

The Application of Halogen-free Intumescent Flame Retardant in Polyolefin

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Abstract

Halogen-free intumescent flame retardant is a kind of flame retardants with a quick development in recent years. However, in practice, we found a lot of problems which limited the use of such flame retardants in polyolefin. Research showed that different processing technology and additives have obvious influence to the flame retardancy and other properties of the material. Meanwhile, polyolefin have many different types and grades, like PP and PE. Different type and even different grade has different requirement for the flame retardant. This paper mainly studied the processing method of polyolefin with the halogen-free intumescent flame retardant, the related additives and the influence of the grades of polyolefin to the final flame retardancy of the material.

Key Words:

Halogen-free, Intumescent, Flame Retarded, Polyolefin, Additive

1. Background

Over the past 10 years, halogen-free intumescent flame retardant (IFR) technology had been one of the important development trends in the flame retardants region. Many papers and researches studied on how to manufacture and use halogen-free flame retardants in polyolefin and other polymers. Some suppliers have manufactured a series of halogen-free intumescent flame retardants at smaller industrial scale. For example, there are Exolit AP750, AP760 of Clariant, Budit 3076 of Budeheim and PNP1 series of JLS. The mechanism of such systems is same. Though the acid donor, carbon donor and gas donor of the flame retardant system work together and form intumescent isolating carbon shell(char), it prevents the molten polymer from getting in touch with oxygen, heat and combustible gases¹. In practice, we found that successful example in a large scale application of such IFR system is very few because of the peculiarity of such halogen-free intumescent flame retardants.

For a successful halogen-free intumescent flame retardant polyolefin compound, it needs so many additives to work together besides the flame retardant, include dispersant, lubricant, modifier, antioxidant and etc. Such additives sometime caused problem to IFR system. It is possible that a few amount of such additives change the char forming processing and, they could bring the fateful influence to flame retardancy. On the other hand there is water-proof limitation commonly for such systems. We can modify the water-proof property, but any modification also could bring influence to flame retardancy. In addition, we must pay attention to the dispersion and extrusion processing.

Because of all these problems, it was difficult to get stable and perfect flame retardancy when we use IFR.

2. Flame Retardant Mechanism of halogen-free intumescent flame retardant

Based on P-N system, JLS-PNP1 series flame retardant is a high efficient halogen-free, intumescent, low smoke, non toxic and environmental friendly flame retardant. In fire, the acid donor, carbon donor and gas donor work together to form intumescent isolating carbon shell, which prevents the molten polymer from getting in touch with oxygen, heat and combustible gases. The flame retarded mechanism is taken place in the solid phase. **Fig1** shows the mechanism.

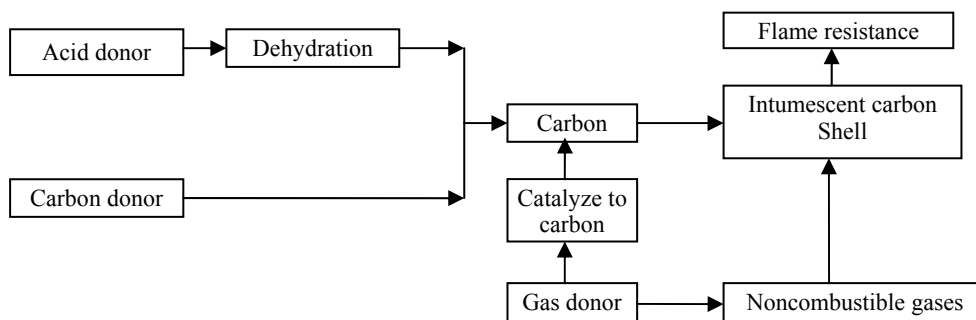


Fig1: Flame retardant mechanism of JLS-PNP1series

In this paper, we take JLS-PNP1C of JLS-PNP1 series as an example. In **Fig2**, intumescent flame retarded system makes the material self-extinguish when the cable leaves the fire and hinders after-glow effectively. It makes the cable to pass VW-1 test (single vertical burning) easily.

At the beginning of fire, the IFR system starts dehydrating and decomposing to give out a lot of noncombustible gas, help molten polymer forming char to reduce combustible gas. While the fire is going along, it is forming the intumescent char shell. The char shell is strong and with excellent heat insulation. It owes to the thickness and lacunose structure with close skin of the char shell².



Fig 2: The intumescent char forming procedure of PE with JLS-PNP1C

3. Surface Treatment - Flame Retardancy

3.1. The influence of coupling agents treatment

There are a lot of polar groups on the surface of halogen-free intumescent flame retardant, for example -NH₂, -OH and etc, but polyolefin is no polar, the flame retardants should be treated by coupling agent to ensure disperse. Normally we can use silane coupling agent, titanate coupling agent and fatty acid, see **Table 1**.

Table 1: Flame Retardancy -Coupling agents Treatment

(Based on 100phr PP+ 38phrJLS-PNP1, LOI=30)

Addition ¹	Silane coupling agent (KH550)	Titanate coupling agent (KR-138)	Stearic Acid
0. 2%	30	30	28
0. 5%	32	31	26
1. 0%	33	33	24
2. 0%	32	33	24
Surface	Smooth	Smooth, little yellow	Disperse badly
Weigh Loss at water ² , %	1.86	2.23	12.00

1. Addition: Based on flame retardant. After treating flame retardants, add flame retardants in the compound

2. Dip method: Based on 1% addition, the sample with $\delta = 1\text{mm}$ and $120 \times 120\text{mm}$ plate dip in water (70°C X 168 hours). Weigh Loss ratio base on the total weigh of the sample plate. If used no treatment flame retardants, Weigh Loss= 2.1%.

In **Table 1**, we find that for stearic acid(SA), it makes IFR difficult to disperse in PP, which makes the flame retardancy very bad. The reason is probably that -COOH of SA can react with -NH₂ of IFR and then to cause IFR powder agglomeration. SA also changes carbon structure too much to form the tight carbon armor. Silane coupling agent and titanate coupling agent can make the IFR to disperse easily, KR-138 contain of pyrophosphoric ester which it is no influence to flame retardant. However, at 210 °C, the compound contain of titanate coupling agent and IFR becomes instable, we find it a little yellow. Also there is negative influence to flame retardancy when the addition of silane coupling agent is above 2%. In fire silane coupling agent changes to SiO₂ which increases the specific gravity of intumescent foam to reduce expandable ratio.

In the paper we treat IFR with thermoset resin to modify the flame retardants water-proof. Thermoset resin contain of silicon resin, epoxy resin, MF resin and so on, which make IFR more dispersive and better water-proof, of course there is somewhat negative influence to flame retardancy. When surface coated, the IFR could not contact polymer straightly before the coating resin breaks up, see **Fig3**.

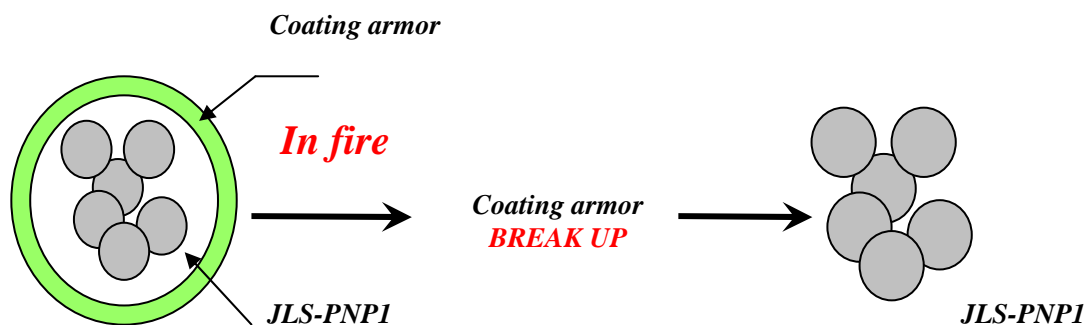


Table 2: Thermoset Resin treatment - Flame Retardancy

(Based on 100phr PE + 55 phrJLS-PNP1, LOI=35)

Item	Silicon resin	Epoxy resin	MF	No treatment
2%	32	33	30	LOI=35
5%	30	32	27	
Weigh Loss at water, %	0.61	1.02	0.03	4.12

1. Base on 5%wt resin treatment

In **Table 2**, there is negative influence to flame retardancy enormously. The influence of MF resin is the biggest. For epoxy resin, it is smaller. The reason is that epoxy is oxygen polymer, which can advance IFR to form the intumescent carbon shell. At the same time we found that IFR decreased the heat stability of the epoxy resin. At 200°C, the compound is becoming yellow.

3.2. The influence of particle size of IFR

IFR is solid powder, whose particle size brings some influence to flame retardancy. In PE, 15-20 μm particle size is better than 8-12 μm at flame retardancy and tensile strength. The bigger the surface area of the finer particle size powders makes them more difficult to disperse and then reduces the tensile strength by 11%. We treat it by coupling agent to improve dispersion in polyolefin. An example of PE compound is showed in **Table 3**.

Table 3: The Particle size of IFR - Flame retardancy

(Based on 100phr PE + 52 phr JLS-PNP1)

Average diameter μm	8-12	15-20	20-25	8-12 (1% silane coupling agent treatment)
LOI	31	30	29	32
Weigh Loss at water, %	4.6	2.1	2.1	1.9
Tensile, Mpa	15	17	14	19

4. How Additives Impact Flame Retardancy

In this paper we find that ordinary additives bring some influence to IFR, for example filler, lubricant and so on.

4.1. The influence of different fillers

We often add fillers in plastics. In brominated flame retardants system, we must add fillers (for example Talcum) as synergists to attain no dipping. How do the fillers affect the IFR, see **Table 4**.

Table 4: How different fillers do affect the IFR (in LOI)

(Based on 100phr PE + 52 phr JLS-PNP1, LOI=32)

Item	CaCO ₃	TiO ₂	SiO ₂	Carbon black	Zinc Borate	Talcum	Mg(OH) ₂
2%	32	33	29	30	34	35	28
5%	27	31	27	26	31	26	<23
10%	<23	—	—	—	<23	<23	—

In **Table4**, we choose a series representative filler to show the influence, contain of inert filler of CaCO₃, color of TiO₂, SiO₂ and carbon black, synergists of zinc borate, Mg(OH)₂ and talcum. Above 5% addition, any filler all bring negative influence. The reason is that overfull filler prevent the tight char shell forming, the other way round we get an open char surface, whose flame retardancy is bad. Of course the proper talcum, zinc borate and TiO₂ are beneficial to flame retardancy, they can react with acid donor to form a glass phase material,

help the tight char shell form at the proper temperature. But $Mg(OH)_2$ released water vapor at 270-300°C, soften the formed carbon foam to influence the intumescent effect. The same is for zinc borate. In addition, EU countries restrict zinc borate because it is harmful to aquatic.

4.2. The influence of glass fiber

The glass fiber (GF) is often used in plastics as modifier material. We study it and find a unique phenomenon in IFR system. It is very different to halogen flame retardant system, see *Table 5*.

Table 5: GF takes an influence to flame retardancy in IFR system

(Based on 100phr PP +39phr JLS-PNP1D)

Addition of GF	0	5	15	25
LOI ¹	31	34	34	30
LOI ²	31	26	<23	<23

1. Use short GF of 10-15mm, hold the length of GF at 4-8mm after processing;
2. Two times extrude makes the length of GF below 1mm

“Candlewick phenomenon of glass fiber” is not obvious in halogen-free intumescent flame retarded system. At the addition of 5-15phr glass fiber, which helps IFR system play a role and makes char shell more stable because of GF framework function. In case the GF be cut too short, it makes the IFR system become worse. The compound can not form continuous char shell in fire, no any flame retardancy. Thereby we must pay an attention to how to process glass fiber.

4.3. The influence of wax

We must add processing additive when we use IFR. First, halogen-free intumescent flame retardant is powder. Secondly, it is because we must add much IFR to attain flame retardancy. The addition is above 25% (wt) for PP and 35% for PE, see *Table 6*.

Table 6: Different Wax - IFR

(Based on 100phr PE+55phr JLS-PNP1C)

Item	Blank	PE wax	Lignite wax	EVA wax	Fluoride wax
0.5%	LOI=36	33	34	35	37
1.0%		30	34	34	37
MI ¹	0.50	1.05	1.21	1.34	2.23
Weigh Loss at water ² , %	4.30	3.70	1.63	2.12	1.23

1. The addition of wax is 1%
2. Weigh Loss at water when the addition of wax is 1%

From *Table 6*, there is big difference between the blank and compound, MI of polyolefin reduces 80% (MI of pure PE=3). It is necessary that we add wax in formulation as lubricant and dispersive agents. However wax is harmful to flame retardancy. The addition of wax reduces LOI above 2 in general. The key phase is the beginning of forming char in fire, once the char shell formed, it is very difficult to enkindle again. As known the melt point of wax is low to perspire easily at fire, the wax influences nascent char shell and disturbs the processing of forming char. But fluoride wax has synergism with IFR. At the beginning, it release HF which has flame retardancy in gas phase. And the wax itself protected the char shell because LOI of fluoride wax is above 40.

5. The Influence of Processing

A good formulation is corresponding to a certain processing method. The thermal decomposing temperature (in TGA) of IFR is designed at about 270°C, which is a little lower than that of polyolefin(about 300°C). If IFR is too stable, it is not good to get flame retardancy. The decomposing temperature of IFR should be lower than that of polyolefin. But in the twin extruder IFR is decomposed from 230-250°C, the more strong shearing force is, the lower decomposing temperature is. We can improve it by adding processing additives. If IFR is decomposed during processing, the flame retardancy is becoming bad very fast, see **Table 7**.

Table 7: Different processing temperature of PP-LOI

(Based on 100phr PP+ 40phrJLS-PNP1)

The highest Temp. of processing	210°C	230°C	250°C
LOI	32	31	26
Phenomena	Smooth surface	A little sparkle	Sparkle very much
Analysis	OK	Decompose a little	Decompose a lot

In fact, at 250°C, the IFR decomposed, gives out water vapor and decomposed matter, which makes the molten viscosity go up. The processing loading go up from 45% at 210°C to 90% at 250°C. It makes negative influence to flame retardancy. You will find same phenomenon when the moisture of IFR is higher.

6. Conclusions

To use halogen-free intumescent flame retardants in Polyolifin, we must choose the proper additives and processing method to meet IFR and ensure flame retardants to give a play normally.

1. In IFR system, you can not use stearic acid. You can use silane coupling agent with the amount below 2%. If you want to improve water-proof property, you can use thermoset resin. But you must immolate a part of flame retardancy.
2. When we make IFR more fine, we must treated it by coupling agents.
3. The addition of fillers must control below 2%. TiO₂, talcum and zinc borate help char shell forming. If adding above 5%, also there are negative influence to flame retardancy. Mg(OH)₂, SiO₂ and carbon black have the big influence to flame retardancy.
4. “Candlewick phenomenon of glass fiber” is not obvious in IFR system, but shear too intensively make the flame retardancy bad.
5. In halogen-free intumescent flame retardant system, we can add wax as lubricant and dispersive agent. Fluoride wax can promote the flame retardancy.
6. In IFR system, we must pay attention to moisture and processing temperature, which could cause decompose of IFR and to make IFR difficult to dispersion. It makes the flame retardancy bad.

7. References

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