreading on the polyurethane foam, due to the joint action of the carbonization barrier of CH and the incombustible gas released by PVS.[270b]

Intumescent nanocoatings can better combine the above gas-condense dual phase flame-retardant effect. The first intumescent flame-retardant LbL nanocoating was developed in 2011 by using polyallylamine (PAH)/sodium and hexametaphosphate (PSP) to treat cotton fabrics.[272] Cotton acted as a natural carbon source, PSP was used as an acid source, and PAH acted as a forming. When encountering a flame, a dense intumescent char will be formed immediately, which further isolated the heat transfer and release of combustible volatiles. Consequently, the coating not only significantly reduced the pHRR value of 43% and the THR value of 51%, but also made the fabric self-extinguish in the vertical flame test. Subsequent researches improve the LbL coating by adding additional carbon sources to make it more versatile and efficient.[246]

The organic LbL method provides an opportunity to build fully bio-based coatings with good renewability and sustainability.[246,273] Various all-biomass polyelectrolyte systems, such as CH/alginate, CH/Phytic acid, CH/DNA, etc., have been developed for flame-retardant fabrics and foams.[246,248,274] For example, DNA containing the structures of polyphosphoric acid, polyhydric char sources, and the nitrogen-containing bases is a natural self-intumescent polyelectrolyte.[248] When combined with CH, the obtained nanocoating made cotton fabric self-extinguish in the horizontal flammability test, increased the LOI value by 24.0%, and reduced the heat release rate by 40%. Although self-extinguishing effects can be achieved, most organic LbL coatings are difficult to reduce or even worsen smoke release, due to incomplete burning of additional organic matter on the surface of the substrate.

4.4.3. Hybrid LbL Coating

The hybrid LbL coating can combine the flame-retardant effects of inorganic nanoparticles and organic components to achieve synergistic high fire safety. Typically, the hybrid nano-coating composed of organic materials with high carbonization ability

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Table 2. Flame retardant performances for representative LbL assembly and polyelectrolyte complex coatings.

	Substrate	Coating	Number	Result	Ref.
Inorganic LbL coating	PET fiber	SiNP+/SiNP-	5BL	CCT: TTI -45%, pHRR -20%	[241]
	Cotton	POSS+/POSS-	20 BL	MCC: pHRR -20%	[242c]
	Cotton	Al_2O_3+/Al_2O_3-	20 BL	Slight increase in LOI	[242a]
	PUF	Boehmite (BMT)/VMT (vermiculite)	1 BL	CCT: pHRR -50%, TSR -50%; eliminates melt dripping	[245]
Organic LbL coating	Cotton	CH/phytic acid	30 BL	VFT: self-extinguishment; CCT: pHRR -60%	[246]
	Cotton	CH/PSP (poly(sodium phosphate))	30 BL	VFT: self-extinguishment	[247]
	Cotton	CH/DNA	20 BL	VFT: self-extinguishment; LOI: 24.0%; CCT: pHRR -40%	[248]
	Cotton	Starch/Poly(phosphoric acid)	2 BL	HFT: self-extinguishment; CCT: pHRR -50%	[208]
	Ramie	PEI/APP	20 BL	VFT: self-extinguishment; MCC: pHRR -65%, THR -68%; CCT: pHRR -42%, THR -25%	[249]
	PA66	PSP/PAH	40 BL	MLC: pHRR -60%	[250]
	PET	Polysiloxane/PA	5 BL	VFT: enhanced charring, reduced burning rate; CCT: pHRR -65%, THR -59%, TSR -72%, LOI: 31.4%	[251]
	PUF	CH/phosphorylated cellulose nanofibers	5 BL	HFT: no melt-dripping; CCT: pHRR -31%	[252]
	PUF	CH/lignosulfate	8 BL	HFT: no melt-dripping; CCT: pHRR -42%	[253]
	PUF	PAA/CH/poly(phosphoric acid)/CH	5 QL	Burn-through torch test: temperature on back side kept under 100 °C; LOI: 23.0%	[254]
Hybrid LbL coating	Cotton	BPEI/MMT	20 BL	VFT: 13% residue remains	[239]
	Cotton	Phosphorylated GO/PEI	10 BL	CCT: pHRR -27%, THR -21%; VFT: cohesive residue	[255]
	Ramie	PEI/ZrP + PEI/APP	5 + 5 BL	MCC: pHRR -53%, THR -56%; VFT: cohesive residue	[256]
	PET-cotton	SiO_2+/ SiO_2-/CH/APP	10 QL	CCT: TTI +37%, pHRR -11%, THR -22%; VFT: no after glow	[257]
	PA66	PAH/PSP/PAHTiO_2	15 BL	MCC: pHRR -26%	[258]
	PUF	PEI/GO/Melanin nanoparticles	2 TL	Torch test: self-extinguishment; CCT: pHRR-39%, THR -12%, TSR -59%	[259]
	PUF	MMT/PAH/PSP	4 to 10 TL	Torch test: self-extinguishment; CCT: pHRR -54–62%, THR -8%	[260]
	PUF	CH/VMT + CH/APP	4 + 20 BL	Torch test: self-extinguishment; CCT: pHRR -66%, THR -11%, TSR +41%	[261]
	PUF	CH/MXene (Ti_3C_2)	8 BL	CCT: pHRR -57%, THR -66%, TSR -71%	[262]
Polyelectrolyte complex coating	Cotton	APP/BPEI	PEC	VFT: self-extinguishment; CCT: pHRR -51%	[263]
	Cotton	BPEI+PSP	PEC	VFT: self-extinguishment; MCC: pHRR -53%	[264]
	Nylon-cotton	PEI+APP/MEL	PEC	VFT: self-extinguishment; MCC: pHRR -65%, THR -28%	[265]
	PET-cotton	Polyallylamine (PAAm)/PSP	PEC	VFT: self-extinguishment; MCC: pHRR -78% (cotton), -31% (PET), THR -30%	[266]
	Wool fiber	CH/PA	PEC	VFT: self-extinguishment	[267]
	PAA fiber	CH/MMT	PEC	VFT: self-extinguishment; CCT: TTI +46%, pHRR –62%, THR –49%, TSR –49%	[268]
	PUF	APP+PEI/GO	PEC + LbL	VFT: self-extinguishment; pHRR –64%	[269]

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and inorganic nanoparticles can jointly form a ceramic barrier during the pyrolysis process, thereby playing a more effective role as a flame-retardant barrier.[275] It was reported that the CH/MMT nanocoating prevented the melting of the polyurethane foam even burnt by a butane torch, and reduced the pHRR value by up to 52%.[275a] Similar synergistic systems have been extensively developed, such as CH/VMT, CH/MXene, PEI/SEP-alginate, CH-CNT/MMT/alginate, etc.[275b,276] Even nanoparticles of different shapes (spherical, rod-like, and layered) are used together to obtain a better flame retardant effect.[277] It is worth noting that this collaborative system can simultaneously achieve self-extinguishing and smoke suppression. Combined the lamellar shield of graphene oxide (GO) and radical trapping effect of synthetic melanin nanoparticles (SMNPs), one-trilayer PEI/GO/SMNPs coating extinguished the fire of polyurethane foams in the torch burn test, and reduced the values of pHRR (by 38.9%) and TSR (by 58.7%).[259]

Inorganic nanoparticles can also be combined with intumescent systems to construct hybrid LbL coatings.[257,260,261] It is expected that the intumescent carbon layer formed during burning can be hybridized and reinforced by inorganic particles to achieve a better flame retardant effect. The first report of an intumescent hybrid LbL coating was to deposit CH/APP/SiO_2 nanocoating onto the surface of cotton-PET fabrics.[257] The complex architectures suppressed the afterglow in the vertical flammability test, while the morphology had a key influence on flame retardancy. In another work, a multiple hybrid LbL nanocoating composed of the first layer PAA/MMT (barrier to volatile release), the second layer BOH (gas phase diluting), and the third layer APP/MMT (hybrid intumescent insulation) was designed to endow polyurethane foams with fire safety (extinguishing, decrease of pHRR by 50% and TSR of 34%).[278]

Despite many advances, LbL nanocoatings still face many challenges. First, the operation is more complicated, and a lot of layers always need to be deposited to achieve a certain flame retardant effect, which has become one of the main reasons limiting its practical application. A promising solution may be to change impregnation methods (such as spraying), develop professional and efficient equipment, and construct more efficient LbL components (such as hybrid synergistic systems). Second, the wash durability of the LbL coating should be largely improved. In fact, the interactions between the substrate and different layers are quietly weak, due to the LbL assembly based mainly on electrostatic forces. In the future, the improvement of the durability of LbL coatings can be probably achieved from the following two aspects. 1) In order to increase the water resistance, additional hydrophobic layer can be applied on the surface of the LbL coating. 2) The interaction between the LbL layers can be enhanced by combining other surface treatments such as sol–gel, UV curing, coordination crosslinking techniques, etc.[279]

4.5. Emerging Surface Flame-Retardant Treatment

As discussed above, plasma/ultraviolet-assisted, sol–gel, and LbL assembly technologies have been widely developed for advanced flame-retardant treatments. These methods have their own advantages and drawbacks, and gradually formed a complete technical system. In the next paragraph, we will focus on the new surface flame-retardant treatment methods that have emerged in recent years. These methods have not been extensively studied, but they may be new trends in the future.

4.5.1. Polyelectrolyte Complex Coating

Recently, a novel one-pot strategy, namely polyelectrolyte complex coating, has been explored to eliminate the inconvenience of repeatedly applying multiple layers of conventional LbL coatings.[264,279c] In a typical polyelectrolyte complex coating, as shown in Figure 8b, flame-retardant components with opposite charges are mixed in water to form an insoluble polyelectrolyte complex, and then adsorbed on the substrate by simple dipping.[264] The first report of polyelectrolyte complex coatings combined PSP and PEI to construct a complex for cotton fabrics, which reduced the THR value by 52.7% at a loading of only 2.3 wt%. When the gain weight achieved 23 wt%, the treated cotton could self-extinguish in the vertical flammability test. The soaking time in the complex solution directly determined the loading weight and flame retardancy. Although this simple one-pot coating can reach high efficiency, the strength of the interaction between the polyelectrolyte complex and the substrate may be so weak that the coating is easily peeled off. Meanwhile, the unstable polyelectrolyte complex suspension can only be used once in a limited amount of time after preparation.[279c]

The subsequent work tries to improve the polyelectrolyte complex coating by a post-treatment of pH crosslinking. The weak polyelectrolyte can be used to prepare a stable water-soluble suspension (such as polyamine-polyphosphate with a pH of 9–12), which is applied to a substrate. After drying, the polyelectrolyte mixture on the surface of the cotton cloth is further cured by an acid buffer and converted into insoluble matter.[265,279c] Compared with the original precipitation process, this treatment allows the stable polyelectrolyte composite solution to be used multiple times over time and extends the shelf life, while maintaining the high flame retardancy of the coating. Further, the polyelectrolyte composite coating can be assisted by UV curing to increase durability. CH, phosphorylated chitosan, and poly-acrylate sodium were together deposited onto the surface of the PA66 fabric by one-pot LbL assembly and subsequent UV-cross-linking.[279d] After 5 washing cycles, the treated fabric could maintain flame retardancy in the vertical burning test. Until now, similar polyelectrolyte complex coatings have been developed for flame-retardant cotton fabrics, nylon-cotton blends, epoxy resins, wools, woods, etc.[280] Although the fire safety protection effect (such as smoke suppression) still has a gap with sol–gel and LbL treatments, polyelectrolyte composite coatings and other treatments using similar mechanisms provide new opportunities for the construction of fast and environmentally friendly coating construction. Based on the success of polyelectrolyte complex coatings, the adjustable, facile, and high-efficiency complex coatings can be expanded for flame-retardant surface treatments in the future.[268]

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4.5.2. Infrared Reflective Coatings

Until now, the condensed phase flame-retardant effect of coatings mainly comes from the barrier/insulation of heat, oxygen, and combustible gas, however, the dominant radiation heat transfer in medium or large-scale fires lacks effective approaches of suppression. In 2012, Schartel et al.[57,281] proposed an infrared (IR) reflective flame-retardant coating to reduce the transfer of radiant heat to the protected polymer substrates (PA/PC). The infrared-mirror coating composed of a silica layer, an adhesive layer, and an IR-reflective copper layer could significantly extend the TTI by 5–8 times, limit the flame spread and flame growth index, and reduce the MAHRE value at a thickness of less than 1 μm. The flame-retardant mechanism of the copper-mirror coating was mainly to isolate the radiant heat through infrared reflection, so that the substrate was kept at a low temperature from being ignited/decomposed. Later, researchers took over IR-reflective flame-retardant methods such as using indium tin oxide on PMMA, vanadium dioxide on steel, aluminum on LDPE, etc.[282] Although these studies confirmed that the IR-reflective coatings were effectively to delay TTI, it failed to prevent ignition if the heat source was continuously applied. Once ignited by fire, the IR-reflective coating had almost no effect on the pHRR and THR of the polymer substrates. In addition, in the small fire test, the protective effect of the infrared reflective coating may be weak due to the igniter of non-radiant heat.

Despite many dilemmas to be tackled, it is no doubt that the infrared mirrors provide a new approach for the development of flame retardant coatings. In the existing work, the IR-reflective coatings have been used to the substrate with a smooth surface through the back coating, while their applications in textiles and foams via other coating technologies remain to be developed, due to the negative impact of roughness on the IR mirror. As for the limitations of comprehensive fire safety (LOI, UL-94, pHRR, THR, etc.), one possible solution is to use infrared reflective coatings together with other flame retardant ways. For instance, Bourbigot and co-workers[283] deposited Al/Al_2O_3 IR-reflective coating on PA6 and PP filled with commercial flame retardants of EG, melamine polyphosphate, and aluminum diethylphosphate, which showed a beneficial complementary flame retardancy of high TTI and low pHRR. In the future, surface treatments combined with IR mirror and barrier effect may become a popularized technology to achieve high flame retardancy in small, medium, and large fires.

4.5.3. Biomimetic Flame-Retardant Treatments

Bio-inspiration in micro/nanomanufacturing processes has enabled the design and fabrication of functional materials in many fields. Recently, biomimetic flame retardant treatments have gradually appeared in the eyes of researchers, mainly including: 1) imitating the micro-nano structure existing in nature to enhance the flame-retardant effect, 2) imitating the interface effect in nature and developing new coating construction methods. In the former case, the highly oriented layer microstructure of nacres has been introduced into flame-retardant coatings because of their thermal resistance and gas barrier effects.[284] For example, a low-viscosity solution containing both a high concentration of inorganic nanosheets (MMT) and PVA binders was applied to the surface of the substrates by means of directional flow (**Figure 9**a), during which MMT and PVA were assembled together to form a highly ordered layered structure with dozens of layers.[284a] Due to the nacreous layered microstructure, the resulting nanocoating shows high mechanical strength, transparency, and fire-extinguishing performance. In fact, the microstructure and flame-retardant mechanism used in this study are very similar to LbL assembly, while the construction method of nano-coating with a high concentration of well-arranged nano-sheets is easier and more convenient. Interestingly, this nacre-like concept is also used in the LbL flame-retardant nanocoating. It was reported that CH/MMT nacre-mimetic LbL nanocoating increased the LOI value of cellulosic paper up to 35.0%.[284b] The high-concentration oriented inorganic nanostructure of the nacre-like layer can be used as a reference for LbL to further improve the flame retardant performance.

For the second case, by imitating the high-strength adhesion existing in nature, the interaction between the flame-retardant coating and the substrate can be improved. Typically, polydopamine (PDA, a molecule containing catechol) as an mimic of adhesion proteins in the feet of common mussels has been widely used as a general-purpose surface adhesion modifier in bioengineering.[286] Ellison and co-workers[287] proposed a flame-retardant PDA nanocoating, consisting of a planar sublayer and a secondary particle layer structure, which evolved together and eventually became a dense and uniform layer. The study found that the PDA nano-coating closely adhered to polyurethane foam could reduce pHRR of by 67% and extinguish the fire in a torch burn test at a loading of 16 wt%, due to the multiple flame-retardant actions of PDA (char formation and radical scavenging). These results were further improved by adding GO, which resulted in a reduction in peak HRR (65%) with less coating loading of 5 wt%.[288] Although the polymerization of PDA takes a long time (several days) to achieve satisfactory flame-retardant properties, this work provide a new way for biomimetic flame-retardant treatments.

Further, the strong biomimetic interface adhesion can be used to construct nano-coatings with high durability. In a recent study (Figure 9b), inspired by the adhesion mechanisms of snails and tree frogs, a flame-retardant nanocoating with phase-separated micro/nanostructures was fabricated through the radical copolymerization of hydroxyethyl acrylate and sodium vinylsulfonate.[285] Due to interfacial hydrogen bonding and mechanical interlocking like those of tree frogs, the resultant nanocoating showed strong interfacial adhesion to various surfaces. Meanwhile, because of the high carbonization ability of the nanocoating, the treated polyurethane foam can reach V-0 rate in the vertical burning test and show low pHRR and TSR values. In addition, the biomimetic treatment is introduced for flame-retardant cotton fabric with washing durability. Inspired by the dye-fixing process, a biomass coating without conventional elements (such as Cl, Br, P) was developed to impart long-lasting flame retardancy to cotton fabrics.[197b] In this coating, tannin used as a carbonization agent was fixed onto the fiber surface by tartar emetic through dye fixation, while the further coordinated Fe^{2+} catalyzed the formation of graphited

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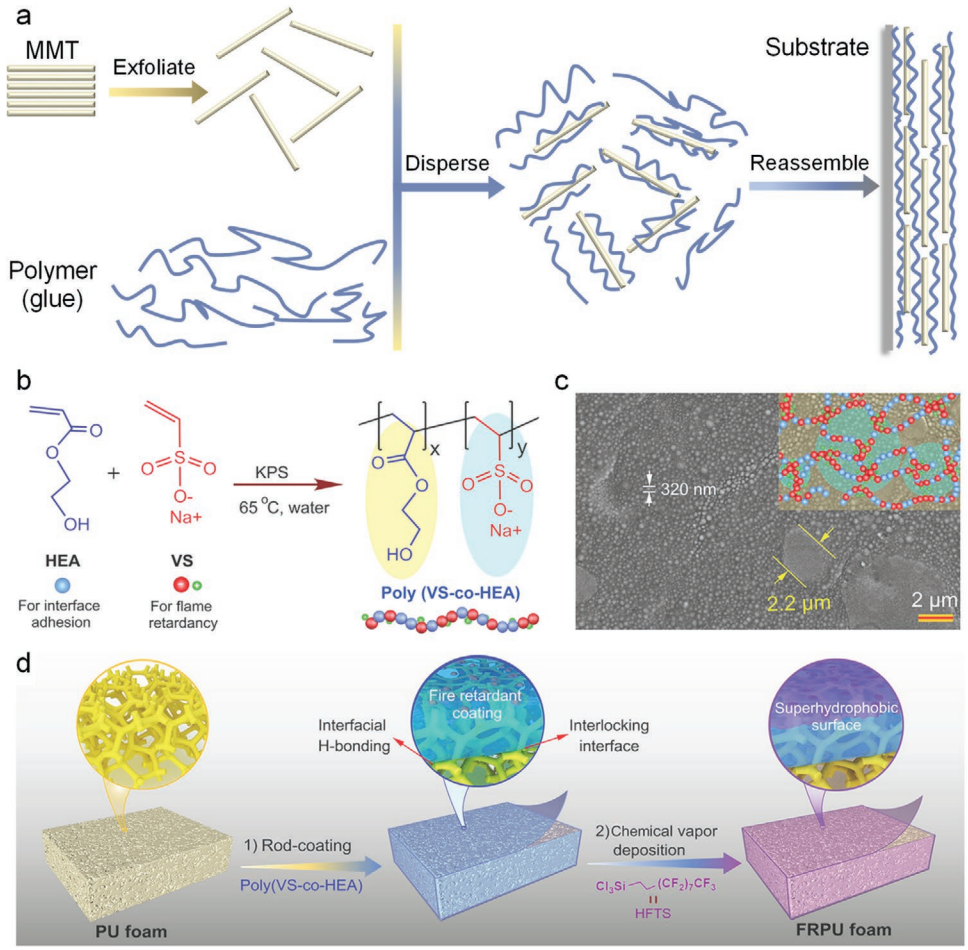


Figure 9. a) Schematic of one-step coassembly for nacre-inspired nanocoatings. b–d) Synthesis (b) and micro/nanostructure (c) of frog-inspired coatings and their application on polyurethane foam (d). b–d) Reproduced with permission.[285] Copyright 2021, American Chemical Society.

char from tannin and cotton fibers to achieve high flame retardance. The treated fabrics remained a high LOI of ≈27.0% and easily passed the horizontal flammability test even after 100 washing or friction cycles. These works provide a new bio-inspired strategy for creating advanced durable flame-retardant coatings, which may attract more in-depth research in the future, making them more valuable in practical applications.

5. Conclusion and Future Perspectives

5.1. Conclusion

Flame retardancy of polymeric materials can be realized by either bulk or surface treatment. For bulk-additive flame-retardant methods, many advanced flame-retardant methods have been developed based on organic–inorganic hybrid, "all-in-one" intumescent flame retardants, nanocomposites, in situ reinforcing TLCP and biomaterials, which totally or in some degree solve the drawbacks of conventional additive flame retardants such as low flame-retardant efficiency, bad compatibility with polymer matrix, and deterioration of products' overall performance. Nevertheless, some issues such as the high cost and processing difficulty of organic–inorganic hybrid and nanocomposites, the applicability of controlled carbonization, as well as the poor thermal stability of some biomaterials, need to be comprehensively investigated and addressed before the commercial application of these flame-retardant methods. Bulk-copolymerization flame-retardant method is believed to be a potential choice to solve the "PBT" issue of additive flame retardants, and has little influence on the processibility (especially the spinnability) of polymers, however, the corresponding research is relatively fewer than those focusing on additive flame-retardant methods. More importantly, the "flame-retardant-free" (containing no conventional flame-retardant elements such as P, Br, etc.) intrinsic char-forming flame-retardant method based on thermal self-cross-linking and rearrangement is the most efficient method ever-reported that can solve the halogen-free/phosphorus-free issue of flame retardants, the dilemma between flame retardancy and anti-dripping performance, etc., and is recognized as an important development direction of flame-retardant polymers. However, some issues like the flame-retardant efficiency and the cost are urgent to be addressed for this novel flame-retardant method, and the applicability of this method in different polymer matrices should be further studied.

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In regards to surface flame-retardant methods, a vast range of advanced treatments including plasma/ultraviolet-aided modification, sol–gel treatments, LbL assembly, polyelectrolyte complex, and biomimetic flame-retardant coatings have been developed to reduce fire hazards of the substrate. Compared with conventional flame-retardant coatings, these advanced technologies have their own advantages in terms of efficiency, diversity, and durability, but there are also some shortcomings that need to be resolved. In summary, plasma (pre-treatment for substrate activation) and UV-curing (post-treatment for coating cross-linking) modifications both have the advantages of simplicity, friendliness, and durability, but the selectivity, efficiency, and designability of their effective components are more limited. Sol–gel treatments usually show high flame-retardant performances benefitting from the abundant, variable, and designable precursors, while their hydrolysis and crosslinking conditions (such as acidity and heating) and drying processes may affect the inherent properties of the substrate. The LbL coatings, characterized by mild preparation conditions, diverse components, and high flame-retardant efficiency, have defects such as complicated steps and poor water resistance, which seriously hinder its practical application. Polyelectrolyte complex coatings effectively tackle the problems of repeatedly applying multiple layers of LbL assemble but are trapped by the pKa-dependent component selection and unproven washing durability. The recent emergence of biomimetic flame-retardant treatments provides new strategies for durable coatings, which require further development to form a more complete system. Therefore, researchers should make effective use of the advantages of these technologies and establish regulations to avoid their weaknesses, and the collaborative use of two or more technologies may be a promising approach.

5.2. Challenge and Future Perspectives

The rapid development of science and technology, the increasing awareness of environmental issues and energy crisis, and the introduction of government policies, have all put forward new requirements for flame-retardant polymeric materials. The following technical and scientific considerations need to be addressed in the future. 1) Environmental friendliness and low toxicity. The eco-friendliness and low toxicity of flame-retardant methods has gradually become a prerequisite for polymeric materials. This not only requires the low migration of additive flame retardants containing halogen or even phosphorus, but also the release of low/no formaldehyde and other VOCs from flame-retardant coatings. The raw materials and preparation process of flame-retardant polymers should also be as environmentally friendly as possible. 2) Multifaceted fire safety. Conventional flame retardation (only considering inhibition of ignition, reduction of combustion heat, etc.) can no longer meet the requirements of some cutting-edge fields (such as high-rise buildings, high-speed vehicles, etc.). Smoke suppression and reduction of toxic gas release of flame-retardant polymers will receive more attention. 3) High flame-retardant efficiency. The amount of flame retardants (additive, reactive, and surface treatment) should be as low as possible to minimize the negative impact on the inherent properties of the polymer matrix. Thus, it is important to achieve high flame-retardant efficiency to obtain high-performance flame-retardant polymers. 4) Flame-retardant persistence. The migration of additive flame retardants from the matrix, and the washing of coated materials will lead to significant deterioration of flame retardancy. Particularly the later one, for which the flame-retardant performances of most surface treatments are largely reduced after 50 washing cycles or less. Consequently, it is important to develop novel additive flame retardant to inhibit the migration, to develop hydrolytically stable actions to improve the washing durability of coatings. 5) Polymer-type flame retardants, especially those showing the in situ reinforcing effect, are perfect choice not only for obtaining flame-retardant polymeric materials with good overall performance, but also for solving the "PBT" issues. Thus, it is an important future development direction of polymeric materials. 6) "Flame-retardant-free" flame retardants (flame retardants containing no conventional flame-retardant elements), which were represented by the reactive flame-retardant monomers based on self-cross-linking and thermal rearrangement, are truly environmentally friendly. The development of these kinds of flame retardants (both additive and reactive) is the priority of future flame-retardant polymeric materials. 7) Recyclability. With the introduction of the carbon neutral strategies all over the world, it is important to realize the full-lifecycle application of flame-retardant polymers. Thus, the development of bio-based, bio-degradable, and recyclable flame retardants and flame-retardant polymeric materials are attracting increasing attention.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

bulk additives, bulk-copolymerization, flame-retardant methods, polymeric materials, surface treatment

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