

# Effects of Intumescent Flame Retardant Based on THEIC-based Oligomeric Ester as Char Forming Agent on Thermal, Mechanical and Flame Retardant Properties of HDPE Composites

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## Abstract

In this study, a new phosphor-ester (TPE) was prepared by one-spot polycondensation of tris (2-hydroxyethyl) isocyanurate (THEIC) and phenyl phosphonic dichloride (PPDC) and used as charring agent in combination with ammonium polyphosphate (APP) to develop new intumescent flame retardant (IFR) for high density polyethylene (HDPE). The thermal and flame retardant properties of composites were investigated by thermogravimetric analysis (TGA), limiting oxygen index measurement (LOI) and cone calorimetry (CCT), while the morphology and chemical structure of the char residue were analyzed by scanning electron microscopy, Fourier transfer infrared spectroscopy, and laser Raman spectroscopy. The results showed that the LOI value of the composite HD/APP/TPE containing 25 wt. % of APP/THE reaches 28.2 %. The CCT test suggested that peak heat released rate (PHRR) of the flame retardant composite is decreased by 37 % compared to that of pure HDPE. The use of IFR based on APP and TPE produces a compact char residue that acts as barrier for heat, oxygen and other combustibles volatile and protects the underlying polymer. Besides TPE can produce the PO type radicals that show some gas phase flame retardant action. However, the tensile strength of the composites are still lower than that of pure polymer.

**Keywords:** Intumescent flame retardants, charring agent, flame retardancy, HDPE composites

## 1. Introduction

In recent years, the use of polymer/plastic-based materials is increasing enormously such that it is hard to find the areas of daily life where polymeric materials do not find their applications. The outstanding properties such as low weight-to-strength ratio, good mechanical behavior, chemical and corrosion resistance, etc. make polymeric materials promising alternatives to metal-based materials. However, their highly flammable nature brings a threat of fire hazards and limits their use in areas where fire safety is a prime concern. In this context, the design of polymeric materials with necessary fire safety

standards is extremely important and researchers are focusing on the development of flame retardant polymeric materials. Among the various polymer, polyethylene (PE) is an important commodity plastic having a wide range of applications such as packaging, cable and wires, household items, pipes and fittings and nonstructural exterior uses like lawn furniture, etc. PE is a flammable polymer and is susceptible to potential fire hazards, therefore, it is necessary to improve the flame retardant properties of PE-based materials for human safety. [1-4].

The flame retardant properties of PE can be improved by incorporating different flame retardant additives during processing. Traditionally, halogenated flame retardants with antimony oxide were regarded as a promising economical route for improving the flame retardant properties of PE due to their low cost and high efficiency. However, these additives produce toxic and corrosive gaseous substances during combustion that have a great impact on human health and the environment, and thus non-halogenated flame retardants are the area of current research focus [5, 6]. Intumescent flame retardants (IFRs) are promising non-halogenated flame retardants due to their low smoke, low toxicity, anti-dripping, and environmentally friendly characteristics. IFRs mainly act by condensed phase mechanism by promoting the formation of expanded carbonized char layer on the surface of polymer that acts as an insulating barrier for heat, oxygen, and other combustible volatiles, thus improving the flame retardant properties. IFR systems require three different agents namely, an acid source, a charring agent and a blowing agent, and their efficiency depends upon the quality of intumescent char [7-12]. Ammonium polyphosphate (APP), a promising phosphorous-based flame retardant, shows a dual role as the blowing agent and acid source in IFR systems.

IFRs are successfully applied to improve the flame retardant properties of non-polar polymers like PE and PP [13-16]. However, the majority of research focus on flame retardant PP composites, and comparatively fewer reports are available for PE. Different types of the IFR formulations are reported for PE, and different synergistic agents like montmorillonite (MMT) [17, 18], metal chelates [2, 19], zeolites [20, 21], layered double hydroxide [22], etc. are also combined with them for further improvement of flame retardant properties. APP alone or in combination with melamine phosphate (MP) is used as an acid source in the IFR systems, and microencapsulated APP is used to improve water resistance in some cases [21, 23]. Different charring agents are combined with APP to make IFRs for PE. Some examples of charring agent used

in PE are pentaerythritol (PER), polyamide (PA) and polyamide/MMT nanocomposite (nPA), char forming agent (SPEPO) prepared from PER [24], phosphorus containing carbonizing agent (CA) from PER [2] and triazine ring based charring agents [1, 21, 25, 26]. An integrated IFR such as melamine salt of pentaerythritol phosphate for HDPE [27], and reactive extrusion of PER/MP for LDPE [19] are also reported. This suggested that the majority of research focuses on the development of new charring agents and/or the use of synergistic agents to improve the efficiency of existing IFR systems, and the triazine derivatives are gaining more popularity due to their excellent flame retardant properties and water resistance. 1, 3, 5-tris (2-hydroxyethyl) isocyanurate (THEIC), a derivative of triazine compound, can act as a charring agent in polyolefin homopolymer and copolymer [28]. THEIC and its chemical modification are used to improve the flame retardant properties of PP and polylactic acid [29-34]. In our previous study, it is found that use of APP/THEIC in 3:1 ratio improves the flame retardant properties of the HDPE, and the LOI value of the composite reached 31.5 % at 30 wt.% of IFR [3]. THEIC is a water soluble small molecule and has higher migration instability that motivates the chemical modification of THEIC into water insoluble macromolecular charring agents.

In this study, a new phospho-ester (TPE) was prepared by one-spot polycondensation of THEIC and phenyl phosphonic dichloride (PPDC) and was characterized by Fourier transform infrared spectroscopy (FTIR), and gel permeation chromatography (GPC). TPE was combined with APP to make flame retardant HDPE composites, and their thermal, mechanical and flame retardant properties were studied by thermogravimetric analysis (TGA), tensile property, limiting oxygen index (LOI) measurement and cone calorimeter test (CCT). The morphology and chemical structure of char residue were studied using scanning electron microscopy (SEM), Fourier transfer infrared spectroscopy (FTIR) and laser Raman spectroscopy (LRS) to elucidate the flame retardant mechanism

## 2. Experimental

### 2.1 Materials

Ammonium polyphosphate (APP, phase II, DP > 1000) was supplied by Jinan Taixing Fine Chemical Co., Ltd. (China). Tris (2-hydroxyethyl) isocyanurate (THEIC), phenyl phosphonic dichloride (PPDC) and triethylamine were obtained from Shanghai Macklin Biochemical Co. Ltd., (Shanghai, China). High density polyethylene (HDPE, density: 0.93 g/cm<sup>3</sup>; melt index: 20 g/10min @ 190 °C/2.16 kg) was obtained from Fushun Petrochemical Co., Ltd., (China).

### 2.2 Preparation of the oligomeric char forming agent

The char forming agent was prepared by polycondensation of PPDC and THEIC in 1:1 mole ratio. In a typical procedure, 26.12 g (0.1 mol.) of THEIC and 19.48 g (0.1 mol.) of PPDC were taken and 200 mL of dichloromethane was added. 20.24 g (0.2 mol.) of triethylamine was added drop-wise to the solution at reaction temperature of 0-5 °C, left stirred for 5 hr., and then the temperature was elevated to 25 °C and kept overnight. The reaction mixture was washed with water three times, collected organic layer using separating funnel and subjected to rotatory evaporation at 40 °C. White solid product collected was crushed into powder. The char forming agent is named as THEIC-phosphoester (TPE) in subsequent text. The yield of TPE was 82 %.

### 2.3 Preparation of composites

HDPE composites were prepared using internal mixer (HL-200) at 170 °C at 60 rpm. The HDPE was processed for 2 min and the flame retardants (APP and TPE in 3:1 weight ratio) were added and processed for another 6 min. The composites were pressed into a sheet using a hot press (BL-6170-A-25J, Baolun Precision Testing Instruments Ltd., Shanghai, China) at 170 °C at a pressure of 10 MPa for 5 min. The composite is denoted as HD/APP/TPE

### 2.4 Measurement and Characterizations

The FTIR spectra were recorded on Nicolet 6700 spectrometer (USA) in an optical range of 400 to 4000 cm<sup>-1</sup> at a scannumber of 32 and a resolution of 4 cm<sup>-1</sup> using KBr method.

Flame retardant properties were evaluated using LOI measurement and CCT test. LOI measurement was performed using an oxygen index instrument (JF-3, Jiangning Analysis Instrument Factory, China) according to ASTM D-2863. CCT was performed using FTT2000 cone calorimeter according to ISO 5660-1. A sample of (100 × 100 × 4) cm<sup>3</sup> was placed in a horizontal position and a heat flux of 35 kW m<sup>-2</sup> was applied during test.

The SEM images of char residue after the CCT test was taken on a field emission scanning electron microscope (S-4800, Hitachi Japan). Samples were sputtered with a thin layer of gold before observations.

Thermogravimetric analysis (TGA) was performed using a thermogravimetric analyzer (Netzsch STA 409 PC, Germany) from room temperature to 700 °C at a heating rate of 10 °C/min in both air and nitrogen atmosphere of 30 mL/min.

The tensile properties were determined according to Chinese standard GB-T 1040.3 2006 on a universal testing machine (MTS E 44) at a crosshead speed of 10 mm/min. Five samples were examined, and the average values were reported

## 3. Results and Discussion

### 3.1 Characterization of the TPE

The polycondensation of the THEIC and PPDC was carried out taking the monomer in a mole ratio of 1:1. Based on the mole ratio it is expected that the terminal group will be hydroxyl group of THEIC. The reaction scheme and the FTIR spectra of TPE are shown in Fig. 1.

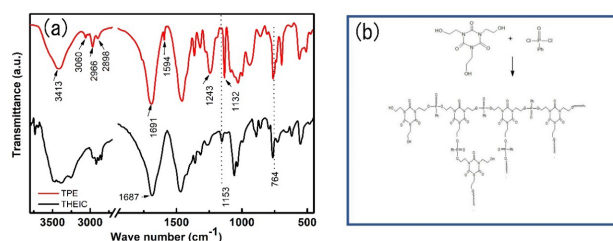


Fig. 1 a) FTIR spectra of THEIC and TPE b) reaction scheme of polycondensation of THEIC and PPDC

In the FTIR spectra of THEIC (Fig. 1 a), the wide and broad peak at 3390 cm<sup>-1</sup> is attributed to O-H stretching vibration, peaks at 2918 and 2851 cm<sup>-1</sup> correspond to

C–H stretching vibration of the saturated hydrocarbon chain, band at  $764\text{ cm}^{-1}$  corresponds to triazine ring skeletons, band at  $1153\text{ cm}^{-1}$  correspond to C–O absorption, and band at  $1687\text{ cm}^{-1}$  corresponds to C=O absorption of THEIC [4, 29, 32]. In the spectra of TPE, the peak at  $3413\text{ cm}^{-1}$  is assigned to stretching vibration of O–H, peaks at  $3060\text{ cm}^{-1}$ ,  $2966\text{ cm}^{-1}$  and  $2898\text{ cm}^{-1}$  are assigned to C–H stretching vibration of the Ph–H and  $-\text{CH}_2-$  respectively. The intensity of the O–H stretching of TPE is relatively small as compared to that of THEIC. The peak at  $1594\text{ cm}^{-1}$  corresponds to the benzene skeleton. The decrease of C–O absorption band intensity and the appearance of new peaks at  $1243$ ,  $1086$ ,  $1132\text{ cm}^{-1}$  corresponding to P=O, P–O–C and P–Ar, respectively in TPE indicate the formation of phospho-ester linkage. The molecular weight of the oligomer was acquired from GPC analysis. The number average and weight average molecular weight of the TPE are found to be  $802\text{ Da}$  and  $1153\text{ Da}$ , respectively with a poly dispersive index of 1.4.

### 3.2 Flame retardants properties

The flame retardant properties of the composites were evaluated by LOI and CCT. The LOI value of HD/APP/TPE composite containing IFR consists of APP and TPE reaches  $28.2\%$ , while that of pure HD is only  $18.2\%$ . The weight ratio of APP/TPE was chosen as 3:1 based on a preliminary experiment of heating a different weight ratio of APP/TPE in a muffle furnace and the composition that produces more char was selected. LOI value of the composite HD/APP/TPE is higher than that of composite containing APP/THEIC in our previous study, suggesting that the TPE shows good flame retardant behavior than THEIC when combined with APP [3].

CCT is a successful test to evaluate the flammability of the materials and often simulates the full-scale fire behaviors. It can provide various parameters such as heat release rate (HRR), total heat release (THR), peak heat release rate (PHRR), time to peak heat release (t-PHRR) as given in Table 1. The representative HRR and THR curves are given in Fig. 2.

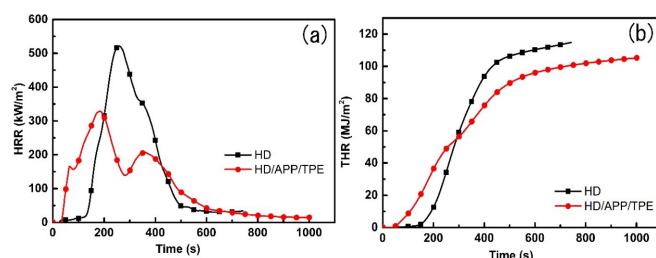


Fig. 2 a) HRR and b) THR curves of HD and HD/APP/TPE composite

The HRR curve (Fig. 2 a) of the pure HD is sharp and PHRR value is  $538\text{ kW/m}^2$ . HDPE is highly flammable and burns rapidly without leaving any char residue. The PHRR and av-HRR of HD/APP/TPE composite are  $339\text{ kW/m}^2$  and  $116\text{ kW/m}^2$ , which are  $37\%$  and  $41\%$  lower than that of pure HD. HRR curve of HD/APP/TPE composite shows two peaks. Initially the APP/TPE degrades and an intumescent shield is formed that protects the underlying polymer, and HRR begins to decrease after reaching first peak. This shield degrades during intense heat and the HRR increases again. Finally, a new intumescent shield is formed corresponds to second peak in HRR curve. The THR curve (Fig. 2 b) of HD/IFR/TPE composite is higher at the beginning due to the early decomposition of flame retardants, after that the THR curve is always lower than that of HD. The total heat evolved at the end of test (THE) for the HD/IFR/TPE composite is slightly lower than that of pure HD. Specific extinction area (SEA) is an important parameter related to smoke production and the use of the flame retardant APP/TPE leads to an increase in SEA value. The IFR produces the intumescent char residue and prevents the supply of oxygen. Due to this, incomplete combustion takes place producing more smoke. Effective heat of combustion (av-EHC) of HD/APP/TPE composite is lower than that of pure HD, suggesting some gas phase mechanism of flame retardancy. The average CO and  $\text{CO}_2$  production and ratio of CO/ $\text{CO}_2$  of the flame retardant composite is higher than that of pure HD. The increased ratio of CO/ $\text{CO}_2$  means more incomplete combustion products (CO) and less complete combustion products ( $\text{CO}_2$ ) which in turns suggests the inhibition of combustion of volatiles [35].



Table 1 Combustion performance obtained from CCT at a heat flux 35 of kw/m<sup>2</sup>

	HD	HD/APP/ TPE
PHRR (kW/m <sup>2</sup> )	538	339
Av-HRR (kW/m <sup>2</sup> )	199	116
t-PHRR (s)	250	163
THE (MJ/m <sup>2</sup> )	109	104
MARHE (kW/m <sup>2</sup> )	242	206
Av-Sp-MLR(g/s.M <sup>2</sup> )	8.8	6.3
Av-EHC (MJ/kg)	38	34
SEA (m <sup>2</sup> /Kg)	276	484
CO (kg/Kg)	0.031	0.12
CO <sub>2</sub> (kg/kg)	3.77	3.96
CO/CO <sub>2</sub> weight ratio	0.008	0.030

### 3.3 Thermal and mechanical properties of the composite

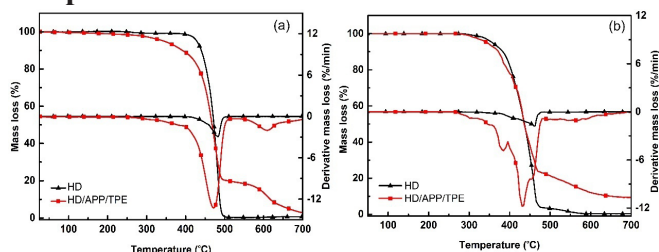


Fig. 3 TGA/DTG curves for HD and composite HD/APP/TPE a) in nitrogen b) in air

The thermal degradation behaviors of HD and HD/APP/TPE composite were studied in the nitrogen atmosphere and the results are shown in Fig. 3 a. Initial decomposition temperature (taken as  $T_{5\%}$  and  $T_{10\%}$ , temperature of 5 and 10 % weight loss), temperature of 50 % weight loss and char residue at 600 °C for HD/APP/TPE composite and pure HD are collected in Table 2.

Table 2 Thermal properties of composites in nitrogen and air atmosphere

In nitrogen atmosphere				
Samples	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	Char at 600 °C
HD	428	440	473	0.3
HD/APP/TPE	365	410	470	9.1
In air atmosphere				
Samples	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	Char at 600 °C
HD	356	383	436	0.8
HD/APP/TPE	344	372	436	12.1

The main degradation mechanisms of HDPE involve chain scission and chain branching, which occurs simultaneously resulting in a single mass loss step in non-oxidative environment. HD/APP/TPE shows a major weight loss step with maximum decomposition at 471 °C. The initial decomposition temperature ( $T_{5\%}$ ) of the composite is lower than that of pure HD due to earlier decomposition of the APP and TPE. After the major decomposition step, the char residue is stable for a while and decomposes at a higher temperature showing a small second stage weight loss in DTG. The use of APP and TPE promotes the char formation and protects the underlying polymer. The thermal degradation behaviors of HD and HD/APP/TPE composite were also studied in an air atmosphere. TGA and DTG curves are shown in Fig. 3 b and the thermal degradation parameters are shown in Table 2. The degradation process of HDPE primarily involves the radical chain reaction in an oxidative environment and PE begins to degrade earlier in the oxidative environment. The initial decomposition temperature ( $T_{5\%}$ ) of the flame retardant composite is lower than that of pure HD due to early decomposition of the APP and TPE. It is found that APP/TPE promotes the formation of char residue at higher temperature.

The mechanical property of composite was monitored by measuring the tensile strength. The tensile strength of pure HDPE is  $22 \pm 2.9$  MPa, whereas that of HD/APP/TPE is  $17.7 \pm 0.7$ , which is 19.5 % lower than that of pure HDPE. In our previous study, the flame retardant composite containing 25 wt. % of APP and THEIC showed a decrease of tensile strength by 23.6 % [4]. It suggests that modification of THEIC into TPE slightly improves the tensile strength. However, the tensile strength is still lower than pure HD.

### 3.4 Morphology and chemical structure of char

The flame retardant action of the IFR system is based on the formation of intumescent char on the surface of polymer, which acts as a barrier for heat, oxygen and other combustible volatiles and inhibits the spread of flame. Due to this, microstructure of the char plays an important role in the flame retardant properties of composites. The digital photo and SEM image of the char residue of HD/APP/TPE composite after the CCT test are shown in Fig. 4 (a, b). The SEM image

shows the formation of compact, smooth char with a small bubble like structure. The gases produced from decomposition of IFR components make expansion or blowing of char layer which eventually produces bubble like structure in surface of char.

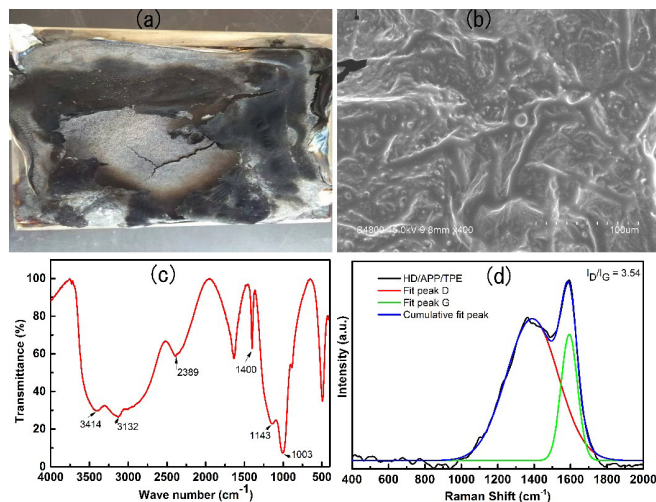


Fig.4 a) Digital photo, b) SEM image, c) FTIR, and d) Raman spectra of the char residue of HD/APP/TPE composite after CCT test

The chemical structure of the char residue was studied using FTIR as shown in Fig 4 (c). In the FTIR spectra, the peaks in the region 3100-3300  $\text{cm}^{-1}$  correspond to the stretching vibration of N-H and that at 3414  $\text{cm}^{-1}$  corresponds to stretching vibration of O-H structure. The absorption band at 2389  $\text{cm}^{-1}$  is assigned to OH-bond in O=P-OH structure. The absorption bands in the region of 1150-1300  $\text{cm}^{-1}$  are due to P-O-C bond of phospho-carbonaceous structure. The bands at 1143 and 1003  $\text{cm}^{-1}$  are assigned to symmetric stretching of P-O-C bond and symmetric vibration of  $\text{PO}_2$  and  $\text{PO}_3$  structure. The absorption band at 1634  $\text{cm}^{-1}$  is assigned to stretching vibration of C=C in cyclic structure suggesting poly-aromatic structure and the absorption band at 1400  $\text{cm}^{-1}$  is due to C-N structure. The main characteristic peak of C=O stretching vibration at 1687  $\text{cm}^{-1}$  and skeleton vibration of nitrogenous heterocyclic at 764  $\text{cm}^{-1}$  of THEIC moiety in TPE disappear in char residue indicating the decomposition of the triazine ring [3, 36]. It is anticipated that char residue consists of the polyaromatic structure linked with phospho-carbonaceous structure *via* P-O-C bond. The nitrogen atoms probably occurred in five or six membered ring of aromatic structure and/or in phosphoric acid salts.

The absorption band for P-Ar structure at 1132  $\text{cm}^{-1}$  is disappeared in char residue. TPE decomposes into PO type radicals and aromatic volatiles before involved in formation of char residue. Raman spectroscopy is usually used to characterize the graphitic structure of the char residue. The Raman spectra of the char residue are shown in Fig. 4 (d). The spectra show two characteristic bands, D band at 1390  $\text{cm}^{-1}$  corresponds to defect or disorder in graphitic layer, and G band at 1593  $\text{cm}^{-1}$  corresponds to the  $E_{2g}$  mode of the vibration of hexagonal graphite. The presence of the two bands suggest the formation of graphitic char with ratio of the integrated intensities of D to G band ( $R=I_D/I_G$ ) of 3.54.

From the chemical analysis of char, it is anticipated that intumescent char has poly-aromatic structure linked with phospho-carbonaceous structure *via* phospho-ester linkage (P-O-C). TPE decomposes into THEIC moiety, PO type radicals, and benzene during combustion. The THEIC moiety undergoes decomposition and carbonization by polyphosphoric acid produced by the decomposition of APP to give the intumescent char. The  $\text{NH}_3$  and  $\text{N}_2$  gas act as a blowing agent for expansion of the char. Thus formed intumescent char acts as physical barrier for heat, oxygen and other combustible volatiles between fire and underlying polymer, and hence improves the flame retardant properties. Besides, the PO type radicals produced by the decomposition of TPE quench the highly reactive H and OH radicals in the gas phase, and thus enhance the flame retardant properties. In conclusion, the combination of gas phase and condensed phase flame retardant mechanism is proposed.

#### 4. Conclusions

In this study, TPE was prepared by one-spot polycondensation of THEIC and PPDC, and was characterized by FTIR and GPC. TPE was combined with APP to make flame retardant HDPE composites, and their thermal, mechanical and flame retardant properties were studied. The LOI value of the HD/APP/TPE composite containing 25 wt. % of APP/TPE reaches 28.2 %. The CCT test suggests that PHRR and av-HRR of the composite are decreased

by 37 % and 41 %, respectively as compared to pure HD. The use of TPE and APP leads to formation of a compact char that acts as barrier for heat, oxygen and other combustibles volatiles to the underlying polymer, and hence improves the flame retardant properties. Besides, there is the formation of PO type radicals that shows some gas phase flame retardant action. This simple method of modification of THEIC into oligomeric char former will help to remove the shortcoming of THEIC produced by high solubility in

water. Further research are still needed to compare the durability of the IFR based on charring agent THEIC and its chemical modified products.

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