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Research Progress in Halogen-Free Flame Retardant Rigid Polyurethane Foam

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Abstract. The article reviews the research advances on halogen-free flame retardant rigid polyurethane foam (HFR-RPUF), mainly covering three categories of flame retardants: additive, reactive and coating. The additive category includes different types such as organic, inorganic, bio-based, microencapsulated, expandable graphite. The reactive category introduces some flame retardants that can react with isocyanate or hydroxyl groups. The coating category presents examples of some organic, inorganic and carbon nanomaterial flame retardants. The article analyzes the effects and factors of various flame retardants, and contrasts their strengths and weaknesses. Lastly, the article summarizes the characteristics and development directions of HFR-RPUF, and offers future perspectives and recommendations. The review aims to provide references for researchers in the field of flame retardant rigid polyurethane foam.

Keywords: rigid polyurethane form, additive flame retardant, reactive flame retardant, surface coating flame retardants.

1. Introduction

Rigid polyurethane foam is a porous polymer material, which is generated by chemical reaction of isocyanate and polyol under the action of foaming agent, catalyst and other additives. Rigid polyurethane foam is mostly closed-cell structure, with excellent properties of thermal insulation, heat insulation, water resistance, insulation, sound insulation, etc.

However, polyurethane foam also has a fatal drawback, which is flammability. Because it contains a lot of combustible gas and combustible groups, it is easy to self-ignite or support combustion when exposed to open fire or high temperature, producing a lot of heat and thick black smoke as well as toxic gases such as CO, NO, HCN, etc., causing serious harm to human health and environment. According to statistics, every year there are many fire accidents caused or aggravated by polyurethane foam. Therefore, flame retardant modification of polyurethane foam is an important measure to improve its safety performance and extend its service life. Flame retardant modification can significantly improve the flame retardant of polyurethane foam, making it less flammable, slow flame spread, low smoke generation, low toxic gas generation, and even achieve self-extinguishing， so that it can not only protect polyurethane foam itself, but also protect the objects attached or wrapped by it, reducing casualties and property losses in fires. At the same time, other properties of polyurethane foam can also be improved, such as mechanical properties, aging resistance, thermal conductivity, etc., improving its comprehensive performance and application value.

In recent decades，an increasing attention focus on halogen-free Flame Retardant due to environmental and biological friendliness, a great deal of research has been reported. This paper reviews the research progress of three types of flame retardants: reactive, additive and surface coating. Finally, it draws conclusions and prospects for the future.

2. Research Progress Of Flame Retardants

2.1 Additive Flame Retardants

Additive flame retardant is to add the halogen-free flame retardant to the raw materials or prepolymers of polyurethane by physical mixing, without chemical bond connection with the matrix, and rely on dispersion or coating methods to improve its dispersibility and stability. Additive flame retardants are usually inorganic salts or organic compounds containing elements such as phosphorus, boron, silicon, etc., such as ammonium polyphosphate, aluminum hypophosphite, intumescent flame retardant, etc. The advantages of additive flame retardants are that they do not affect the foaming reaction and foam density of polyurethane, easy to operate and adjust, but the disadvantages are that they are easy to migrate, volatilize and hydrolyze, and may reduce the mechanical and aging properties of polyurethane foam.

2.1.1 organic flame retardants

Organic flame retardants used in rigid polyurethane foam are a class of organic compounds that can improve the flame retardancy of foam plastics. For example, phosphoric acid ester flame retardants (DMMP, DEEP), etc., which do not contain halogens, are low-toxic, low-smoke, have high flame retardant efficiency and good thermal stability. These flame retardants can react with polyols to form polyurethane molecules with phosphorus linkages, thus improving the carbonization ability and anti-dripping property of foam plastics. Phosphorus-nitrogen composite flame retardants (DOPO and its derivatives, MPP, etc.), which contain both phosphorus and nitrogen elements in their molecules, can exert synergistic flame retardant effects in both condensed and gas phases. The advantages of organic flame retardants are low dosage, good compatibility with polymers, small impact on material properties, easy processing, etc. But there are also some disadvantages, such as easy volatilization, migration, aging, generation of toxic and corrosive gases, etc. Therefore, when choosing and using organic flame retardants, factors such as their effectiveness, safety, environmental impact, etc. need to be considered comprehensively.

Han et al.[19] studied the flame retardant effect of a flame retardant system based on diethyl bis(2-hydroxyethyl)aminomethyl phosphonate (DBHP) and in situ exfoliated clay on rigid polyurethane foam (RPUF). The OMMT/DBHP system significantly increased the LOI value from 19.2% to 29.9%, and improved the UL94 rating from no rating to V-0 rating. In addition, the OMMT/DBHP system also reduced the pHRR value from 275.4 kW/m2 to 136.4 kW/m2, the TSR value from 404.4 m2/m2 to 337.8 m2/m2, and increased the char yield from 12.0% to 32.3%.

Lin et al.[20] synthesized a phosphorus-nitrogen containing halogen-free flame retardant HAPO, and applied it to rigid polyurethane foam (PU). HAPO can promote the carbonization and radical trapping of PU, forming a dense carbon layer, hindering the heat and oxygen transfer, and reducing the heat release rate, total heat release, and total smoke production of PU. When the addition amount of HAPO was 10 wt%, the limiting oxygen index of PU/HAPO composite increased from 20% to 23.5%, UL-94 reached V-0 level, and cone calorimeter test showed that its peak heat release rate, total heat release, and total smoke production decreased by 36.6%, 12.3%, and 38.8%, respectively.

Zeng et al.[21] designed three phosphorus-containing monohydroxy molecules (DOM, DPM and DPE), and used them to modify polyurethane foam (PUF). DPM had the best dispersibility and reactivity, and could form molecular-scale side chains and micron-scale particles during the foaming process, constructing phosphorus-containing multiscale energy dissipation networks (PMNs). The PUF with 2.8 wt% DPM had 26.5%, 59% and 92% higher fracture strength, fracture elongation and toughness, respectively, than pure PUF. DPM could impart PUF with rapid self-extinguishing ability at a lower loading (1.8 wt%), meeting the vertical burning test requirements of Cal TB 117. This was mainly attributed to the release of effective free radical scavenger PO· at lower temperature by DPM, which interrupted the combustion cycle of PUF.

Zemla et al.[22] used three phosphorus-containing liquid additive flame retardants (TEP, DMPP and CT901) to modify rigid polyurethane foam (RPURF). DMPP had the most significant flame retardant effect on both RPURF systems (with or without bio-polyether), reducing the MARHE by 29% and 37%, respectively. DMPP also showed the highest OI values, 26.6% and 27.3%, respectively. CT901 had the greatest impact on the cell structure, increasing the cell number and closed-cell ratio, but also increasing the water absorption. Bio-polyether also affected the cell structure and mechanical properties of RPURF, making it have more and smaller cells and lower compressive strength.

Dong et al.[23] successfully synthesized a novel nitrogen and phosphorus-containing flame retardant (DN), which was derived from renewable camphor. During combustion, DN promoted the formation of a phosphorus-rich protective char layer on polyurethane foam. The non-flammable gases released by the decomposition of DN lowered the surface temperature and oxygen concentration of PUF, reducing its flammability. The limiting oxygen index (LOI) of DNPUF-2 was 24.1%, which was 41.7% higher than that of PUF. The residual char yield was 18.4%, which was 60.1% higher than that of PUF. In addition, the peak heat release rate (PHRR) of DNPUF decreased by 40.3%. Compared with unmodified PUF samples, the compressive strength of DNPUF samples increased by 166%.

Zhang et al.[26] studied the effect of hexaphenoxy cyclotriphosphazene (HPCTP) and glass fiber (GF) on the flame retardant performance of rigid polyurethane foam (RPUF). When the HPCTP content was 15 wt% and 20 wt%, the peak heat release rate (PHRR) of RPUF was 154.43 kW/m2 and 162.22 kW/m2, respectively, which was almost half of that of RPUF without HPCTP. When the HPCTP content was 20 wt%, the THR was 4.49 MJ/m2 lower than that of RPUF without HPCTP. When the HPCTP content was 20 wt%, the LOI of RPUF reached 28.7%, which was 9.8% higher than that of RPUF without HPCTP, and the LOI of RPUF-GF5-HPCTP20 reached 29.0%, which was 0.3% higher than that of RPUF-HPCTP20.

Riyapan et al.[29] studied a novel rigid polyurethane foam, which was prepared based on modified waste palm oil (MUPO) as the raw material. The authors added triphenyl phosphate (TPP) as a flame retardant in the formulation. When the TPP content reached 20% or 30%, the foam self-extinguished after 12 seconds or 5 seconds of the first ignition, while the foam without TPP continued to burn. TPP could promote the formation of a char layer on the foam surface, preventing the escape of combustible gases and the transfer of heat, and consuming active free radicals in the flame zone, thus inhibiting the degradation of polymer chains.

Strakowska et al.[30] used three chlorinated polyhedral oligomeric silsesquioxanes (POSS-Cl) as flame retardants and reinforcing agents for rigid polyurethane foam (RPUF). The POSS-Cl with aromatic structures, POSS-Ar-Cl and POSS-Ar-Et-Cl, showed the best flame retardancy for RPUF, reducing the peak heat release rate (pHRR) by 30% and 30.6%, respectively, and the total smoke release (TSR) by 5.3% and 11.4%, respectively. The flame retardant mechanism of POSS-Cl may be related to the formation of a protective carbon layer in the initial decomposition stage, and the release of chlorine atoms as radical scavengers to inhibit the combustion reaction.

2.1.3 inorganic flame retardants

Inorganic flame retardants have the advantages of non-toxicity, stability, non-volatility, non-migration, smoke suppression, etc., which have less impact on the environment and human health. They can decompose water or other non-combustible or low-combustible gases at high temperature, absorb heat, reduce flame temperature, inhibit free radical reactions, thus slowing down or stopping the combustion of materials. But inorganic flame retardants generally have low flame retardant efficiency and need a large amount of addition. Otherwise they have no good flame retardant effect. But a large amount of addition will inevitably lead to poor fluidity of the material during resin mixing and molding, affecting the processing performance and mechanical properties of the material. At the same time they have poor acid resistance and dispersibility. They will dissolve quickly in acid and easily produce aggregation phenomenon, affecting the uniformity and stability of the material.

Li et al.[31] studied a novel flame retardant and smoke suppressant composite material, namely decorating the porous surface of polyurethane foam (PUF) with silica aerogel (SiO2), forming a SiO2/PUF composite with a hierarchical porous structure. The SiO2/PUF composite exhibited self-extinguishing performance in the vertical burning test, reaching the UL-94 V-0 rating, with a limiting oxygen index (LOI) of 32.5%, while pure PUF could not pass any UL-94 rating, with a LOI of only 20.5%. Meanwhile, the peak heat release rate (PHRR) and peak smoke production rate (PSPR) decreased by 40.4% and 45.6%, respectively, and the total heat release (THR) and total smoke production (TSP) also showed significant reductions.

Yuan et al.[32] studied a novel flame retardant Cu2O-MoS2, and prepared Cu2O-MoS2 hybrids with layered structure and different ratios by hydrothermal and wet chemical methods. The Cu2O-MoS2 hybrids could effectively prevent the restacking of MoS2 nanosheets, and provide abundant active sites, realizing the physical adsorption of MoS2 and the catalytic effect of Cu2O. The flame retardant effect of Cu2O-MoS2 hybrids was related to the ratio of Cu2O and MoS2 and the thickness of the hybrids. When the Cu2O/MoS2 ratio was 1:1 and the hybrid thickness was 600 microns, the polyurethane foam had the highest flame retardancy, reaching UL-94 V-0 rating, with an LOI value of 35.5% and a PHRR reduction of 87%.

Xu et al.[33] synthesized three novel carbon-coated transition metal oxide particles, Cu@C, Fe2O3@C and Cu2O@Fe2O3@C. The carbon-coated transition metal oxide particles had spherical or octahedral morphologies, and the metal oxides were completely wrapped by carbon layers. Fe2O3@C particles had the most significant flame retardant and smoke suppression effects on RPUF, and when their mass fraction was 5%, the peak heat release rate of RPUF decreased by 40.5%, and the char residue increased by 6.12%. The pHRR and THR values of RPUF decreased by 40.5% and 34.9%, respectively.

Peng et al.[34] studied the effect of different contents of aluminum hydroxide and magnesium hydroxide on the flame retardant performance of rigid polyurethane foam composites. When 20 wt% of aluminum hydroxide was added, the LOI of rigid polyurethane foam composite reached 29.5%, while when 20 wt% of magnesium hydroxide was added, the LOI was 26%. This was because aluminum hydroxide decomposed more water than magnesium hydroxide, and the generated Al2O3 formed a denser protective layer than MgO. Aluminum hydroxide and magnesium hydroxide could also synergize with organic phosphorus flame retardant (FR-047), forming a more uniform and dense carbon layer, improving the structural stability and flame retardant performance of rigid polyurethane foam composites during combustion.

Yuan et al.[35] found that different sizes of Cu2O crystals had different effects on the combustion performance of RPUF composites. Nano-sized Cu2O crystals increased the peak heat release rate of RPUF composites by 4.7%, while submicron-sized Cu2O crystals decreased it by 17.5%. Micron-sized Cu2O crystals had no significant effect on the peak heat release rate of RPUF composites. Meanwhile, different sizes of Cu2O crystals had different effects on the smoke toxicity of RPUF composites. Nano-sized Cu2O crystals decreased the CO concentration and total smoke density of RPUF composites by 67.6% and 16.1%, respectively, while submicron-sized Cu2O crystals decreased them by 41.2% and 21.6%, respectively. Micron-sized Cu2O crystals only slightly decreased the CO concentration and total smoke density of RPUF composites.

Chai et al.[36] studied the effect of inorganic additive flame retardants on the fire hazard of polyurethane external wall insulation materials. When the ratio of aluminum trihydrate (ATH) and magnesium hydroxide (MDH) was 1:3, the ignition time could be extended by about 14.33 s, the peak heat release rate and total heat release could be reduced by about 50.79 kW m-2 and 2.60 MJ m-2, respectively, and the peak carbon monoxide release rate could be reduced by about 0.0096 g s-1. The water and oxides produced by the decomposition of ATH and MDH could absorb the heat in the combustion zone, lower the temperature, cover the surface of polyurethane, form an insulation layer, and inhibit the combustion process. Meanwhile, polyurethane also formed a carbonized layer in the decomposition process, which played a role in suppressing smoke.

Tao et al.[37] incorporated P/Cu-hybridized silica aerogel (m-SA) into rigid polyurethane foam (RPUF). At 5 wt% m-SA loading, the peak heat release rate (PHRR) and total heat release (THR) of RPUF/m-SA-5 decreased by 18% and 10.4%, respectively, compared with pure RPUF. The total smoke production (TSP) and average carbon monoxide yield (av-COY) decreased by 18.4% and 23.4%, respectively, compared with pure RPUF. The residual carbon content was 25 wt%, which was 33.0% higher than that of pure RPUF. The thermal conductivity decreased from 40.3 mW/(m·K) for pure RPUF to 37.1 mW/(m·K) for m-SA. The flame retardant mechanism of m-SA might be related to its internal P, Cu elements and silica aerogel three-dimensional network structure, which played the roles of catalytic charring, free radical scavenging, physical barrier, etc.

Alves et al.[38] studied the flame retardant performance of polyurethane/vermiculite foam composites (PU/VMT). The composite with 15% vermiculite had the best flame retardant effect, with a total afterflame time of 0 seconds, while the pure polyurethane foam had a total afterflame time of 10 seconds. At this moment, as the vermiculite content increased, the mass ratio of PU per unit volume decreased. In turn, it required more oxygen to maintain the combustion after adding clay. Excessive vermiculite hindered the homogenization of the matrix, resulting in an uneven residual carbon layer after combustion, which led to a decrease in flame retardant performance when the vermiculite content exceeded 15%.

2.1.4 organic-inorganic composite flame retardants

Organic-inorganic composite flame retardants are a kind of flame retardants that use the synergistic effect of organic and inorganic different types of flame retardants to improve the flame retardancy of materials. For example, organic-inorganic hybrid flame retardants are those that combine organic and inorganic flame retardants together by chemical reaction or physical mixing to form new flame retardants with special structure and performance. For example, organic flame retardants containing phosphorus or halogen are prepared into organic-inorganic hybrid flame retardants with oxides, silicates, hydroxides and other inorganic flame retardants by sol-gel method, hydrothermal method, self-assembly method and other methods. These flame retardants have the advantages of high efficiency, low toxicity, low smoke, anti-aging, etc., and can improve the condensed and gas phase flame retardant effects of materials. Organic-inorganic composite granular flame retardants are those that mix organic and inorganic flame retardants in a certain proportion and then make them into uniform dispersed composite granules by spray drying, ball milling, extrusion and other methods. For example, red phosphorus or its microcapsules are mixed with aluminum hydroxide or magnesium hydroxide and other inorganic flame retardants to make composite granules. These flame retardants have the advantages of easy processing, good dispersibility, low migration, etc.

Xu et al.[39] prepared a novel silicon-nitrogen-zinc ternary hybrid (ZMD) by loading ZIF-8@MA coated with silica on diatomite, and adding it to rigid polyurethane foam. ZMD has a core-shell structure, which can effectively prevent the thermal decomposition and oxidation of ZIF-8, and provide a large number of active sites, realizing the synergistic catalysis of ZIF-8, silica and diatomite. ZMD can promote the carbonization of polyurethane foam, forming a protective layer with high char yield, inhibiting heat release, smoke release and mass loss, and improving its self-extinguishing and limiting oxygen index. The flame retardant effect of ZMD is related to the ratio of ZIF-8, silica and diatomite, and the content of ZMD. When the ratio of ZIF-8/silica/diatomite is 1:1:2, and the content of ZMD is 10 wt%, the polyurethane foam has the highest flame retardant performance, reaching UL-94 V-0 level, LOI value of 25.4%, and PHRR reduction of 50.1%.

Akdogan et al.[40] prepared rigid polyurethane foam (RPUF) containing three different flame retardants (triphenyl phosphate, aluminum hydroxide, zinc borate) or their binary mixtures. The authors found that all three flame retardants could reduce the peak heat release rate (pHRR) and total heat release (THR) of RPUF, among which aluminum hydroxide and zinc borate could promote the formation of a protective char layer, while triphenyl phosphate could inhibit the flame in the gas phase. Some binary mixtures could produce synergistic effects, increasing the limiting oxygen index (LOI) and decreasing the flame spread rate of RPUF. For example, RPUF containing 30% aluminum hydroxide and 10% triphenyl phosphate had a LOI of 21.5%, higher than the theoretical value of 21.1%, while RPUF containing 20% aluminum hydroxide and 20% zinc borate had a flame spread rate of 0 mm/min, lower than that of single flame retardants.

Li et al.[41] prepared a novel flame retardant composed of ammonium dihydrogen phosphate (APP) and β-cyclodextrin (β-CD), and prepared APP/β-CD nanocomposites with different ratios by surface modification and ultrasonic dispersion methods. The flame retardant effect of APP/β-CD nanocomposite was related to the ratio of APP and β-CD, and the content of nanocomposite. When the ratio of APP/β-CD was 4:1, and the content of nanocomposite was 25 wt%, the polyurethane foam had the highest flame retardant performance, reaching UL-94 V-0 level, LOI value of 24.9%, and PHRR reduction of 43.8%.

Caliskan et al.[42] synthesized a novel flame retardant with phosphorus-nitrogen dual-functional structure and aromaticity, namely bis(3-hydroxyanilino)phenyl phosphine oxide (BHAPPO). When the mass fraction of BHAPPO was 8%, the limiting oxygen index (LOI) of RPUF increased from 18.5% to 21.0%. When the mass ratio of BHAPPO and APP was 6:2, the LOI of RPUF reached 22.0%, and the thermogravimetric analysis (TGA) showed that its char yield was 9% at 850°C. Cone calorimeter test indicated that BHAPPO could prolong the ignition time of RPUF, reduce its average heat release rate (Avg. HRR) and average effective heat of combustion (Avg. EHC), but also increase its carbon monoxide (CO) production.

Li et al.[43] investigated the synergistic flame retardant effect of dimethyl methylphosphonate (DMMP) and modified ammonium polyphosphate (MAPP) on rigid polyurethane foam (RPUF). The ratio of 10% DMMP/10% MAPP achieved the highest LOI value (26.0%), which was 7.0% higher than that of 20% MAPP alone. The ratio of 6% DMMP/14% MAPP had the lowest peak heat release rate (pk-HRR, 137.6 kW/m2) and total heat release (THR, 7.5 MJ/m2). DMMP and MAPP could act as flame retardants in both gas and condensed phases. DMMP decomposed at low temperature and released PO· and PO2· radicals, which had a gas phase quenching effect in the early stage; MAPP decomposed at high temperature and released NH3, H2O, PO· and PO2 radicals, which had a gas phase dilution and quenching effect in the middle and late stages.

Wu et al.[44] prepared three kinds of rigid polyurethane foam (RPUF) composites with different phosphorus-based flame retardants (PEPA, PCP and ADP) blended with APP, which were labeled as RPUF-1, RPUF-2 and RPUF-3. Compared with pure RPUF, the limiting oxygen index (LOI) of RPUF-1, RPUF-2 and RPUF-3 increased by 5.2%, 5.2% and 4.8%, respectively; the peak heat release rate (p-HRR) decreased by 38%, 41% and 52%, respectively; the total heat release (THR) decreased by 31%, 33% and 37%, respectively. APP and PEPA mainly formed a protective carbonaceous layer in the condensed phase, increasing the char yield; PCP and ADP could scavenge radicals in the gas phase, reducing the combustion degree of flammable volatiles, but also increasing the smoke release and carbon monoxide production.

Tao et al.[46] used the following additives: zinc borate (ZB), aluminum hydroxide (ATH), tris(2-chloroisopropyl) phosphate (TCPP), ammonium phosphate salts (PABs), stearic acid or hydroxystearic acid coated zinc borate (ZB-SA or ZB-HSA) to prepare RPUF composites. At the same total amount of additives (30 php), the ZB/ATH/TCPP/PABs system had the best flame retardant performance, with a limiting oxygen index (LOI) of 28.6%, UL-94 test reaching V-0 level, and peak heat release rate (PHRR) decreasing by 48.2%. The ZB/ATH/TCPP/PABs system had the best smoke suppression effect, with the total smoke production (TSP) decreasing by 57.9%, and the CO and CO2 production decreasing by 49.8% and 38.7%, respectively.

Music et al.[49] studied the effects of two flame retardants, ammonium polyphosphate and 2,4,6-triamino-1,3,5-triazine, on the properties of two-component polyurethane foam. The fire behavior of different PUR samples depended on the fire conditions. Under the ignition conditions of the UL 94 standard, the additives in PUR successfully reduced the flame spread. Under the cone calorimeter test conditions simulating a fully developed fire, the samples reacted differently. Compared with PUR 0 sample, the additive samples had longer burning time, lower heat release rate, but higher total heat release. The smoke production rate of the additive samples was lower than that of PUR 0 sample, and the total smoke production was also lower, especially for PUR 2 sample. When comparing the weight loss rate, PUR 0 sample had the highest LOI value, about 95%. PUR 1 sample had the lowest LOI value, about 65%.

Zhu et al.[50] investigated the effects of phosphorus-based flame retardants on rigid polyurethane foam (RPUFs). The RPUF-3 containing 10 parts APP/10 parts DMMP had the highest LOI (29.1%), the lowest PHRR (161.1 kW/m2) and THR (21.8 MJ/m2). Among them, the RPUF-2 containing 20 parts APP had the lowest TSP (2.4 m2), TSR (272.1 m2^{2}[2] /m2) and CO/CO2 weight ratio (0.052). EMF and phosphorus-based flame retardants could promote the formation of thick and dense phosphorus-containing char layer on RPUFs at high temperature, thus protecting the internal polymer from further decomposition. The RPUF-3 containing 10 parts APP/10 parts DMMP had the thickest and densest char layer.

Jia et al.[53] synthesized a flame-retardant polyether polyol containing a melamine derivative, phosphate and acetylene groups, which was used to prepare rigid polyurethane foam (PUF). Compared with the PUF without the flame-retardant polyether polyol, the PUF with 23.2% MB3F3 had an increased limiting oxygen index (LOI) from 20.4% to 24.3%, a decreased peak heat release rate (p-HRR) from 345.2 kW m-2 to 247.7 kW m-2, a decreased total heat release (THR) from 13.1 MJ m-2 to 9.1 MJ m-2, and an increased residual mass from 1.4% to 21.7%.

2.1.5 biobased flame retardants

Biobased flame retardants are a kind of flame retardants that use biobased materials or their derivatives to improve the flame retardancy of polymers. Biobased flame retardants have the advantages of renewability, biodegradability, low toxicity, low smoke density, etc., which conform to the concept of green environmental protection. Biobased flame retardants are a new type of green flame retardant with broad application prospects. However, there are still some problems in the application and development of biobased flame retardants, such as the source and cost of biobased flame retardants, the compatibility and dispersibility of biobased flame retardants with RPUF, etc.

Acuna et al.[54] prepared a bio-based rigid polyurethane foam (RPUF) from plant oil (castor oil), and improved its flame retardant performance by introducing phosphorus-containing flame retardant and carbon-based materials (expandable graphite and graphene oxide). RPUF containing 6 wt% expandable graphite and 0.5 wt% graphene oxide (BIO2/EG/GO) had the best flame retardant performance, with a LOI value of 27.2 vol %, UL94 level of V-0, and peak heat release rate (HRR), total heat release (THR) and total smoke production (TSP) in CCT reduced by 54%, 24% and 15%, respectively, compared with BIO1.

Yang et al.[55] used a malic acid-based bio-polyol (MAP) to prepare rigid polyurethane foam (RPUF), and studied its structure and thermal degradation performance. MAP-based RPUF had a lower thermal conductivity (0.019~0.025 W/(m·K)), which had better thermal insulation performance than commercial polyol GR4110-based RPUF (0.0298 W/(m·K)). The residue rate at 700 °C was 18.5~24.6 wt%, higher than GR4110-based RPUF (10.9 wt%). Meanwhile, the self-extinguishing time of MAP-based RPUF was 9~24 s, much lower than GR4110-based RPUF's 43 s, and the limiting oxygen index (LOI) was 21.2~22.1%, higher than GR4110-based RPUF's 19.3%. The thermal degradation mechanism of MAP-based RPUF was mainly through the cleavage of urethane bonds and intramolecular cyclization reactions, producing CO2, aromatics, olefins, aldehydes, alcohols and isocyanates as volatile products.

Xing et al.[56] synthesized a novel bio-based P-N containing intumescent flame retardant, called PSTM, which was obtained by chemical reaction of starch, phytic acid and melamine. When the PSTM content was 30%, the limiting oxygen index (LOI) of PU foam reached 25.9, the vertical combustion test (UL-94) reached V-0 level, and the cone calorimeter test (CONE) showed that its peak heat release rate (PHRR) was 308 kW m−2, total heat release (THR) was 25 MJ m−2, and smoke production rate (SPR) was 0.092 m2 s−1. The flame retardant mechanism of PSTM in PU/PSTM composite was to expand into a dense carbonized layer, which blocked the contact between the polymer surface and the flame, and suppressed the transfer of combustible gas and heat.

Wang et al.[57] synthesized a novel bio-renewable resource maleopimaric acid-based polysiloxane flame retardant, which grafted maleopimaric acid onto amino polysiloxane by imidization reaction. The synthesized flame retardant was used as a part of the soft segment, and rigid polyurethane foam was prepared by "one-pot method". The influence of different contents of maleopimaric acid-based polysiloxane on the flame retardant performance of rigid polyurethane foam was evaluated by limiting oxygen index, thermogravimetric analysis infrared spectroscopy, cone calorimeter and other methods. It was found that when the mass fraction of maleopimaric acid in the flame retardant was 20%, the rigid polyurethane foam had the best flame retardant performance, and its minimum supporting combustion concentration increased by 39.7%, and the peak heat release rate decreased by more than 50% compared with pure rigid polyurethane foam. The LOI value of modified RPUF (RPUF-2) was 23.9%, and the char residue was 16.3%, which increased by 39.7% and 31.5% respectively compared with pure RPUF.

Wang et al.[58] studied the synthesis of a bio-based flame retardant FPASO-DOPO from rosin as a raw material. Silicon and phosphorus had an obvious synergistic effect in FPASO-DOPO, which increased the residual yield of FR-RPUF (from 1.30% to 9.09%). Most importantly, the LOI value of FR-RUF was 26.1%, and it had self-extinguishing property in air for 9 s. The TSR of FR-RPUF decreased from 818 to 675.1 m2/m2, showing good smoke suppression performance. Cone calorimeter showed that PHRR decreased by 33.7%.

Jeong et al.[59] discovered a new bio-inspired fire retardant, namely adenosine triphosphate (ATP), which consists of three phosphate groups, a ribose and an adenine, and coated ATP on polyurethane foam (PU) and cotton fabric by a simple impregnation method. PU foam coated with 30 wt % ATP hardly burned in direct combustion test and had self-extinguishing property; its peak heat release rate decreased by 94.3%, ignition time was extended by 282 s, and LOI reached 31%.; in UL94 HBF test, it achieved HF-1 level.

Tang et al.[60] developed a phosphorus-containing soybean oil-derived polyol (PESO) as a bio-based flame retardant for preparing rigid polyurethane foam (RPUF). When the PESO content was 12.3 wt%, the RPUF-3 sample reduced the peak heat release rate, total heat release and total smoke production by 40%, 35% and 49%, respectively, compared with the unmodified RPUF. The flame retardant mechanism of PESO was to promote the carbonization of RPUF matrix, forming a protective barrier layer, which suppressed the heat release and smoke emission.

2.1.6 microencapsulated flame retardants

Microencapsulated flame retardants are a kind of flame retardants that use microencapsulation technology to coat flame retardants. They can convert gaseous or liquid flame retardants into solid microcapsules, which are convenient for blending and processing with polymer materials. According to different polymer substrates, suitable wall materials can be selected to improve the compatibility and dispersibility of flame retardants with polymers, reduce the impact on the mechanical properties and transparency of polymers, reduce the release of toxic components or irritating gases in the flame retardants during the processing process, avoid polluting the environment and harming human health, reduce the migration and volatilization of liquid flame retardants in the polymer interior, reduce the loss and leakage of flame retardants, and improve the flame retardant efficiency. They can also mask the irritating odor of flame retardants, change their color, adjust their density, volume and other characteristics, and increase their aesthetics and practicality.

Tang et al.[65] prepared microencapsulated ammonium polyphosphate (MFAPP) with melamine-formaldehyde resin as the shell material, and applied it to rigid polyurethane foam (RPUF) composites to improve their flame retardancy. RPUF/MFAPP30 (containing 30% MFAPP) had excellent flame retardant performance, achieving V-1 rating in UL-94 test, with a limiting oxygen index of 21.3 vol%. It maintained good flame retardancy even after soaking in water for 15 days. The compressive strength of RPUF/MFAPP30 was 0.295 MPa, which was 13.5% higher than that of RPUF/APP30 (containing 30% APP), indicating that MFAPP improved the interfacial compatibility between APP particles and RPUF matrix. RPUF/MFAPP30 released lower intensities of CO and isocyanate compounds than RPUF/APP30, indicating that RPUF/MFAPP30 had better fire safety. RPUF/MFAPP30 had more compact char residues, and had higher degree of graphitization, which effectively hindered the mass and heat transfer during combustion.

Cheng et al.[66] studied a novel flame retardant microcapsule POAPP, which was prepared by interfacial polymerization method using polyurea as the shell material and ammonium polyphosphate (APP) as the core material. POAPP could effectively reduce the heat release rate (HRR) and total heat release (THR) of RPUF, and increase the limiting oxygen index (LOI) of RPUF. When the content of POAPP was 20 wt%, the HRR and THR of RPUF decreased from 336.52 kW/m2 and 11.5 MJ/m2 to 203.84 kW/m2 and 7.6 MJ/m2, respectively, and the LOI increased from 18.2% to 24.8%. When the content of POAPP was 10 wt%, the maximum compressive strength of RPUF reached 8.16 MPa, which was 13.2% higher than that of RPUF without POAPP. The preparation process of POAPP was successful, and the polyurea shell layer could protect APP from the environmental moisture, improving its flame retardant effect and storage stability. The water solubility and hygroscopicity of POAPP were much lower than those of APP.

Li et al.[67] prepared a flame retardant microcapsule (PMAPP) by encapsulating ammonium polyphosphate (APP) with poly(methyl methacrylate) (PMMA) as the shell material, and added it to rigid polyurethane foam (RPUF). When 25 wt% of PMAPP was added, the LOI of RPUF increased from 18.4% to 25.3%, and the peak heat release rate (PHRR) and total heat release (THR) of RPUF decreased from 256.45 kW/m2 and 14.03 MJ/m2 to 169.9 kW/m2 and 8.53 MJ/m2, respectively.

Cheng et al.[68] studied a novel phase change microcapsule modified with iron oxide/carbon nanotubes (FeeC-PCM). FeeC-PCM had better thermal stability than ordinary phase change microcapsule (R-PCM) and carbon nanotube phase change microcapsule (C-PCM). RPUF-Fe-C-PCM had a peak heat release rate (pHRR) of 428.53 kW/m2, which was 22.1% lower than RPUF; a total heat release (THR) of 36.9 MJ/m2, which was 17.8% lower than RPUF; and a total smoke production (TSP) of 6.92 m2, which was 23.6% lower than RPUF.

Niu et al.[69] studied the preparation and characterization of a multifunctional phase change material microcapsule, in which the shell material was poly(methyl methacrylate), the core material was decanoic acid, and carbon nanotubes (d-CNT) modified with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) were also added. The residual mass of d-CNT microcapsule (d-c-MPCM) was 15.88% and 10.91% higher than that of microcapsule without d-CNT (r-MPCM), respectively. Meanwhile, the peak heat release rate (pHRR) and total heat release (THR) of RPUF/d-c-MPCM were 44.73% and 13.92% lower than those of pure foam (p-RPUF), respectively, while the residual mass ratio was increased by 84.52%.

Yang et al.[70] prepared microencapsulated ammonium polyphosphate (SiAPP) with gel-silica as the shell material by sol-gel method, and used it to improve the flame retardancy of rigid polyurethane foam (RPUF). The LOI values of RPUF/APP30 and RPUF/SiAPP30 increased from 18.8vol% and 22.8vol% of the original RPUF to 23.2 and 22.8Vol%, respectively. With the increase of soaking time, the LOI value of RPUF/APP30 decreased rapidly. After soaking for 15 days, its LOI was 21.7vol%, and it failed in the UL-94 test. The LOI of RPUF/SiAPP30 decreased from 22.8% to 21.8% after soaking in water for 5 days, but its UL-94 rating still reached V-0 level. The char residues of RPUF/SiAPP30 had higher degree of graphitization and thermal stability, indicating that SiAPP could promote the formation of dense carbon layer, effectively blocking the propagation of gas and heat, and thus improving the flame retardancy of RPUF/SiAPP30.

Additive flame retardants are a kind of flame retardants that mix with the substrate by physical or chemical methods, thus improving the flame retardancy of the substrate. The advantages of additive flame retardants are that they can be applied to various substrates, do not affect the original properties of the substrate, and have low cost. The disadvantages of additive flame retardants are that they are prone to migration, volatilization or hydrolysis, leading to a decrease in flame retardant effect, and may cause harm to the environment and human health. The market size of additive flame retardants continues to grow, mainly driven by the demand from the fields of electronics, construction, transportation, etc., and inorganic flame retardants occupy the main market share. The technical development direction of additive flame retardants is mainly to improve the flame retardant efficiency, reduce toxicity and smoke generation, enhance compatibility and stability, and develop multifunctional and intelligent products.

2.1.7 EG and its related flame retardants

Expandable graphite(EG) which is a kind of inorganic flame retardant, widely used in various plastics and coatings. Its flame retardant mechanism is to rapidly expand at high temperature, forming a dense carbon layer, which isolates the oxygen and heat transfer, thus inhibiting the combustion of the material. EG has the advantages of abundant resources, simple manufacturing, low cost, non-toxicity, low smoke, etc., but it has poor flame retardant effect when used alone, and generally needs to be used with other flame retardants to form a synergistic effect.

Liu et al.[1] synthesized a novel phosphorus-nitrogen flame retardant, nano zirconium amino tri(methylene phosphonate) (Zr-AMP), and used it together with expandable graphite (EG) for the flame retardant modification of rigid polyurethane (RPU) foam. The RPU foam with 3 wt% nano Zr-AMP and 12 wt% EG (RPU/12EG/3Zr-AMP) reduced the PHRR and THR values by 39.3% and 54.8%, respectively, in the cone calorimeter test. Nano Zr-AMP facilitated the formation of a dense char layer, increased the graphitization degree and thermal stability of the char, and generated non-flammable products to dilute the flammable volatiles. EG produced a “worm-like” char layer that provided a protective barrier, hindering the heat and mass transfer.

Chen et al.[2] synthesized a novel halogen-free intumescent flame retardant DPES, which contained three flame retardant elements of silicon, nitrogen and phosphorus, and could synergize with ionic liquid modified expandable graphite (IL-EG) to improve the flame retardant performance of rigid polyurethane foam (RPUF). When the mass ratio of IL-EG and DPES was 1:1, the limiting oxygen index (LOI) of RPUF reached 28.5%, which was 18.8% higher than that of pure RPUF; cone calorimeter test showed that the peak heat release rate (PHRR) decreased by 60.5%, the total heat release (THR) decreased by 45.0%, and the total smoke release (TSR) decreased by 69.0%. IL-EG decomposed and expanded at high temperature, forming a porous carbonized layer, which blocked the transfer of oxygen and heat; DPES decomposed at high temperature to produce viscous polyphosphoric acid liquid, which catalyzed the formation of carbonized layer, and generated gas-phase flame retardants such as PO· or HPO· that consumed radicals; meanwhile, the silicon bonds in DPES enhanced the strength and barrier performance of the carbonized layer.

Yun et al.[3] prepared cellulose-based flame retardants (CF and GCF) and mixed them with expandable graphite (EG) to obtain PUF composites with high flame retardancy and high mechanical strength. Compared with EG15, GCF3 had a higher compressive strength (increased by about 21%), while maintaining a proper limiting oxygen index (LOI) value (above 25%). GCF not only significantly improved the compressive strength of PUF, but also acted as an auxiliary flame retardant, suppressing the “popcorn effect” of the char layer produced by EG, which was prone to fall off.

Wang et al.[4] designed and synthesized a bifunctional flame retardant PDEP containing two phosphorus groups for rigid polyurethane foam (RPUF), and investigated its synergistic flame retardant effect with expandable graphite (EG). PDEP successfully connected two phosphorus groups, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and diethyl phosphate (DEP), on the two carbonyl groups of 1,4-benzaldehyde. PDEP started to decompose at around 200 °C, releasing phosphorus oxides containing PO and PO2 radicals, which had gas-phase flame retardant action; meanwhile, PDEP also produced a high content of char residue (32.2 wt%) at high temperature, which had condensed-phase flame retardant action. The limiting oxygen index (LOI) of RPUF/12%PDEP/8%EG sample increased from 18.5% to 27.2%, and passed the UL-94 V-0 level vertical combustion test.

Wang et al.[5] prepared a flame retardant rigid polyurethane foam (RPUF) containing expandable graphite, diethyl phosphate and 2-carboxyethyl (phenyl) phosphinic acid. RPUF-6 showed the best flame retardant performance, achieving UL-94 V-0 level, and had the lowest PHRR (160kWm-2), THR (16.3MJm-2) and PSRR (0.268m2s-1). After observing the char morphology of the cone calorimeter test by SEM, it was found that pure RPUF remained a small amount of irregular carbon layer; after adding expandable graphite, a large amount of worm-like expanded carbon layer remained; after adding expandable graphite, diethyl phosphate and 2-carboxyethyl (phenyl) phosphinic acid, a uniform and dense carbon layer remained, indicating that these flame retardants could synergistically form a dense protective layer.

Chen et al.[6] used three flame retardants, namely modified ammonium polyphosphate (MAPP), expandable graphite (EG) and dimethyl methylphosphonate (DMMP). When the mass ratio of DMMP/EG/MAPP was 4/12/4, RPUF had the best flame retardant performance, with a limiting oxygen index (LOI) of 31.9%, a peak heat release rate (pk-HRR) reduced to 97 kW/m2, a total heat release (THR) reduced to 7.6 MJ/m2, and a total smoke release (TSR) reduced to 347 m2/m2. In the condensed phase, the “graphite worms” produced by EG were wrapped and connected by the combustion products of MAPP, forming a “connected worm-like” structure, which had a good isolation and protection effect, effectively blocking the transfer of heat and oxygen; in the gas phase, DMMP/EG/MAPP released PO and PO2 radicals throughout the combustion process, playing a gas-phase quenching effect.

Ma et al.[7] synthesized a phosphorus-containing hyperbranched polyether polyol (POCHP), and combined it with expandable graphite (EG), incorporating POCHP and/or EG into RPUF. With the addition of EG, the foam density increased, and the compressive strength and thermal insulation performance deteriorated. POCHP had an adverse effect on them, ERPUF50 increased the compressive strength by 12.8%, and the density and thermal conductivity slightly decreased. ERPUF50 achieved 30.0% LOI and UL-94 V-0 level, and had immediate self-extinguishing behavior after removing the flame. Compared with the original foam, ERPUF50 reduced PHRR, THR and TSP by 71.1%, 52.2% and 71.1%, respectively. The combustion gas analysis results showed that POCHP and EG both reduced the production of CO. ERPUF50 showed a 52% reduction in CO and a 40% reduction in NOx, but HCN increased by 26%.

Zhang et al.[8] used sodium alginate (SA), diethyl aluminum phosphate (ADPO2) and expandable graphite (EG) as flame retardants. When the ratio of ADPO2, SA and EG was 2:3:3, RPUF had the best flame retardant performance, with a LOI value of 25.5%, UL-94 level of V-0, peak heat release rate (PHRR) reduced by 22.6%, total heat release (THR) reduced by about 6 MJ/m2, and total smoke release (TSP) reduced by 1.5 m2/m2, showing good flame retardant and smoke suppression effects. There was a synergistic flame retardant effect between ADPO2, SA and EG, which could promote the formation of carbonized layer on the surface of RPUF, prevent the transfer of heat and oxygen, and generate phosphorus-containing compounds in the gas phase, inhibiting the diffusion of flame.

Lee et al.[9] prepared flame retardant RPU foam by incorporating flame retardant materials containing CC and ATH into RPU foam. RPU/IFR1 sample (containing 15 php of APP/PER/MC/EG/CC and 3 php of ATH) had the lowest PHRR (82.12 kW/m2) and THR (15.15 MJ/m2), which were 41.3% and 39.5% lower than pure foam, respectively. RPU/IFR1 sample had the highest LOI value (36%), which was 14% higher than pure foam. RPU/IFR1 sample had the highest residual char amount (42.67%) at 800 ℃, which was 18.87% higher than pure foam.

2.2 Reactive Flame Retardants

Reactive flame retardant is to make the halogen-free flame retardant react with the raw materials of polyurethane, such as isocyanate or polyol, and make it part of the polyurethane molecular chain, thus improving its compatibility and stability with the matrix. Reactive flame retardants are usually organic compounds with active groups, such as hydroxyl, amino, isocyanate, etc., such as melamine, ethylenediamine, aluminum diethylphosphinate, etc.. The advantages of reactive flame retardants are that they are not easy to migrate, volatilize and hydrolyze, and can improve the mechanical and aging properties of polyurethane foam, but the disadvantages are that they may affect the foaming reaction and foam density of polyurethane, and need to optimize the formulation and process.

Jia et al.[83] synthesized phosphoric acid triglyceride (POG) and introduced it as a reactive flame retardant into the cross-linked structure of rigid PUF. The thermal conductivity of PUF-2 with POG addition decreased from 2.91 10 2 W m 1 K 1 without POG to 2.72 10 2 W 1 K 1, the char yield of PUF-3 at 700°C increased from 3.6% of PUF-0 to 23.2%, and the LOI of PUF-3 reached 22.3% with the increase of POG. THR decreased from 12.9 MJ m2 of PUF-0 to 9.0 MJ m2 of PUF-3, a reduction of 30.2%. The TTF of PUF-3 shortened by 51s.

Wu et al.[84] synthesized a novel reactive phosphorus-containing flame retardant, namely phenylphosphoryl ethylene glycol ether oligomer (PPGE), and introduced it into rigid polyurethane foam (RPUF), along with expanded graphite (EG), to improve the flame retardancy of RPUF. When the phosphorus content was 2%, the LOI value of RPUF increased from 20.0% to 24.5%, and the UL-94 rating increased from no rating to V-1 rating. When the phosphorus content was 2%, and the EG content was 15%, the LOI value of RPUF reached 34.5%, the UL-94 rating reached V-0 rating, and the HRR and THR decreased by 65% and 56%, respectively. At the same time, the total smoke release (TSR) decreased by 23.7%, and the peak values of CO and CO2 decreased by 82.4% and 15%, respectively. PPGE decomposed at high temperature to produce phosphorus radicals, which inhibited the further decomposition of combustible gases in the gas phase; EG promoted the formation and expansion of carbon layer, which isolated the oxygen and heat transfer in the condensed phase.

Cui et al.[85] synthesized two novel reactive phosphorus-containing flame retardants, namely phenylphosphoryl ethylene glycol ether oligomer (FRC) and dimethyl methylphosphonate phenyl ester (FRD), by ester exchange reaction without solvent and catalyst, and introduced them as polyols into rigid polyurethane foam (RPUF). When the phosphorus content was 2%, and the FRD content was 10%, the LOI value of RPUF reached 29.8%, the UL-94 rating reached V-0 rating, and the HRR and THR decreased by 31.4% and 47.8%, respectively. FRD could reduce the pHRR of RPUF from 261 kW/m2 to 179 kW/m2, and the THR from 40.8 MJ/m2 to 21.3 MJ/m2. It also increased the residual carbon content of RPUF at 800°C from 7.9% to 24.2%. FRC and FRD decomposed at high temperature to produce phosphorus radicals, which inhibited the further decomposition of combustible gases in the gas phase; meanwhile, they promoted the formation and expansion of carbon layer, which isolated the oxygen and heat transfer in the condensed phase.

2.3 Surface Coating Flame Retardants

Surface coating flame retardant is to cover the surface of polyurethane foam with a layer or film of halogen-free flame retardant, forming an effective protective barrier, isolating the external oxygen and heat transfer, protecting the matrix from further decomposition and combustion. Surface coating flame retardants are usually polymer materials containing elements such as carbon or silicon, such as silicone or siloxane resin, etc., such as siloxane resin, borosiloxane resin, etc. The advantages of surface coating flame retardants are that they do not affect the thermal insulation and dimensional stability of polyurethane foam, and can improve the fire resistance and weather resistance of polyurethane foam, but the disadvantages are that the coating may have problems such as cracking and falling off, and need to improve the adhesion strength between the coating and the matrix.

Ma et al.[71] developed a waterborne poly(VS-co-HEA) fire-retardant polymer coating by biomimetic design, which achieved strong adhesion with the foam substrate through interfacial hydrogen bonding and mechanical interlocking. The coating could form a dense char layer during combustion, reaching the UL-94 V-0 level of flame retardancy. The flame retardancy of the coating was related to the VS/HEA ratio and the coating thickness. When the VS/HEA ratio was 60/40 and the coating thickness was 600 microns, the coated foam had the highest flame retardancy, with an LOI value of 35.5% and a PHRR reduction of 87%.

Huang et al.[72] developed a novel UV-curable IFR/MXene nanocomposite coating. The IFR/MXene coating could rapidly form a fire barrier composed of an intumescent char layer and a MXene blocking network during combustion, effectively blocking the release of heat and volatiles, and protecting the underlying substrate from further burning. The polyurethane foam treated with the IFR/MXene coating exhibited fast self-extinguishing behavior and significantly reduced heat and smoke generation. After adding 1 wt% of m-MXene to the IFR system, the UL-94 V-0 level was achieved, with an LOI value of 32.5%, a PHRR reduction of 40.4%, a PSPR reduction of 45.6%, and a Ds reduction of 55.7%.

Wang et al.[73] used a hybrid coating of a silicone resin (poly-DDPM) and expandable graphite (EG), which was applied on the surface of RPUF by brushing. The coating increased the weight by about 8.5 mg/cm2, and improved the limiting oxygen index (LOI) of RPUF from 18 to 32.3, the UL 94 rating from no rating to V-0, the peak heat release rate (pk-HRR) decreased by 55%, and the peak smoke production rate (pk-SPR) decreased by 59%. The coating could form a dense protective layer composed of expanded graphite flakes and deposited nano-silica when heated, thereby inhibiting the combustion of RPUF. The coating also increased the compressive strength of RPUF by 10%, and had good flame retardant durability under specific conditions.

Ma et al.[74] developed a multiscale organic-inorganic hybrid flame retardant coating inspired by lava, by combining GP, BN and flame retardant PVH polymer. After being treated with only 200 μm thick hybrid coating, PU foam could self-extinguish within 30 seconds, achieving UL-94 V-0 rating, and had a limiting oxygen index (LOI) of 35.8%, much higher than untreated PU foam (19.1%). The coating also significantly reduced the HRR (-34%), THR (-33%), TSR (-53%) of PU foam. When exposed to flame, GP, BN and PVH in the hybrid coating synergistically produced an integral ceramic char layer with a porous internal structure, and the char layer acted as a fire/thermal barrier, providing effective fire protection for the underlying substrate.

Ma et al.[75] prepared a three-layer “sandwich-type” flame retardant coating to improve the fire resistance and fire alarm capability of rigid polyurethane (PU) foam. The coating consisted of modified flame retardant copolymer (PVH), phosphoric acid (PA), graphene oxide (GO), carbon nanotubes (CNTs) and boron nitride (BN). Using only 200 μm thick coating, the PU foam exhibited a fast fire alarm response (about 8 s) and continued to emit fire alarm signals at high temperature. In addition, the foam showed self-extinguishing behavior, with a high limiting oxygen index of 58.0 vol%, and significantly reduced peak heat release rate (PHRR), total heat release (THR) and total smoke release (TSR), which were 49%, 33% and 42% lower than those of uncoated PU foam, respectively, indicating its effective inhibition of flame spread and smoke generation.

Tang et al.[76] combined CS, GEL and PA-Na to prepare CS/GEL/PA-Na. The experiments showed that CS/GEL/PA-Na had high flame retardant efficiency and other related properties in PUF by surface coating. The pHRR and THR of PUF decreased from 247.2 kW/m2 and 6.8 MJ/m2 to 115.0 kW/m2 and 3.5 MJ/m2, respectively. Compared with PUF, the burn-through time of the tin foil and the burn-through temperature of the modified PUF increased from 36 s to 60 s, and decreased from 729 ℃to 469℃.

Chen et al.[77] found that RPUF was quickly ignited (TTI of 7 s), while the coated RPUF had a greatly increased TTI. PAAm-MXene showed a TTI extended to 172 s, but the coated RPUF with m-MXene had a shorter ignition time. PAAm-MXene coated rigid polyurethane foam had the longest ignition time (172 s), while PAAm-m2 coated rigid polyurethane foam had the lowest peak heat release rate (265.0 kW/m2), total heat release (55.9 MJ/m2) and total smoke production (6.7 m2/m2), exhibiting the best flame retardant performance.

Huang et al.[78] proposed a green and efficient flame retardant strategy based on a dual-network hydrogel coating, using polyacrylamide-dopamine (PAAm-PDA) dual-network hydrogel as the flame retardant coating, which had good toughness, adhesion, water retention and carbonization abilities. The hydrogel coated RPUF showed excellent flame retardant performance in cone calorimeter test, compared with uncoated RPUF, the ignition time was extended by 6 times, the average heat release rate and total smoke production were reduced by 39.7% and 42.2%, respectively. The flame retardant mechanism of the hydrogel coating included the cooling effect of water evaporation, the physical barrier formed by hydrogel carbonization, the oxygen dilution effect of water vapor in the gas phase, and the free radical scavenging ability of catechol groups in dopamine.

Huang et al.[79] applied a halogen-free UV-curable self-extinguishing coating on the surface of rigid polyurethane foam (RPU), and prepared a surface flame retardant RPU foam system (SFR-RPU). SFR-RPU foam had efficient flame retardant performance, and could quickly self-extinguish and maintain the internal foam structure intact with a coating thickness of 25 microns. The limiting oxygen index (LOI) of SFR-RPU foam increased from 18.2% to 24.8%, the afterflame time (t1) after the first ignition in the vertical burning (UL-94) test decreased from 37.2 s to 5.0 s, and in the cone calorimeter (CCT) test, the mean heat release rate (mean HRR) decreased by 33.2%, and the mean effective heat of combustion (mean EHC) decreased by 15.7%. SFR-RPU foam maintained excellent flame retardant performance without affecting its own mechanical and thermal insulation properties. Compared with pure RPU foam, the compressive strength of SFR-RPU foam increased by 9.8%, and the thermal conductivity did not change significantly.

Surface coating flame retardants are a kind of flame retardants that coat a layer of flame retardant coating on the surface of the substrate, thus improving the flame retardancy of the substrate. The advantages of surface coating flame retardants are that they can be applied to various substrates, do not affect the original properties of the substrate, and can provide aesthetic and protective effects. The disadvantages of surface coating flame retardants are that the coating may fall off, age or damage, leading to a decrease in flame retardant effect, and that the preparation and construction process of the coating may cause environmental pollution. The market size of surface coating flame retardants continues to grow, mainly driven by the demand from the fields of construction, furniture, electronics, automobiles, etc., and organic halogen series and organic phosphorus series occupy the main market share. The technical development direction of surface coating flame retardants is mainly to improve the adhesion, stability, weather resistance and fire resistance of the coating, and develop multifunctional and intelligent products.

3. Conclusion

Halogen-free flame retardant rigid polyurethane foam refers to rigid polyurethane foam that does not contain halogen elements (such as chlorine, bromine, etc.) in the flame retardant, which has the following advantages compared with traditional halogen-containing flame retardant rigid polyurethane foam: lower toxicity. Halogen-free flame retardants do not release toxic or carcinogenic halides, such as dioxins, furans, etc., when burning or decomposing, causing less harm to human health and environment. Higher efficiency. Halogen-free flame retardants can achieve higher flame retardant effect with lower addition amount, reduce the impact on the substrate material, and improve its mechanical properties and aging resistance. Better compatibility. Halogen-free flame retardants can be compatible or react with rigid polyurethane raw materials, improve their dispersibility and stability, and avoid phenomena such as migration, volatilization and hydrolysis. Smaller environmental impact. Halogen-free flame retardants can reduce the environmental load of the material during its life cycle, improve its recyclability and degradability, and conform to the concept of green environmental protection.

Halogen-free flame retardant rigid polyurethane foam also has some shortcomings, mainly as follows. Unstable flame retardant effect. Halogen-free flame retardants may show different flame retardant effects under different fire conditions, such as temperature, oxygen concentration, flame intensity, etc., or even fail. Therefore, it is necessary to consider various complex influencing factors, optimize the formulation and process, and improve the stability and reliability of the flame retardant effect. Higher flame retardant cost. Halogen-free flame retardants are usually more expensive than traditional halogen-containing flame retardants, and require higher purity and quality. In addition, halogen-free flame retardants may need to be used with other types of flame retardants or additives to exert synergistic effects, increasing the flame retardant cost. Unclear flame retardant mechanism. The flame retardant mechanism of halogen-free flame retardants in rigid polyurethane foam is not very clear, especially their mode and process of action in gas phase and condensed phase. Therefore, it is necessary to explore the interaction and reaction mechanism between halogen-free flame retardants and rigid polyurethane foam in depth, providing theoretical basis for designing more efficient and environmentally friendly halogen-free flame retardants.

I think the future development direction of halogen-free flame retardant rigid polyurethane foam may include the following aspects. Biobased polyols. Using biomass resources, such as vegetable oil, lignin, cellulose, etc., to synthesize biobased polyols, replacing traditional petroleum-based polyols, improving the renewability and degradability of polyurethane foam, reducing its impact on the environment. Reactive halogen-free flame retardants. Developing organic halogen-free flame retardants with active groups, such as hydroxyl group, amino group, isocyanate group, etc., making them react with polyurethane raw materials to become part of the polyurethane molecular chain, improving their compatibility and stability with the substrate, avoiding migration, volatilization and hydrolysis phenomena. Surface treatment technology. Using coating, film, layer-by-layer assembly and other technologies to cover a layer of halogen-free flame retardant on the surface of polyurethane foam, forming an effective protective barrier, isolating the external oxygen and heat transfer, protecting the substrate from further decomposition and combustion. Catalytic carbonization technology. Using compounds or nanomaterials containing metal or non-metal elements as catalysts, promoting rapid carbonization of polyurethane foam when burning, forming a dense and stable carbon layer, enhancing its heat insulation, oxygen isolation and structural strength, improving its flame retardancy.

In future work, the development and innovation of halogen-free flame retardants should be strengthened. Combining biotechnology, nanotechnology, surface modification technology, etc., developing new types of halogen-free flame retardants, improving their flame retardant efficiency and performance, reducing their toxicity and environmental impact, meeting the needs and standards of different fields. Strengthening the evaluation and testing of halogen-free flame retardants. Establishing a sound evaluation and testing system for halogen-free flame retardants, including physical properties such as flame retardancy, mechanical properties, aging resistance, thermal conductivity, water absorption rate, etc., and environmental properties such as toxicity, biodegradability, recyclability, etc., providing scientific basis for the selection and application of halogen-free flame retardants. Promoting the application and popularization of halogen-free flame retardants. Strengthening the propaganda and education of the application and popularization of halogen-free flame retardants, improving public awareness and acceptance of halogen-free flame retardants, promoting their wide application in rigid polyurethane foam, providing safe, environmentally friendly and efficient flame retardant materials for the fields of construction, furniture, automobiles, aviation, etc.

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