Research progress on flame-retarded silicone rubber

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Abstract. Silicone rubber (SR) is widely used for its excellent temperature resistance, weathering resistance, chemical resistance and good transparency. In order to improve the flame retardancy of SR, many types of flame retardants (FRs) have been investigated. This paper summarized the research progress on flame-retarded SR, introduced different types of FRs for SR, analyzed the mechanisms of FR in condensed and gas phase, and finally predicted the prospective of flame-retarded SR.

1. Introduction
Silicone rubber (SR) is widely used in various fields including electrical, aerospace and automobile industries due to its excellent temperature resistance, weathering resistance, chemical resistance and good transparency [1-6]. However, SR is considered to be flammable [7-8], and it can’t meet the strict flame-retarded requirements in many applications.

In order to improve the flame retardancy of SR, researchers have investigated many types of FRs [9], among of which, halogen-contained FR proves to be effective. For example, SR with 25 wt % of decabromodiphenyloxide reaches V-0 rating and LOI value of 46% [10]. However, it does harm to the environment by releasing toxic smoke and corrosive fumes when exposed to fire.

Therefore, halogen-free FR for SR has been paid great attention. Usually, it plays roles in both condensed and gas phase. In the former, a continuous charring layer forms as an isolation of the heat and gas in combustion; in the latter, combustion is prevented by quench of free radicals.

In addition, incombustible gases that are generated in combustion of SR can reduce the combustion through concentration dilution of oxygen and combustible gases. Moreover, endothermal reactions reduce the combustion rate by reducing the reaction temperature.

2. Inorganic flame retardant
The inorganic FR performs excellent flame retardancy by reducing proportion of the combustible and changing thermal conductivity, stickiness and other performances of the matrix. The most widely used inorganic FRs for SR are platinum, metal hydroxide, expanded graphite (EG), metallic oxide and zinc borate(ZB).

Platinum or platinum compounds as a high temperature catalyst [11] is significantly effective in flame-retarded SR, which can improve the cross-linking density and residue char of SR at only 200~600 ppm. However, it hardly make SR reach V-0 rating without incorporation of other compounds, and its activity is damaged easily when contacting with P, N, S, Pb, Zn, etc.

Aluminum trihydrate (ATH) and magnesium hydroxide (MH) are widely used metal hydroxides for low cost, halogen-free and nontoxic smoke. They can reduce the proportion of available fuel, dilute concentration of oxygen, absorb heat and produce a char layer. However, they are effective only at a
high loading, which damages the mechanical property of SR greatly. Therefore, it is important to improve the adhesion and dispersion of metallic hydroxides in SR [12].

In addition, the effect of metal hydroxide is inconspicuous when used alone. Therefore, it is incorporated with synergist to promote the formation of char residue. For example, with the synergistic effect of red phosphorus (RP), the LOI of SR reaches 49% and 32.8% with 38 wt % of ATH and 20 wt % of MH, respectively [13-14]. In addition, the LOI of SR is 46% when the mass ratio of ATH and EG (37.5 wt %) is 1:1 [15].

EG is increasingly an effective FR. SR with addition of 25 phr of EG (50~80μm) is V-0 rating and reaches LOI value of 47%, which is 22% higher than that of pure SR [16].

Metallic oxide and ZB are cheap flame-retarded and smoke-suppressed synergists [17]. For example, 2.0 wt % of ZnO with intumescent flame retardant (IFR) reduces the peak heat release rate (PHRR) of SR and makes the char layer compact [18]. SR that contains ZB, B4C and hollow bead achieves LOI value of 27.1% when the content exceeds 12 wt %, which proves to behave well in heat insulation and flame retardancy [19].

3. Phosphorus-contained flame retardant

Phosphorus-contained FR is environmental friendly and effective. It plays important roles in both condensed and gas phase. In condensed phase, polyphosphoric acid that is generated through the breakage of the P-C bond can improve the dehydrated carbonization of the matrix, which plays a barrier effect. In gas phase, the free radicals PO·, PO2· and HPO· generated from FR scavenge radicals H· and HO· so as to reduce the combustion [20].

RP is a very effective inorganic phosphorus-contained FR synergist in small quantity (less than 10%), which is thermally stable up to 450°C. However, it has a major disadvantage that it can react with atmospheric moisture to form toxic phosphine gas. So it is often encapsulated in an appropriate polymer matrix for commercial use.

APP is an inorganic salt of polyphosphoric acid and ammonia, the chain length (n) of which is usually greater than 1000. It can contribute to improving thermal stability of SR composites [21-22]. After 10 wt % of APP is added, the LOI of SR is 31.2% [23], so is SR added with APP and other inorganic fillers [24].

Recently, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) has been investigated as an effective organic phosphorus-contained FR. It can improve flame retardancy and thermal stability of polymers as the cyclic O=P–O chain is more thermally stable than the open O=P–O chain [25-26]. As the P-H bond in DOPO molecule is highly reactive, DOPO can react with a series of unsaturated compounds. For example, DOPO is used to react with the epoxy group of siloxane monomer to obtain a SR containing phosphaphenanthrene structure. With the introduction of DOPO, SR is V-0 rating and achieves LOI value of 42.3%. At the same time, the HRR is greatly reduced [27].

Besides, FRs of other organic phosphorus compounds such as phosphonates and phosphonolipid also perform well in flame retarding and char forming [28].

4. Nitrogen-contained flame retardant

Usually, phosphorus-contained FR has poor heat resistance and high volatility in combustion, and the char residue of SR is quite loose. Therefore, as the isolation between material underneath and the outer is weak, flame retardant that contains phosphorus only can’t enhance the flame retardancy of SR in condensed phase effectively [29].

In this case, nitrogen-contained FR such as melamine is added as a gas resource, which can make the char layer intumescent. More importantly, it can improve the flame retardancy of SR by heavily absorbing heat when decomposed and releasing incombustible gases. The nitrogen and phosphorus system is called IFR, which is effective with the combined action of gas and condensed phase [30-31]. It has advantages including less smoke production, low toxicity and antidripping [32-33], and the intumescent char layer can not only isolate the transfer of the mass and heat between SR and flame, but also protect SR from the action of the heat flux or a fire [36-37].
Recently, IFR has been widely investigated (Figure 1). For example, the IFR mentioned above, which is synthesized with phosphorus acid, melamine and pentaerythritol, is effective for SR with the synergist ZnO [18]. The flame retardancy of SR proves to be the best with 16 wt % of PMP and 4 wt % of FeOOH [38]. After incorporating 18 wt % of HPTT, SR has LOI value of 31% and reaches V-0 rating [39]. Meanwhile, the residue of SR/HPTT is much higher, more compact and stable than that of SR.

IFR can make SR produce a stable and compact char layer to realize self-extinguishment and achieve excellent flame retardancy. However, they also have drawbacks including decline of mechanical property, decrease of transparency and loss of elasticity [16].

5. Silicon-contained flame retardant

SR is a polymer with structure of Si-O-Si chain which can generate SiO2 in combustion. The SiO2 is a ceramic layer consisting of carbon, silicon and oxygen, which can isolate the transfer of heat and combustible gas and oxygen. Therefore, SR can be added into other polymers as a flame retardant. Recently, the silicon-contained FR with low HRR and burning rate is environmental friendly. Due to their low surface energy, they can concentrate on the surface of polymer to form a silica layer, which can protect the polymer residue from further thermal decomposition [40].

As a silicon-contained FR, octaphenyl polyhedral oligomeric silsesquioxane (OPS) is composed of cage-like hybrid molecules of silicon and oxygen with a rigid hollow silica core, which contributes to flame retardancy and oxidation resistance [41-42].

Usually, silicon-contained FR is used with other types of FRs such as phosphorus-contained FRs to achieve better flame retardancy. For example, SPDV and DOPO-PMVS (Figure 1) are based on P and Si. DPA-SiN and DVN (Figure 2) consist of P, N and Si [43-46], and it indicates that the LOI increases with the decrease of P and increase of Si and N contents at the same loading level of DVN [47].

The silicon-contained FR is effective with synergist. Moreover, the similar structure with SR makes it disperse better in the matrix to maintain basic mechanical property.

6. Nano flame retardant

With progress of nanotechnology and demand for good flame retardancy, nano FRs such as montmorillonite (Mt) and layered silicate are widely studied and applied. With a special structural unit of two tetrahedral sheets, Mt can improve the flame retardancy of SR within a small amount. For example, LOI of SR increases to 28.0% with 15 phr of dendrimer modified organic montmorillonite [48]. In addition, it can also be used with IFR, for example, after adding 10
phr of OMMT and 35 phr of melamine phosphate, SR performs the best comprehensive performance including flame retardancy, mechanical property and heat stability [49]. However, the hydrophilic surface nature of Mt may hinder its dispersion in SR matrix, so the surface of Mt is modified organically [50].

Compared with Mt, functionalized zirconium phosphate (F-ZrP), which is prepared by the intercalation of PMVP (Figure 2) into α-ZrP, exhibits advantages including higher purity, ease of intercalation and exfoliation [51]. It can generate efficient and regenerable free radical scavengers which interrupt and suppress the free radical combustion progress. SR has LOI value of 31.0% and reaches V-0 rating with only 4.0 phr of F-ZrP.

7. Conclusions
Silicone rubber has good chemical resistance due to its stable structure. However, it is flammable and need to improve the flame retardancy. This paper summarized the research progress of flame-retarded SR. Usually, different types of FRs, which are incorporated into SR matrix together, work effectively with the synergistic effect in condensed and gas phase. However, the inorganic FR is effective only at high loading level and it damages the mechanical property of SR more or less. The future trend of flame-retarded SR is to introduce IFR structure to SR matrix and modify the surface of nano FR organically. In a word, different flame-retarded mechanisms will be used together to improve the flame retardancy of SR on the premise of keeping the basic mechanical properties of SR.

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