Application analysis of two flame retardant polymer materials

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Abstract. Flame retardants have become an integral part of the construction industry, not only to bring safety to residents in the event of fire, but also to reduce property damage. As excellent flame retardant materials, common flame retardant polymer composites mainly include two types, that is, traditional flame retardant and nano flame retardant. This research introduces the different flame retardants under the two categories and their corresponding flame retardant mechanisms in detail. And some other flame retardant polymer composites. In terms of mechanism, two important flame retardant mechanisms include dehydration and charring. In this research, the advantages and disadvantages of different flame retardant mechanisms in different polymers and their causes are introduced in detail. In addition, this research will compare the advantages and disadvantages of existing flame retardant materials and look forward to their future development trends, hoping to provide a new idea for the development of new flame retardant materials.

Keywords: Polymer, Flame retardant, Mechanism, Application.

1. Introduction

In recent years, with the process of industrialization, factories tend to be automated management, real estate enterprises become saturated. Due to the characteristics of polymer, such as light weight, high strength and plasticity, a diverse of different polymers has been widely used in various fields, for instance, biomedicine, environmental monitoring, chemical catalysis, home furnishings, building and construction materials and extra.

The use of polymer in the construction of flame retardant composites has many strengths. Firstly, it has the advantage of green environmental protection. It will not destroy and pollute the environment during production and construction, and it has high cost performance. Secondly, it has strong practicability. Facing a variety of construction applications, polymers can perform well in a variety of irregular substrates. This is because of its light weight and high strength. The most important advantage is that it has strong fire resistance, the flame retardant polymer composites can reduce casualties and ensure property safety in the face of fire.

The 2017 fire administration annual report showed more than one million of home fire causing more than 14,000 people injury and 3,000 people dead [1]. With billions of dollars in economic losses. In addition, in 2018, almost the same losses and injuries was happened [2]. While polymers have brought convenience to human life, the huge potential safety hazards behind them should not be underestimated. Therefore, flame retardant polymer composites play an important role in order to ensure personal safety and property safety. The flame retardant polymer composites have become a research hotspot in the field of architectural.

The main reason why flame retardant polymer composites have flame retardancy is the addition of flame retardant in polymers. Chemical composition is an important part of flame retardants, whose purpose is to slow and prevent objects from burning. The main factors of fire are heat, air and fuel [3]. All three conditions must be met for combustion to occur, and if one of them is not met, the combustion will be extinguished. The flame retardant polymer composites can reduce the flammability of fuel, isolate oxygen or cool the fuel so that it does not meet the above conditions to achieve the purpose. Therefore, adding flame retardants to protect the end product from burning is a growing trend.

Flame retardant is an important part of polymer composite formulation, which includes several flame retardant mechanisms [4], for example, gas phase inhibition, polymer breakdown, charring and extra. In the mechanism of gas phase, the flame retardants prevent the combustion of free radicals' mechanism in the gaseous phase [5]. In this way, the exothermic reaction of combustion will stop due to the decreasing of supply of flammable gases. Therefore, the system will cool down. In the gas phase, the reactive radicals HO* and H* will react with halogenated radicals X* which from flame retardant degradation. The combustion kinetics will reduce due to less reactive free radicals. In terms of polymer breakdown, flame retardants can influence the polymer to flow significantly, thus reducing the impact of flame strength. What's more, the mechanism of charring refers to the formation of carbon layer on polymer by flame retardant [6]. This can be achieved by forming double bonds in the polymer with in the process of dehydration of flame retardant. In this way, carbonization insulates the polymer surface and slows down pyrolysis.

At present, two kinds of common flame retardants are traditional flame retardants and nanosized fire retardants. The traditional one include halogenated and phosphorous products. The halogenated flame retardants suspend the gas phase of burning by generating free radicals. This kind of retardants corresponds to the gas phase inhibition mechanism above. While, halogen-free phosphorus-based flame retardants are considered to be the most available alternatives to halogen-containing components. In terms of nanosized fire retardants, metallic and non-metallic particles, zinc oxide, nanoclays, bio-based additives, Cellulose nanofibers, and carbon family-based additives. Adding a small amount of nano filler into polymer composites will often significantly improve the thermal stability.

In this research, flame retardant polymer composites will be introduced in detail, which is divided into three parts: traditional flame retardant materials, nannosized free retardant materials, and some other flame retardant materials. For each flame retardant composite, its flame retardant mechanism, material properties, advantages and disadvantages will be introduced in detail.

2. Traditional flame retardants

In the classification of traditional flame, halogenated flame retardants is occupied the most part of flame retardants. It contain organochlorines and organobromines. For example, chlorinated paraffins, hexabromocyclododecane, tetrabromophthalic anhydride and etc. The reactive radicals HO* and H* react with halogenated radicals X* [7]. In halogen flame retardants, adding different halogens will make great difference in flame retardancy. In the case of halogenated FRs of bromine and chlorine, very small bond energies are required to bond them to the carbon atoms on the polymer. Therefore, in combustion, halogenated flame retardants of bromine and chlorine can participate in the process with very little energy. However, other halogenated flame retardants, such as fluorides, require higher energy because their free radicals need to reach high temperatures to be released. In comparison, halogen flame retardants of brominated and chlorinated organic compounds have a great advantage. Besides, an additive that produces halides and degrades the polymer into a combustible volatile product over the same temperature range. Some effective halogen based retardant are PVC,CPVC,PVDF and additives are CP, DECA, BEOs and etc. The mechanism of halogenated flame retardants is showed below. The flame needs to be in the gas phase to capture free radicals more efficiently. At this point, the volatile antimony species will inhibiting H* radicals when adding antimony trioxide. As a result, the combustion will be interrupt. The synergistic effect between Sb_2O_3 and halogenated compound is proved by this case. Besides halogen in halogenated FRs, phosphorous products are also a traditional flame retardant. It contain organophosphates and phosphonate. For instance, resorcinol bis, ricresyl phosphate, aluminium diethyl phosphinate and etc [8].

Phosphorus flame retardants have three different flame retardants. The most common mechanism is the free radicals forming in the gas phase. Moreover, dehydration and charring are the two main mechanisms [9]. For most phosphorus compounds, thermal decomposition condenses phosphoric acid to produce water molecules and pyrophosphate. The combustion environment will cool down by the water molecules, while pyrophosphate forms a carbide layer to insulate the flame. This insulating carbon layer is protecting the underlying polymer from further combustion and limiting the further diffusion of oxygen. As shown in Figure 1, the mechanism for how phosphorus flame retardants work in epoxy resin is present. In the process of combustion, the free radical of phosphorus are produced in gas phase. The charring layers are formed in condensed phase.

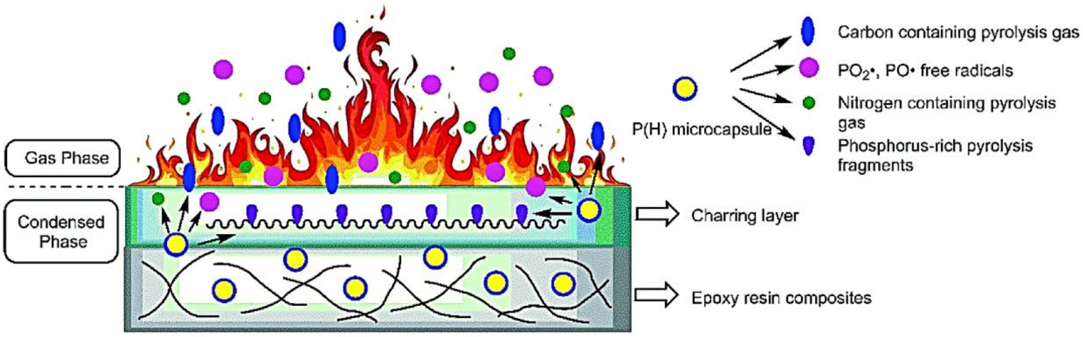

Figure 1. Mmechanism of phosphorous fire retardants in epoxy resin [10]

Common traditional flame retardants are brominated and chlorinated halogen flame retardants and phosphorous products. For halogen flame retardants, decabromodiphenyl ether, tetrabromophthalimide and etc. are the common useful flame retardants. Although the production cost of these halogen flame retardants is very low, they have an irreversible impact on the environment after use. In the process of flame retardation, halogen flame retardants will produce toxic and acidic substances, which will cause land corrosion after a fire. Therefore, many countries and regions prohibit the use of some halogen flame retardants. However, some countries are still used in some countries because of their low cost and high flame retardancy. For phosphorous products, some common flame retardants are triphenylphosphate, phosphinate salts, DOPO and etc. Compared with brominated flame retardants, phosphorus flame retardants have less reactive types. For example, adding phosphorus flame retardant to epoxy resin can effectively improve the value of limited oxygen index. However, phosphorus products have the same shortcomings as halogen flame retardants. In the process of flame retardation, toxic substances harmful to human nervous system will remain in the environment.

3. Nannosized fire retardants

Nanoscale flame retardants use polymer nanocomposites as flame retardants. It is divided into natural and artificial synthetic materials. Natural materials are nanoclay, montmorillonite and so on. Artificial synthetic materials include graphite carbon, metal oxidation and hydroxide and etc. Over the past few decades, the preparation and application of nanomaterials have achieved rapid development and progress. For this reason, the application prospect of nano-filled materials in the field of flame retardant has been rapidly developed. Although nano fillers themselves do not have excellent flame retardancy, adding nano fillers into polymer composites can be able to increase the thermal stability to the prepared materials. The mechanism for the prepared materials by different nanomaterials mainly occurs in condensed matter [11]. For the nanosized fire retardants, their flame retardant mechanism is based on the special structure of the used nanomaterials and their chemical composition [12]. As shwon in Figure 2, the prepared material without nanomaterials could be consumed after 471 seconds, while the samples with nanomaterials took longer to achieve the burnout state. In general, the exist of nano-fillers in the polymer will change the influence of nano-composites in the combustion. The most commonly used nanofillers for flame retardant nanocomposites are summarized in the table.

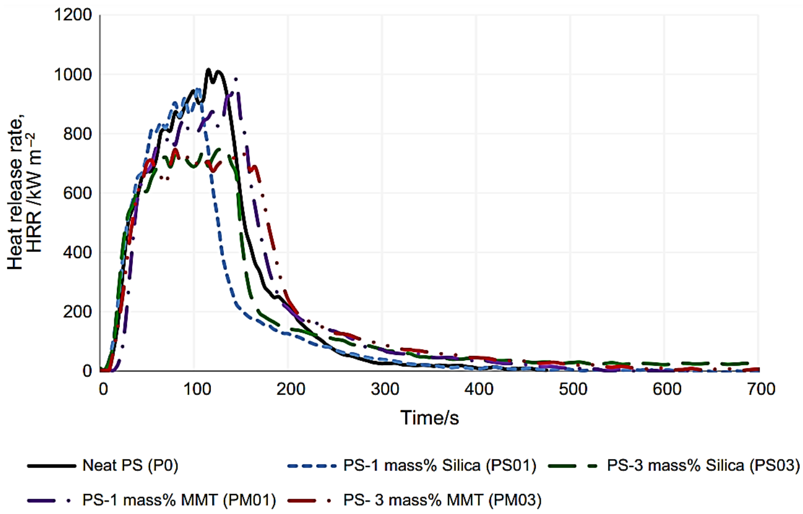

Figure 2. The heat release rate for the different prepared samples [12]

The way of apply of metal nanoparticle as fire retardants in different polymer substrates has attracted extensive attention. Different structures of metal nanoparticles lead to different fire reaction mechanisms. For example, metal hydroxide nanoparticles, when the object burns, water molecules will be released from hydrated minerals. This chemical reaction is endothermic [13]. In this case, the heat absorbed by the water molecules will prevent the combustion process, so as to achieve the cooling effect. Among them, aluminum trihydroxide and magnesium hydroxide are examples of metal hydroxides.

The limited oxygen index to the prepared materials can be significantly increased by the addition of metal hydroxide nanoparticles. In this case, in the polymer surface, there is a formed barrier to block the heat flow of the flame during the combustion. Thus achieving the purpose of flame retardancy. Some nanomaterials can also form carbon layers, such as trihydrate alumina (ATH), whose main function is to delay ignition [14]. In addition, small amount of metal hydroxide flame retardants produce water when they reached high temperatures. The formation of water promotes the dilution of combustible gas, thereby avoiding the effect of oxygen and inhibiting the propagation rate of the flame. Xi et al. prepared a new fire retardant (polyurethane foams) and analyzed its flame retardant effect [15]. As shown in Figure 3, the added ATH showed a better flame retardant as compared to other additives such as AO. Nanoclay is a ubiquitous nano filler which is separated from naturally occurring clay by some means. Nanoclays consist of stacked layers of silicate minerals that form complex clay crystals. Studies show that the composite containing clay particles has three main flame retardant mechanisms: migration mechanism, barrier mechanism and paramagnetic mechanism.

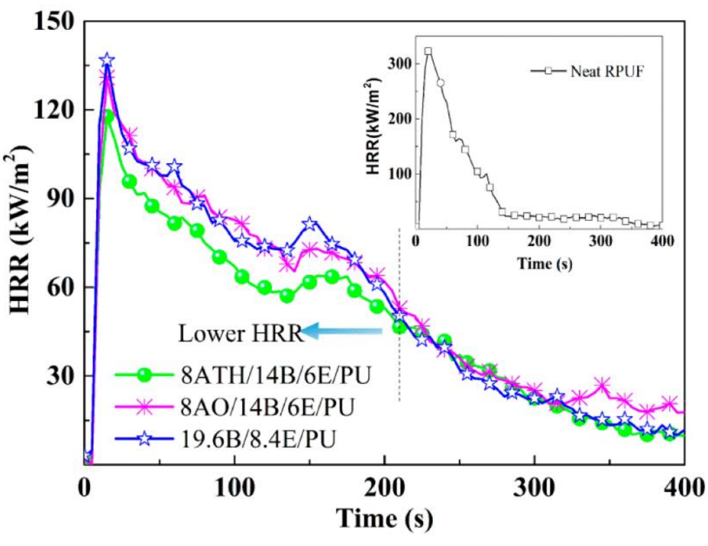

Figure 3. The heat release rate for the prepared fire retardants [12]

Common nano flame retardants include multi walled carbon nanotubes (MWNT), graphene and inorganic nanoparticles. For MWNT, Meyer rod's process is used, so that overlapping network carbon layers will be generated during combustion to prevent flame combustion. This reticulated carbon layer is one of the advantages of MWNT, which can significantly increase the fire resistance the polymer. MWNT has many hydrophilic groups in its structure, which can interact with hydrogen bonds and cellulose to form a protective layer to achieve the purpose of flame retardant. For graphene, its thermal conductivity is very poor. Because of its strong barrier effect and thermal stability. This is a necessary condition for an excellent flame retardant. Graphene is mainly used in epoxy resin, which can greatly improve its fire resistance and combustion stability. Graphene will form carbon residue during combustion to achieve the purpose of flame retardant. The report of Zhang et al. shows that adding graphene to epoxy resin can reduce the value of peak of heat release by 30% and increase the value of limited oxygen index by nearly 6% [16]. For inorganic nanoparticles, aluminum hydroxide and magnesium hydroxide belong to the two most commonly used inorganic flame retardants. For example, Gui et al. prepared the flame retardant ternary composites based on the addition of nanoscale magnesium hydroxide [17], where a better flame retardancy was obtained. The advantage of this material is that it can be more evenly distributed in the polymer than other materials, making it have better fire resistance.

4. Other fire retardants

Cellulose is an abundant organic polymer found in the cell walls of plants and bacteria. Cellulose has multiple glucose units and its extraction method has high degree of polymerization. The fibrous tissue is composed of many cellulose-disaccharide repeating units [18] and the mechanism of carbon formation in cellulosic materials is very complex. During thermal decomposition, cellulose creates a layer of insulating carbon on the surface of a certain size. As shown in Figure 4, cellulose chain organization can induce the generation of microfibrils, and these microfibrils aggregate to further produce cellulose fibers.

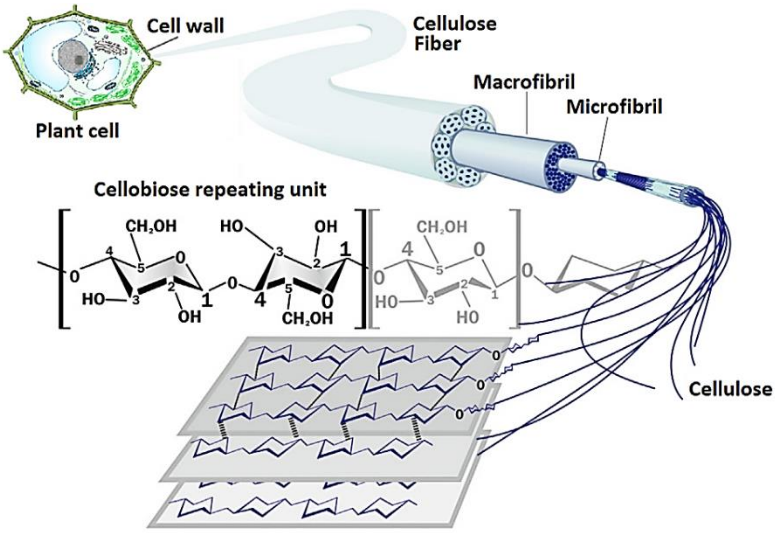

Figure 4. Cellulosic fibrous tissue in plant cell wall [19]

Two dimensional graphite carbon nitride is an carbon nitride with advantage of with thermochemical stability, photochemical and catalytic properties. This material is easily dispersed in a polymer matrix and forms a sustainable protective carbon layer through various accelerators. MXenes is a two-dimensional transition metal carbide. This substance is used in some fields, such as storage of energy, water purification and etc. In recent years, it has been extended to the nanometer filling field and achieved good results. Because it has good thermal stability and mechanical properties. However, MXenes is not widely used because industrial preparation does not allow it to disperse evenly in the polymer.

5. Conclusion

This research outlines the flame retardant combustion process of polymer and the flame retardant technology in recent years. In detail, two different types of flame retardant materials, traditional flame retardants and nano flame retardants, are introduced. The introduction of nano-fillers into polymer substrates to improve the fire resistance and the polymer material's mechanical properties has been widely researched. The flame retardancy of polymer will improved by appropriate nano filler. The addition of some graphite, inorganic nanoparticles or carbon to the polymer matrix in a controlled manner has been shown to advance the ability of flame retardancy of the polymer. Specifically, the nanotubes form a network of protective layers during combustion that protect the matrix of polymer from radiations and the burns of the flame. The interaction between nanoparticles and polymers will increase the concentration of nanoparticles and improve the fire resistance. In addition, the different chemical structure and shape of each type of nanoparticles will affect the fire resistance of polymers. If there is a large contact area between the nano filler and the polymer. The catalyst can better complete the catalysis. Because the catalytic area becomes larger, carbonation or free radicals can be formed faster.

For traditional flame retardants, although they were widely used before, they now have an irreversible impact on the environment. It is now subject to various regulations. These chemicals may volatilize or penetrate into the environment, causing harm to animals, plants and even human beings. In addition, halogenated flame retardants have great side effects in fire. Their flame retardants will produce toxic and acidic substances at the same time, resulting in a large number of corrosion problems after fire. Thus, it is expected that the development of new flame retardant materials can reduce the damage to the environment.

In large fires, excellent flame retardant composite materials are of vital importance. Because in a fire, the loss of property and casualties are terrible numbers. Fire retardant composite materials can reduce fire risk and damage. Flame retardant technology still faces many challenges. However, preparation of new flame retardant materials and related technologies still need continuous improvement. In the future, the research of further study on materials suitable for flame retardants and explore their recyclability. While achieving the purpose of flame retardancy, it can also be recycled. This can not only improve the economic feasibility, but also achieve the role of environmental protection.

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