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Application of halogen-free EPDM flame retardants

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Abstract. Flame retardant materials have been widely used in different fields because of their unique physical and chemical properties, such as aerospace and chemical products. However, although the traditional halogen-based flame retardant has shown excellent application performance in the actual application process, there are serious environmental pollution problems after its use. In order to solve the environmental problems caused by halogen flame retardants, different types of environmentally friendly flame retardant materials have been developed, such as ethylene propylene diene monomer (EPDM) flame retardant. As a new type of energy saving and environment friendly rubber, the EPDM has excellent heat resistance, aging resistance, corrosion resistance and insulation performance, and thus it has been widely used in all walks of life. To this end, EPDM has been used to develop different types of flame retardant materials. Herein, this research will mainly analyze the application performance of different types of EPDM flame retardants and their flame retardant mechanisms, where the research and application of EDPM flame retarder are mainly described from three aspects: intumescent flame retarder, phosphorous flame retarder and inorganic flame retarder.

Keywords: EPDM rubber, flame retardant, application.

1. Introduction

Ethylene propylene diene monomer (EPDM) is a rubber, which can be prepared by copolymerization of ethylene, propylene and a small amount of non-conjugated dienes. Owing to its unique physical and chemical properties, the EPDM has extremely excellent application characteristics, including heat deformation resistance, aging resistance, water resistance, electrical insulation properties, and availability at low temperatures. At the same time, EPDM rubber is widely used in the automotive industry, textile industry, power industry and other fields because of its unique performance advantages. Based on this, EPDM has become one of the most widely used rubbers in non-tire applications in the world, and it can be also known as the third-generation rubber. Not only that, EPDM is also widely used in the preparation of different types of flame retardant materials, which has been widely used in different fields [1].

EPDM-based flame retardant materials belong to a halogen-free flame retardants. EPDM-based flame retardant materials are widely used in some special scenarios due to their good flame retardant performance, high thermal stability, and outstanding mechanical properties and durability. Here are some of the main application scenarios of EPDM flame retardant materials [2]. For power industry, EPDM-based flame retardant can be used for cable accessories for cable termination, cable joints and cable insulation. For construction industry, EPDM-based flame retardant materials can be also used as flame retardant sealing rings, sealing strips and fireproof boards in building materials. For aerospace and railway industry, EPDM-based flame retardant materials are widely used in aircraft and train interiors, cable insulation and other fields to enhance the performance of flame retardant and product safety. For electronics industry, they are used in the fields of fire protection of electronic products and packaging of electronic circuits. In other fields, this type of flame retardant materials can also be used to manufacture flame retardant rubber seals, flame retardant hoses and flame retardant rubber pads to meet the flame retardant requirements in a diverse of different fields.

Compared to traditional halogen-based flame retardants, halogen-free flame retardants have the following advantages [3]. This type of flame retardant does not contain harmful halogen elements and will not cause harm to the environment and human health, which is an environmentally friendly flame retardant material. And in other words, EPDM-based flame retardants have low toxicity and will not cause harm to the human body during use. Halogen-free flame retardants show good thermal stability performance under high temperature conditions, which can effectively inhibit the combustion of materials under high temperature conditions. This type of flame retardants does not produce corrosive gases during the combustion process, and has little impact on the corrosion of sensitive devices, such as electronic products and communication equipment. In addition, halogen-free flame retardants can achieve flame retardant effects without affecting the physical properties of the material. In summary, halogen-free flame retardant has the advantages of environmental protection, low toxicity, good thermal stability, and no corrosive gas, and is an ideal flame retardant.

As a result, this research will discuss the synthesis of different types of EPDM-based flame retardant materials and their application performance. After analyzing the flame retardant mechanism of flame retardant materials, this research will analyze the flame retardant properties and applications of different EPDM-based flame retardant materials separately, which is expected to provide a new idea for the preparation and application of new environmentally friendly flame retardants.

2. Flame retardant mechanism

There are several ways for flame retardants to achieve flame retardant effect [4]. The first way is cooling and flame retardancy. Since heat transfer is the main condition in the combustion process of polymers, by selecting flame retardants with high heat capacity and prone to phase change or reaction to absorb the large amount of heat generated in the combustion process, the surface temperature of burning polymers can be reduced to be lower than the combustible temperature, so as to delay combustion and even flame retardant. The second way is to reduce the concentration of combustion supporting gases. Flame retardants can produce a large number of inert gases through thermal decomposition during the combustion process. The mixture of these inert gases and combustion supporting gases will reduce the concentration of combustion supporting gases in the combustion area as a whole. Because the combustion of polymers requires a certain concentration of combustible volatiles and a large number of combustion supporting gases, when the diluted gas concentration is lower than the concentration required for combustion, the combustion of polymer is blocked to realize self-extinguishing. The third way is to add flame retardants that produce a tight isolation layer. Both polymers and flame retardants decompose during combustion can be used to produce a carbon layer, which is usually stable and dense, so it can not only prevent the escape of combustible gases, but also block the contact between polymers and flame and combustion supporting gases, so as to achieve flame retardancy. The fourth way is to add inhibitory flame retardants. By adding flame retardants with the ability to capture free radicals, the side reactions of oxygen-containing free radicals during polymer combustion can be inhibited, so as to inhibit combustion.

3. Application of EPDM flame retardants

This part of the article mainly introduces three types of EPDM flame retardants, including intumescent flame retardant, phosphorus-containing flame retardants and inorganic flame retardants. At present, the modification of EPDM flame retardant is still by mixing with flame retardant polymer materials and

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adding a large number of flame retardants. To this end, these different modification strategies will be systematically analyzed and their specific application performance will be discussed.

3.1. Intumescent flame retardants

Intumescent flame retardants (IFRS) shows different advantages in the process of application, such as low smoke, low toxicity, high flame retardant efficiency and no corrosive gas release, so it has become a widely used flame retardant. The IFRS are classified into physical and chemical types. The physical type is mainly expandable graphite while the chemical type is mainly carbon source (carbonaceous agent) and gas source (foaming agent) [5]. For example, Cheng et al. prepared the expandable graphite (EG) microcapsule by using in-situ polymerization, and they also obtained the organic shell with high compatibility and thermal conductivity by using the boron nitride (BN) doped [6]. The introduction of BN can be used to improve the thermal conductivity of the prepared EG microcapsules. In addition, BN and EG can form a highway network for heat transfer. The BN-PMEG, which has high thermal conductivity, effectively reduces the risk of rubber burning. This work provides new options for the design and application of rubber composites in construction.

Jiang et al. designed a bio-based enhanced flame retardant based on Enteromorpha [7]. The flame retardant system they designed mainly focuses on the enhancement and flame retardant effect of the EPDM. As shown in Figure 1, because of its intumescent flame retardant mechanism, the bio-based flame retardant holds synergistic flame retardant and smoke suppression effects on the EPDM. In addition, Raman and scanning electron microscopy characterization shows that the APEG system can be used to promote high graphitization and form a carbon layer containing phosphorus carbon structure, which can significantly reduce flammability parameters and fire risk. And also, the addition of a suitable APEG system can also help to improve the mechanical properties of the EPDM. More importantly, EN and GE can effectively compensate for mechanical damage caused by the addition of flame retardants, even under higher load conditions.

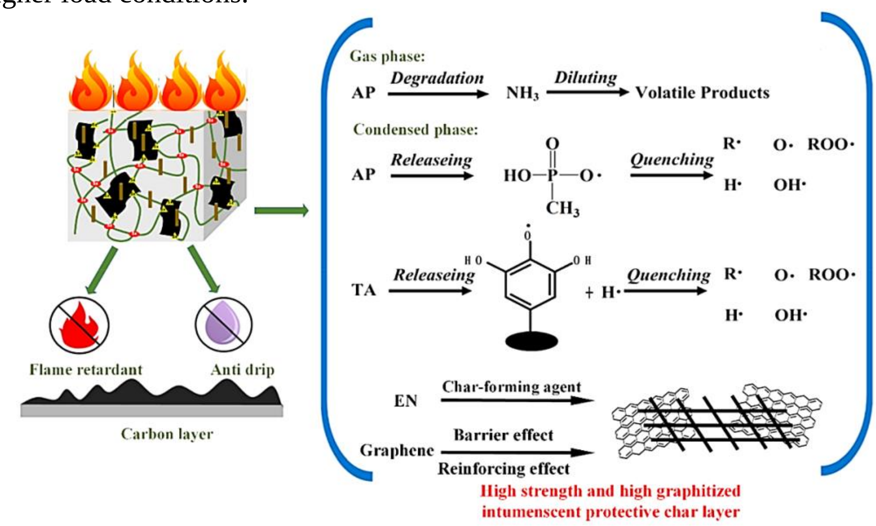

Figure 1. Flame retardant mechanism of prepared EPDM/APEG materials [7].

In order to reduce the fire risk of EPDM, Han et al. synthesized a piperazine/olefin-containing phosphamide oligomer poly (2-butene-1,4-diketopiperazine-fumalyl phenylphosphonate) (PPFPP) and used it as a carbonizing agent, and combined with ammonium polyphosphate (APP) to prepare a new intumescent flame retardant [8]. By incorporating 20 wt% APP/PPFPP into EPDM according to the weight ratio (3:1), the flame retardant EPDM reaches UL-94 V-0 grade, and its limiting oxygen index can reach 27.0%, which is significantly better than the flame retardant EPDM composed of olefin-free controlled flame retardant PPSPP and phenylphosphine-free PPFA. As shown in Figure 2, the prepared target EPDM shows a good flame retardant effect. In this work, the combination of piperazine and olefins with phenylphosphine can be used as carbonizing agents for the preparation of different EPDM-based flame retardant materials.

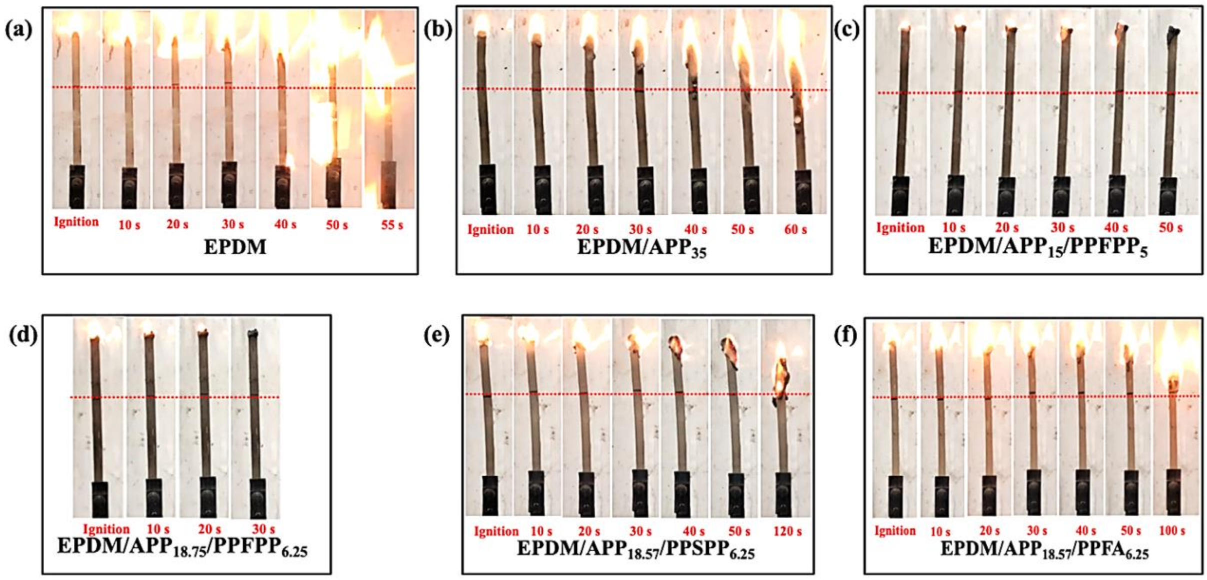

Figure 2. Digital photos for burning EPDM and its composite materials [8].

When triazine carbon forming agent (CFA) and ammonium polyphosphate (APP) are used in flame retardant materials, they can be used to regulate the flame retardant properties of the material [9]. The effect of APP-CFA on the flame retardant properties for the prepared EPDM-based composite materials is analyzed. Their results show that APP-CFA can be used to significantly improve the flame retardant performance of the prepared materials. When the ratio of APP to CFA is 4:1, the limiting oxygen index (LOI) of EVM/EPDM can reach 27.1%.

3.2. Phosphorus-containing flame retardants

Phosphorus and phosphorus compounds have been used as flame retardants for a long time. Their own characteristics enable them to overcome many shortcomings of traditional flame retardants, such as toxic gas emissions, high smoke emissions, and large amounts of additives. Inorganic phosphorus flame retardants can be commonly used as rubber flame retardants include four kinds: phosphate, microencapsulated red phosphorus, red phosphorus and ammonium polyphosphate.

Pegoretti et al. studied the fire performance of elastomer panels prepared with EPDM for the first time [10]. These panels could be prepared with four different flame retardants. To analyze their efficacy, they are selectively dispersed only in the core material, or in the housing, or both. The results show that there is a significant increase in the fire resistance of EPDM/nitrile rubber panels with paraffin wax due to physicochemical and chemical interactions between clay, talc, kaolin and silicon with ammonium polyphosphate. The use of paraffin wax to improve the fire performance of EPDM/nitrile rubber panels offers potential applications in the field of building thermal energy storage.

Wu et al. reported that polypropylene (PP)/EPDM was synergized by modified aramid fiber and ammonium polyphosphate (APP) to improve its flame retardant efficiency [11]. The prepared PP/EPDM materials with 34.5 wt% APP and 0.5 wt% modified aramid fiber can be up to UL-94 V0 and with a LOI of 28%. Moreover, total heat release and total smoke release for the prepared PP/EPDM materials decreased by 23.6% and 47.0%, respectively. In addition, the prepared P/EPDM materials shows a good thermal stability, as shown in Figure 3.

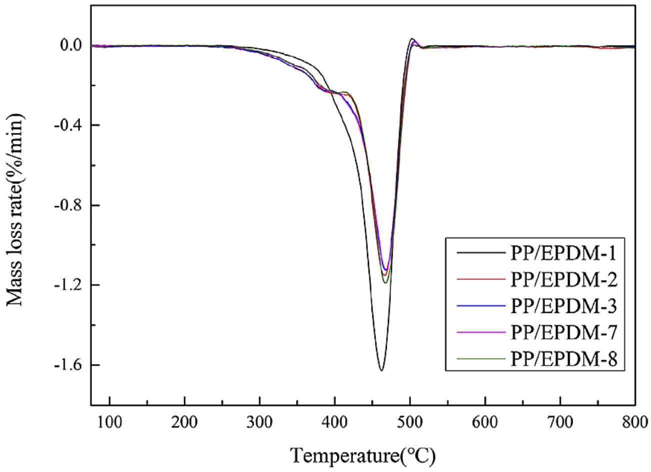

Figure 3. The DTG curves for the prepared PP/EPDM materials [11].

3.3. Inorganic flame retardants

Inorganic flame retardants are mainly metal hydroxides, where the most representative varieties are aluminum hydroxide and magnesium hydroxide. These flame retardants decompose at high combustion temperature, release structural water, generate metal oxides and absorb a large amount of heat from the environment. The released water vapor can be used to dilute and isolate the transport of oxygen, slow down the combustion process and absorb heat from the environment. For example, Yao et al. constructed a thermally reversible crosslinking network by using the Diels-Alder reaction in the flame-retardant EPDM/ magnesium hydroxide (MH) composite [12]. The coordination formed between MH and carboxylic acid groups enhances compatibility between the MH and EPDM matrices. The presence of thermoreversible crosslinking plays a key role in the overall flame retardant. It can be used to improve the flame retardancy and the degradation activation energy. As shown in Figure 4, the prepared flame retardant has good mechanical properties and is always capable of reworking under a high MH load.

George et al. investigated the effects of zinc borate (ZB), MH and APP as flame retardants on the mechanical, curing, thermal and combustion properties of Kevlar fiber (KF)-enhanced EPDM materials [13]. Compared to untreated EPDM/KF materials, the addition of composite fillers can be used to improve the flame retardant properties of EPDM/KF materials. In addition, flame retardant composites containing ZB and APP have significant synergistic effects in terms of thermal stability and flame retardance. If FR is added, the thermal insulation performance of EPDM/KF materials can also be significantly improved. Zirnstein et al. used APP, aluminum hydroxide (ATH) and polyaniline (PANI) to build a new multi-component flame retardant system [14]. The constructed multi-component flame retardant system effectively improves the flame retardancy and mechanical properties of rubber compounds. At the same time, it can also reduce the amount of filler. The APP, pentaerythritol and pyrophosphate can be also used to modify EPDM, which can reduce the effective combustion heat of EPDM by 20% [15]. And also, the mechanical properties and flame retardancy of EPDM have also been improved.

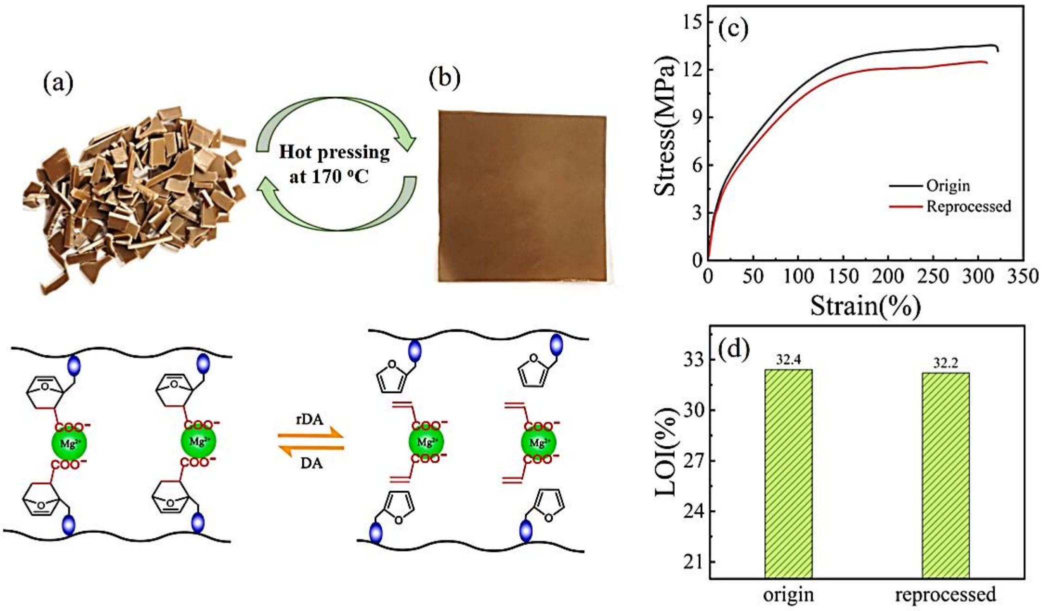

Figure 4. Description and analysis of the reprocessing process [12].

Heinrich et al. prepared fireproof nanocomposites of layered double hydroxide (LDH) and EPDM elastomer [16]. The authors pointed out that 4 phr of LDH could make its thermal stability the best, and this material could significantly improve the inherent slow sulfur curing properties of EPDM rubber. Chen et al. prepared the composite flame retardant and phenanthrene with significant flame retardancy and resistance to γ radiation properties of EPDM materials [17]. The material has the advantages of long ignition time (> 46 s), low peak heat release rate (~341 kW/m^2), and the LOI value greater than 30%, which can make the material widely used in radiation environment.

4. Conclusion

In recent years, the preparation of EPDM-based flame retardants by green and environmental protection methods has attracted extensive attention of scientists at home and abroad. This research analyzes the flame retardant mechanism of EPDM flame retardant materials and their different types of construction methods and applications. The APP can be incorporated into flame retardant systems with different structures to enhance the flame retardant performance. There are still some problems in the current flame retardant system. For example, it has certain hygroscopicity, large amount of additives, high cost, poor compatibility between materials and release of toxic gases. In view of these problems, the main research directions of EDPM flame retardant are as follows.

The surface of flame retardant can be modified to improve the binding efficiency between molecules. It can design new polymer molecules and develop high-efficiency charring agents, and reduce the particle size of flame retardant as much as possible and develop it to nanometer level. At the same time, attention should be paid to the research of flame retardant synergists to improve the flame retardant efficiency. There are some new directions for thinking there, such as to develop new nitrogen-containing phosphorus triazine polymer high-efficiency flame retardants, construct high-efficiency synergistic flame retardant system and improve the water resistance of flame retardants. Of course, some new green synthetic materials can also be developed, such as to develop new bio-based flame retardants. Using bio-based materials has many advantages. For example, the bio-based materials have high carbon content and multi hydroxyl structure, which is convenient for further modification, so they have excellent charring performance. It can not only promote the development of green flame retardant, but also greatly reduce the cost of flame retardant. In addition, the addition of environmentally friendly materials can also be used to improve the flame retardant performance of different flame retardants.

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