

Effect of Charring Agent THEIC on Flame Retardant Properties of Polypropylene

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ABSTRACT: Tris(2-hydroxyethyl) isocyanurate (THEIC) was used as charring agent and combined with ammonium polyphosphate (APP) to form an intumescent flame retardant (IFR) for polypropylene (PP). The flame retardancy and combustion performance of PP/IFR composite was tested by limiting oxygen index (LOI), UL-94 vertical burning test and cone calorimeter. The results showed that PP/IFR composite had highest LOI of 34.8 and obtained V-0 rating when 30 wt % IFR was loaded and mass ratio APP/THEIC was 2 : 1. The peak heat release (PHRR) and total heat release (THR) values of PP composite containing FRs were remarkably reduced compared with that of pure PP. However, water resistant test demonstrated the PP/IFR composite had poor flame retardant durability, both the LOI value and UL-94 V-rating decreased when PP/IFR composite was soaked in water at 70°C after 36 h. The degradation process and the char morphology of IFR and PP/IFR composite were investigated by TGA and SEM images. The possible reaction path between APP and THEIC in the swollen process was proposed. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41214.

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INTRODUCTION

Polypropylene (PP) is an important polyolefin and has been widely used in many fields. However, the use of PP in electric and electronic, building, or transportation is strongly limited because of its easy flammability and dripping tendency.^{1,2} Traditionally, halogen flame retardants are added to promote flame resistant properties. Nevertheless, corrosive fume and toxic gases may release during their combustion process. In recent years, nontoxic and environmental friendly flame retardants are largely required in many fields, such as automobile, airplane, high-speed, mine cable, etc.,³ halogen flame retardants are restrained.

Intumescent flame retardant (IFR) has been reported and used for several decades, which is regarded as a promising way to enhance polymer's flame resistance with little pollution.⁴ Its flame retardant mechanism is based on foamed cellular charred layer, which acts as a physical barrier to slow down the heat and mass transfer between the gas and condense phase.³ Normally, a typical IFR system involves three ingredients, an acid resource, usually phosphoric acid, a charring agent commonly pentaerythritol (PER), and a blowing agent, like melamine.⁵ The most typical and widely studied IFR system is the combination of ammonium polyphosphate (APP) and PER, which was studied by Camino's and Borbigot's groups as early as in 1984.^{6–13}

Charring agent is an important component in IFR system, its charring behavior greatly affects IFR's flame retardancy. Unfortunately, studies on charring agent are not received so much attention compared with other ingredients in IFR system, many studies use PER as charring agent.¹⁴⁻¹⁶ To provide a new perspective into charring agent, development of new charring agent to substitute PER is of great importance. In recent years, some triazine-based oligomer was synthesized and applied in IFR system, it was found triazines and their derivatives were very effective as charring agent.¹⁷⁻²⁰ Ke¹⁹ prepared hyperbranched charring agent (HCA) by using cyanuric chloride, diisopropyl ethylamine and 4,4'-diaminodiphenyl as raw materials, results showed the IFR containing HCA had excellent flame retardant and anti-dripping abilities for PLA. Li²⁰ synthesized a triazine-based char forming agent (CFA) by using cyanuric chloride, ethanolamine and ethylenediamine as raw materials. The IFR consisting of CFA, APP and 4A zeolite showed good flame retardant efficiency on PP. However, all triazine-based charring agents are prepared from cyanuric chloride and need organic solvent, leading to environmental pollution in larger scale production and safety anxieties for workers in operation. Thus, new synthetic process or new charring agent is in urgent requirement.

Tris(2-hydroxyethyl) isocyanurate (short for THEIC), mainly used as stabilizer of polyvinyl chloride (PVC), intermediate of paints,

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dyes and pharmaceuticals, is a derivative of triazine compounds. Its usage as charring agent in IFR system is seldom reported, except for some patents and papers in last century.²¹⁻²³ Recently, Li²⁴ studied the flame retardancy of PP/APP/THEIC system, he found PP/APP/THEIC composite's heat release rate, mass loss rate and total heat release rate decreased obviously, so he believed there was synergistic effect between APP and THEIC. However, Li's work was only emphasized on the advantage of THEIC in IFR system, the disadvantage of THEIC based IFR was not mentioned, such as thermal instability and low flame retardant durability. His study is not comprehensive and may lead to misuse in industrial production. In this article, THEIC was used as charring agent and was combined with APP to form IFR system. The thermal degradation process was studied, the reaction path between APP and THEIC was also proposed. The advantages and disadvantages of THEIC in IFR system were comprehensively evaluated.

EXPERIMENTAL

Materials

PP (T30s, melt-flow rate = 2.3 g/10 min) was supplied as pellets by SINOPEC Maoming Company, China. APP of crystal form II with polymerization degree 1000 was kindly provided by Shandong Shi'an Chemical. THEIC was purchased from Changzhou Lantian Chemical. PER was purchased from Sinopharm Chemical Reagent. All were used without further purification.

Preparation of Samples

APP and THEIC were dried at 60° C under vacuum condition for 8 h before used. Pure PP was mixed at rotate speed of 20 r min⁻¹ at 180°C for 3 min by using an internal mixer (Su 70-1, Suyan Technological Company, China), then APP and THEIC were introduced and mixed for 10 min. The composites were hot-pressed at 180°C into sheets of suitable thickness and size for further flame properties tests. The formulation of all samples was listed in Table I.

Flame Retardancy Test

The flame retardancy was characterized by limited oxygen index (LOI) and UL-94 methods. The LOI values were tested according

Table I. Flame Retardancy of PP/IFR System

	Components			Flame reta	rdancy
Sample no.	PP	APP	THEIC	LOI	UL-94
PPO	100	0	0	17.8 ± 0.1	N.R
PP1	70	30	0	18.9 ± 0.1	N.R
PP2	70	27	3	30.8 ± 0.1	V-0
PP3	70	25	5	32.7 ± 0.1	V-0
PP4	70	20	10	34.8 ± 0.1	V-0
PP5	70	15	15	30.6 ± 0.1	V-0
PP6	70	10	20	24.8 ± 0.1	V-1
PP7	70	5	25	21.2 ± 0.1	N.R
PP8	70	3	27	19.7 ± 0.1	N.R
PP9	70	0	30	18.2 ± 0.1	N.R
PP10	70	20	10	31.6 ± 0.1	N.R

N.R: no rating.

Composite formulation PP/IFR = 70: 30.

to ASTM D2863-97 using an oxygen index instrument (JF-3) produced by Jiangning Analysis Instrument Factory. UL-94 rating tests were conducted on CZF-3 (Jiangning, China) with sheet dimensions of $130 \times 13 \times 3 \text{ mm}^3$ according to ASTM D3801.

Water Solubility

A clean beaker was weighted (W_a). Nearly 100 g sample (APP or THEIC) was solved with 100 mL distilled water in a 250-mL beaker with constant stirring. After 30 min, the mixture was pulled out and centrifuged to get upper clear solution. About 20 mL of the clear solution was put into a clean beaker and dried at 120°C for several hours until the weight was constant (W_b). As a result, the water solubility of APP and THEIC can be calculated as: ($W_b - W_a$)/20 × 100% g/100 mL water.

Water Resistance of Flame-Retarded PP Materials

The specimens were soaked in distilled water at 70°C and were kept at this temperature for various time periods. The specimens were subsequently taken out, dried in the vacuum oven, and evaluated by LOI and UL-94 tests.

Characterization

The thermogravimery analysis (TGA) tests were carried out on EXSTAR 6000 (Hitachi, Japan) at a heating rate of 10°C min⁻¹ under air atmosphere. The TGA data were collected from room temperature to 800°C, the weight of the samples was kept within 4-5 mg. The Fourier transform infrared (FTIR) spectra were obtained using a Bruker-Vertex 70 FITR spectrometer in the range of 400–4000 cm⁻¹ by using the KBr disk method. The combustion properties were evaluated by using a cone calorimeter. All samples $(100 \times 100 \times 3 \text{ mm}^3)$ were exposed to a Stanton Redcroft cone calorimeter under a heat flux of 50 kW m⁻² according to ISO-5660 standard procedures. The morphology of residue char was observed by JSM-6360 scanning electron microscopy with an accelerating voltage of 15 kW. The surface of the char residue was sputter-coated with gold layer prior to measurement. In addition, the IFR's residue char was obtained by heat treatment of IFR in muffle furnace at 400°C for 30 min, and the char of PP/ IFR composites was obtained after LOI tests.

RESULTS AND DISCUSSION

FTIR of THEIC

The FTIR spectra of THEIC are shown in Figure 1.

The absorption peaks at 3512, 3367, and 3251 cm⁻¹ are attributed to O—H and hydrogen bond vibration. The absorptions at 2974 cm⁻¹, 2949 cm⁻¹ are assigned to the asymmetric stretching vibration of $-CH_2$ —, the peak at 2885 cm⁻¹ is attributed to $-CH_2$ — stretching vibration, 1464 cm⁻¹ is attributed to C=O stretching vibration. Absorptions at 1056 and 1035 cm⁻¹ are assigned to C–O vibration. Area at 814 cm⁻¹ is attributed to the skeleton vibration of triazine ring.¹⁸ All the peaks are in good agreement with THEIC functional group.

Flame Retardancy

As stated above, the formulation of all samples is listed in Table I, the flame retardancy test results of PP/IFR composites are also listed in Table I.

It can be seen from Table I, PP is easily burnt, accompanied with droplet, its LOI value is only 17.8. Addition of single 30 wt





Figure 1. FT-IR spectra of THEIC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

% APP (sample PP1 in Table I) or single 30% THEIC (sample PP9 in Table I) has low LOI values, the composites fail to achieve any V-rating and their LOI values are 18.9 and 18.3, respectively. The low flame retardancy (PP1 and PP9) are caused by the poor char forming capacity due to the lack of either acid source or charring agent in IFR system. Thus, coexistence of acid source and charring agent is crucial for the synergistic effect of IFR system. The flame retardancy of PP/IFR composites with different mass proportion of APP/THEIC in PP is studied. It is found that the LOI value improves a lot if the mixture of APP and THEIC was added. When IFR loading was 30 wt % (APP/THEIC = 9:1), the PP/IFR composite's LOI is raised to 30.8, an increase of 72.9% in comparison with that of pure PP. When the mass ratio of APP/THEIC was 2 : 1, the composite's LOI reach the highest value of 34.8. PP10 is a traditional IFR formulation, it has a LOI value of 31.8, lower than 34.8 of PP4. The LOI value indicates the synergistic effect of APP/THEIC in PP4 is better than PP/PER in PP10, the PP/ APP/THEIC composite has a higher flame retardant efficiency. As for UL-94 vertical tests, it is found when the mass ratio APP/THEIC was from 9 : 1 to 1 : 1, V-0 rating can be obtained.

The effect of different ratio of APP/THEIC on flame retardant property is shown in Figure 2.

From Figure 2, it is found the composite's LOI values begin to decrease when mass ratio APP/THEIC was lower than 2 : 1, this phenomenon may be caused by their mixing process. This phenomenon was also mentioned by EP0531110A2,²² because THEIC has low melting point, the melted THEIC and PP are not compatible with each other. THEIC's melt can easily migrates to the surface of PP when they are processed together in the mixer. As a result, a liquid membrane is formed. The degree of mixing in the mixer depends on the friction between the melt and the metal surface, the formed liquid membrane reduces the friction to almost zero, resulting in the occurrence of screw slippage during mixing. Screw slippage merely happens when THEIC's loading exceeded a certain point. In our tests, screw slippage happens when APP/THEIC is lower than 1:1 (30 wt % IFR loading). When APP/THEIC was larger than 1 : 1, screw slippage does not happen, and melted THEIC can act



Figure 2. Effect of different ratio of APP/THEIC on flame retardant property. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

as external lubricant to prevent composites from roll sticking. So the mixing process has close relationship with THEIC's loading, which would further affect the flame retardant effect.

Table II shows the flame retardancy results of PP/IFR composite with different IFR loadings.

According to the LOI results, the most effective IFR formulation is selected, which contains 67 wt % APP and 33 wt % THEIC. As expected, the more amount IFR loading, the higher LOI value. When 30 wt % IFR is loaded, the composite's LOI value is 34.8. When 15 wt % IFR is loaded, the PP/IFR composite's LOI is only 24.9. The UL-94 vertical burning tests further demonstrate the effect of IFR loading on IFR's flame retardancy. When IFR's loading is higher than 25%, the PP/IFR composites obtain a V-0 rating. However, when the loading is lower than 15 wt %, no rating can be achieved. These results demonstrate THEIC is an effective charring agent and it has good synergistic effect with APP.

Water Resistant Tests of PP/APP/THEIC Blends

Water resistant tests were carried out to investigate IFR's flame durability and water resistant property. The PP/IFR composites with 30 wt % IFR loading were soaked in water at 70°C for certain time, the flame retardancy was checked by LOI and UL-94 tests, the results are listed in Table III.

Table II. Effect of IFR Addition on Flame Retardancy of PP-IFR System

	Componer	nts		
Samples	PP	IFR	LOI%	UL-4
PP11	70	30	34.8 ± 0.1	V-0
PP12	75	25	31.5 ± 0.1	V-0
PP13	80	20	28.0 ± 0.1	V-2
PP14	85	15	24.9 ± 0.1	N.R

IFR formulation: APP/THEIC = 2 : 1.



Table III	. Effect	of V	Nater	Soaking	Time	on	LOI	Value	of P	P/IFR
Composi	te									

Samples	Water treated time	LOI value	UL-94 V-rank
PP4	0 h	34.8	V-0
PP4	12 h	32.7	V-0
PP4	24 h	30.2	V-2
PP4	36 h	29.0	N.R
PP4	96 h	26.9	N.R

From Table III, it can be seen the PP/IFR composites' LOI decrease with the increase of water soaking time. After being soaked in water for 12 h, LOI value decreases to 32.7. It drops to 26.9 after 96 h, a decrease of 22.7% in comparison with that of samples before water soakage. The UL-94 tests show that the samples can achieve a V-0 rating when it has been soaked for 12 h, however, after 24 h, dripping is occurred, only V-2 rating can be obtained. When water soaking time is increased to more than 36 h, no V-rating rank can be obtained. The water resistant tests indicate IFR's poor water resistant property and bad flame retardant durability. To describe this water resistant behavior quantitatively, water solubility of APP and THEIC was tested. The results show that their water solubility is 0.34 g/100 g water and 54.35 g/100 g water, respectively, meaning THEIC is far more water soluble. It is assumed the IFR's poor water resistance is mainly caused by THEIC's high water solubility. From this point, it is necessary to decrease THEIC's water solubility to improve the IFR's flame retardant durability. From the chemical point of view, the technology of microcapsule or esterification with organic acid to enlarge THEIC's molecular weight and to decrease its polarity may take effect.

Cone Calorimeter Test. Cone calorimeter is a small-scale test, but it has good correlation with real fire disaster and is commonly used to predict the combustion behavior of materials in real fire. Some important parameters to evaluate the developing, spreading and intensity of fires can be obtained from cone calorimeter, including the heat release rate (HRR), especially the peak heat release rate (PHRR), average heat release rate (Av-HRR), time to peak heat release (TPHR) and the total heat release (THR).

The flame retardant effects of PP/IFR are evaluated by cone calorimeter. The curves of PHRR and THR for PP and PP/IFR composites are shown in Figures 3 and 4, respectively, the relative data are listed in Table IV.

It is found that pure PP burns very fast after ignition and the PHRR value is 1175.84 kW m⁻². However, when 30 wt % IFR with APP/THEIC = 2 : 1 is added, the PP/IFR composite's PHRR remarkably decrease. Its value drops to 251.92 kW m⁻², a decrease of 78.57% in comparison with that of pure PP. There are two peaks in its PHRR curves, it can be explained as follows¹⁸: first, the APP/THEIC degrades and intumescent shield forms. Second, this shield degrades when it faces massive heat and consequently the residual materials also degrade and form a new intumescent filed. The further degradation of the inner PP



Figure 3. HRR of PP and PP/APP/THEIC composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

is prevented due to the formation of the protective char, this char can effectively decreases the amount of heat and gas transmission from burning area to the inner matrix, thus, flame retardancy is achieved. The THR curves of PP0 and PP4 are shown in Figure 4, it can be seen that THR of non-flame retarded PP0 is 94.79 MJ m⁻². With addition of IFR, the THR of PP4 drops to 65.33 MJ m⁻². The above results show that there exists well synergistic effect between APP and THEIC.

Analysis of Char Morphology

The char layer of IFR was obtained by heating IFR in muffle furnace at 400°C for 30 min, its morphology was studied by SEM, the SEM images are shown in Figure 5.

In Figure 5(a), it is found that the char layer's surface has irregular cracks with many obvious bubbles like sheets inside its structure, which is resulted from the release of gaseous substance during combustion. These released gases may be the decomposed product of APP. Many studies^{7,8,10} confirm that non-flammable gases of NH₃ and H₂O are released in APP's thermal degradation process. Figure 5(b) is partial view of



Figure 4. THR of PP and PP/APP/THEIC composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

Table IV. Part Data Recorded in Cone Calorimeter Test

Samples	PHRR (kW m ⁻²)	Av-HRR (kW m ⁻²)	TPHR (s)	THR (MJ m ⁻²)
PP0	1175.84	199.54	109	94.79
PP4	251.92	113.17	156	65.33

Figure 5(a), it can be seen that the IFR's surface is fiber like and very compact. The char layer of PP/IFR composite was obtained after LOI test, its SEM images were taken as well. As shown in Figure 5(c,d), some holes and cracks exist in PP/IFR char layer, which means gaseous substance is also released, leading to a swollen process during combustion. It is also found the PP/IFR composite has a very compact char layer, which is very important to achieve well flame retardancy, because the char layer can effectively slow down the heat and mass transfer between the gas and condense phase.

Thermal Analysis

The thermal degradation curves of APP, THEIC, IFR, and IFR-calculated are shown in Figure 6.



Figure 6. TG curves of IFRa system. (a) THEIC; (b) APP-II; (c) IFR; (d) IFR-calculated. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As shown in curve-a in Figure 6, THEIC decomposes in one step, it initially starts at 275°C and completely ends at 290°C, with no char residue left. Curve-b shows the thermal



Figure 5. SEM images of IFR and PP/IFR composite. (a) SEM image of IFR's char layer (1000 x). (b) SEM image of IFR's char layer (\times 5000). (c) SEM image of PP/IFR's char layer(2000 x). (d) SEM image of PP/IFR's char layer(\times 5000).

degradation process of APP, which have been comprehensively studied by Camino.¹⁰ Below 200°C, Camino¹⁰ considers the main weight loss was attributed to the degradation of unstable structure contained in APP, such as the phosphates with low molecular weight or some adsorbed water. With temperature increasing, the crosslinkage occurred by releasing more amount of NH₃ and H₂O from APP, acidic polyphosphate was formed at this stage. After that, the crosslinked polyphosphate begin to decompose when the temperature was higher than 600°C.

The decomposition process of IFR is shown in curve-c in Figure 6. Three decomposed steps are found in IFR's whole thermal degradation process. The first stage occurs below 280°C and probably corresponds to crosslinking reactions between APP and THEIC by releasing of NH3 and H2O. The second stage occurs from 280 to 400°C and can be ascribed to the occurrence of ester reaction between acidic groups and OH groups in IFR system. The last stage is the decomposition of ester compound. Attention should be paid to the IFR's initial decomposition temperature, it can be seen the IFR is not thermal stable, its initial decomposition temperature is blow 100°C, which is lower than that of single APP or THEIC. Nearly 2 wt % weight loss can be observed at 150°C. However, Li²⁴ obtained an opposite conclusion compared with our results, he assumed APP/THEIC composite's initial thermal stability was enhanced in the presence of APP below 360°C. Very interestingly, Camino⁸ had studied the thermal degradation process of APP and PER, he found that the mixture of APP and PER decomposed at 125°C, which was lower than the initial decomposition temperature of single APP or PER, and he believed it was caused by synergistic effect between APP and PER. Similarly in APP/THEIC system, we consider the decrease of IFR's initial decomposition temperature is caused by the synergistic effect between APP and THEIC.

To fully investigate the synergistic effect, mass residue at different TG temperature and comparison with calculated residue are studied, as listed in Table V.

The TG curve of IFR-calculated is obtained from mathematical fitting of curve-a and curve-b according to mass ratio of APP/ THEIC in IFR system. It is found that the residue weight of IFR-calculated is 0.52 at 500°C, 0.35 at 600°C, 0.23 at 700°C compared with that of IFR, which is 0.51 at 500°C, 0.43 at 600°C, 0.40 at 700°C. When the temperature is higher than 500°C, IFR has a larger residue weight. These weight difference indicates a synergistic effect between APP and THEIC.

 Table V. Mass Residue at Different TG Temperature and in Comparison

 with Calculated Residue

Temperature	IFR ^a	IFR-calculated
200°C	0.96	0.99
300°C	0.87	0.64
400°C	0.62	0.56
500°C	0.51	0.52
600°C	0.43	0.35
700°C	0.40	0.23

^a IFR formulation: APP/THEIC = 2 : 1.



Figure 7. TGA curves of PP and PP/(IFR^b)^a composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The TG curves of PP and PP/IFR composites are shown in Figure 7.

It can be seen that PP/IFR composite has lower initial decomposed temperature than pure PP, PP/IFR composite has 2 wt % weight loss at 200°C, this may be attributed to the decomposition of the IFR. Song²⁵ found that incorporation of additives into the polymer resulted in the decrease of the composite's initial decomposed temperature (T_{onset}), the larger IFR loading in PP, the lower of the T_{onset} . It is also found PP/IFR composite has a larger residue weight when the temperature was higher than 360°C. This is caused by protecting effect of the forming char layer, which can effectively protect the composite from further thermal degradation by slowing down the heat and mass release both in gas and condense phase.



Figure 8. Digital photograph of the samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Swollen Process and Mechanism

Figure 8 shows the digital photograph of four samples, including IFR (8a), IFR after heat treatment (8b), the PP/IFR composite for LOI test (8c) and the composite after LOI test (8d).

It is found that IFR and PP/IFR composite expand when they are heated to a certain temperature, the char layers are formed in this stage. To well understand the swollen process, it is necessary to point out the chemical reaction between APP and THEIC in this stage. The possible reaction path is schemed in Figure 9.

Single molecular THEIC has three OH groups, it can be considered as an alcohol. In this sense, esterification between APP and THEIC is possible. The formation of ester can occur either through alcoholysis of APP (phosphorylation of PER) or through esterification of polyphosphoric acid by elimination of $\rm NH_3$ from APP.¹² Thus, it seems that alcohohysis is the first step which is occurred by heating APP-THEIC mixture, as shown in Figure 9(I). This reaction mechanism is in agreement with the reaction between mono-alcohols and polyphosphoric acid, as reported in literature.²⁶

For the APP's degradation process, NH_3 is constantly evolved when APP was continuously heated. Camino. G^8 once quantita-



Figure 9. Possible rection route between APP and THEIC.

tively measured the evolved NH3 from APP and APP-PER mixture, he pointed out the addition of PER affect the release rate of NH₃ from APP. The more PER was added, the more NH₃ was released. It means the existence of PER can accelerate APP's decomposition rate to form phosphate. Moreover, Camino⁸ noted evolution of NH₃ is accompanied with the formation of cyclic phosphate structures. Similarly, THEIC may play the same role as PER, when NH₃ and H₂O are released from APP-THEIC mixture, a ring closure esterification may happen, which is illustrated in Figure 9(II). According to literature,¹² the alcoholysis may happen between APP and THEIC by release of phosphate group, as shown in Figure 9(III). The formed ring closure ester with -PONH₄ groups can further esterify with OH groups along the chain by releasing of NH₃ and H₂O, as shown in Figure 9(IV). Finally a crosslinking structure is formed.

CONCLUSION

The IFR system containing APP and THEIC can improve the flame retardancy property of PP/IFR composite. The flame retarded composite has the highest LOI value of 34.8 and reach UL-94 V-0 rating. However, its disadvantages of low melting point, thermal instability and easy migration, would affect the mixing process, flame retardant durability and flame retardant effect, thus limiting its usage in flame retardant filed. To further employ THEIC's application in IFR system, chemical modification is needed. Finally, the possible reaction path between APP and THEIC is proposed.

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