Effect of metal chelates on the ignition and early flaming behaviour of intumescent fire-retarded polyethylene systems

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Abstract

Polyethylene (PE) was treated with various formulations containing an intumescent fire retardant, which consists of melamine phosphate (MP), pentaerythritol (PER) and ammonium polyphosphate (APP), and one or none of following metal-chelates: CuSAO, CoSAO and NiSAO. The behaviour of this intumescent system can be enhanced significantly by the addition of small amounts (0.2 %) of metal chelate (CuSAO, CoSAO and NiSAO). The thermal stabilization, burning behaviour and char formation of the fire retardant PE system have been investigated by TGA, LOI, UL-94 test, SEM and cone

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calorimetry. All formulations studied provide good fire retardant behaviour, with LOI≥27.4 and UL-94

V-0 rating. TGA results present more complicated thermal decomposition behaviour after the addition of

small amounts (0.2 %) of metal chelate when compared to that of PE-IFR. Cone calorimetry of

PE-IFR-metal chelate (PE-IFR-CuSAO, PE-IFR-CoSAO and PE-IFR-NiSAO) shows a very significant

decrease in HRR, PHRR, ML, THR and a very significant improvement of TTI compared to samples

without metal chelate. Furthermore, SEM and photographs of the char layer show that the char layer from

PE-IFR-metal chelate has a compact and tough char structure compared to the open porous char layer

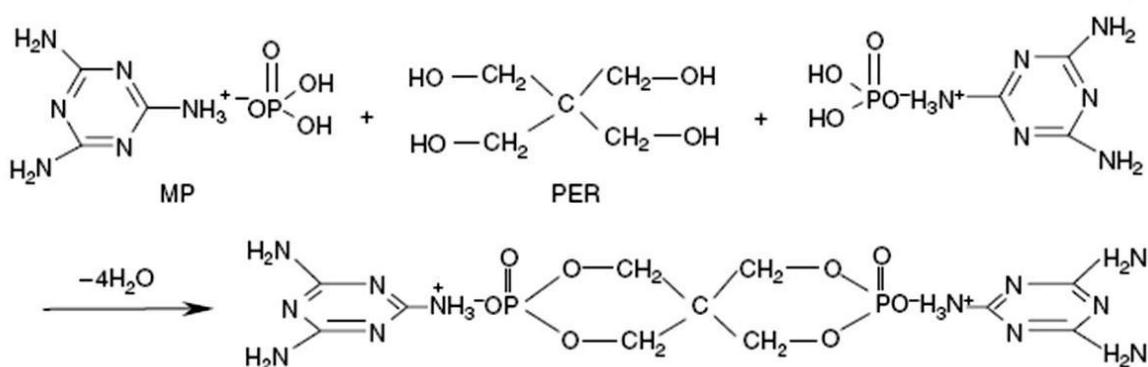produced by sample without metal chelate.

1. Introduction

It is well known that polyethylene (PE) has been widely used in many fields because of its excellent performance, such as low density, low toxicity, excellent electric insulation, mechanical durability, good chemical resistance, ease of processing and moulding, low cost, and so on. Unfortunately, PE burns easily and has poor drip performance. So, there is still a need to improve both fire retardancy and the poor drip performance of PE.

Usually, the common fire retardants for PE can be classified into two kinds: halogen based flame retardants which act in the gas phase; and char forming and intumescent fire retardants (IFR) which incorporate phosphorus or nitrogen in their structures or formulations. However, because of environmental pressure, most halogen based flame retardants are now considered unacceptable. Compared with halogen based flame retardants, intumescent fire retardant (IFR) additives are more promising as an effective and "green" fire retardant for PE based on their excellent intumescent carbonization. Many studies focused on intumescent fire retardant (IFR) have been widely investigated in the fire retardation of polyolefin [1–4]. Generally, they act by a condensed phase mechanism when heating or burning [5–10]. On heating, intumescents form a foamed cellular charred layer on the polymer surface, which acts as a physical barrier and protects the underlying materials from the action of heat and flame. Usually, such formulations contain three ingredients: an acid source, a blowing agent and a carbonization agent. However, the conventional IFR additives also have disadvantages [11–13], such as the higher loading needed in order to obtain the required fire retardant level. Thus, further improvements in the fire retardant efficiency of IFRs are needed.

On the other hand, it is worth noting that some metal chelates can affect the initial stage of polymer degradation [14–16]. In our earlier work, some research on fire retarded PE containing metal chelates has

been carried out [17, 18], meanwhile, reactive extrusion technology was adopted to synthesize a fire retardant (ER), based on the esterification of melamine phosphate (MP) and pentaerythritol (PER) at a particular temperature (shown in Scheme 1). It has been found that ER combined with APP and a small quantity of copper (II)-chelate at pre-selected levels can be an effective IFR for PE yielding good fire retardancy and good anti-dripping behaviour.

In this paper, different metal chelates (Copper (II), Cobalt (II) and Nickel (II)) complexes with salicylaldoxime (SAO) have been investigated. The fire retardant being used in this paper is ER combined with APP. The effect of metal chelates on the thermal stabilization, char formation and burning behaviours of intumescent fire retardant PE has been studied by LOI, UL-94 test, TGA, SEM and cone calorimeter.

Scheme 1. Reaction of melamine phosphate with pentaerythritol.

2. Experimental

2.1. Materials

Melamine phosphate (MP), pentaerythritol (PER), sodium hydroxide, methanol and ethanol were provided by Changzheng Chemical Reagent Corp. (Chengdu, China). Salicylaldoxime (SAO), $Cu(CH_3COO)_2 \cdot H_2O$, $Co(CH_3COO)_2 \cdot 4H_2O$, $Ni(CH_3COO)_2 \cdot 4H_2O$ were supplied by Shanghai First
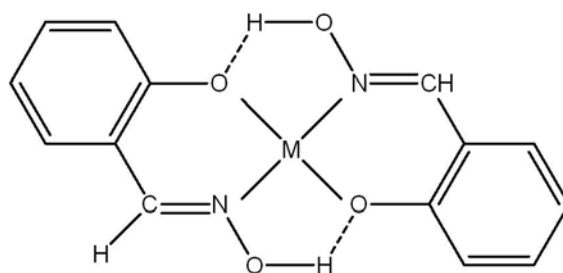
Reagent Plant (Shanghai, China). Ammonium polyphosphate (APP) was provided by Changfeng Chemical Corp. (Shifang, China). Reactive extrusion fire retardant (ER) has been prepared in our lab using MP and PER [18]. Commercial low-density polyethylene (LDPE), 112 A, was supplied by Lanzhou Petroleum Chemical Company (Lanzhou, China).

2.2. Preparation of samples

2.2.1. Metal-chelates [19] (CuSAO, CoSAO and NiSAO)

M $(CH_3COO)_2 \cdot nH_2O$ $(Cu(CH_3COO)_2 \cdot H_2O, Co(CH_3COO)_2 \cdot 4H_2O, Ni(CH_3COO)_2 \cdot 4H_2O)$ (0.01 mol) was thoroughly milled with 0.02mol SAO at room temperature for 0.5 h, this gave rise to a smell of acetic acid. Then the solid phase reaction was kept 30 ^{o}C for 16 h, and the product, MSAO (M= Cu, Co, Ni) was dried in vacuum (80 ^{o}C).

The FTIR spectrum (KBr, pellet) of the metal chelate: 3418-3472 cm^{-1} (-OH), 1520-1580 cm^{-1} (C=C, phenyl), 430-470 cm^{-1} (M-O), 1660-1680 cm^{-1} (C=N) was determined to confirm the structure of the respective chelate. The structure of the chelates is shown in scheme 2. Analysis of the C, H, N, O content of metal chelate was carried out on CARLO ERBA1106 elemental analyser. The detailed results were shown as following. CuSAO：C%=49.84 (calculated 50.07), H%=3.34 (calculated 3.58), N%=8.40 (calculated 8.35), O%=19.12 (calculated 19.08); CoSAO：C%=50.72 (calculated 50.83), H%=3.45 (calculated 3.63), N%=8.52 (calculated 8.46), O%=19.40 (calculated 19.34); NiSAO：C%=50.71 (calculated 50.80), H%=3.46 (calculated 3.63), N%=8.51 (calculated 8.47), O%=19.42 (calculated 19.35). This shows good agreement with the proposed formula.

Scheme 2. The structure of MSAO (M = Cu, Co, Ni).

2.2.2. Fire retardant PE samples

The total content of IFR (W_{APP}: W_{ER}=2:1) in premixed PE was kept at 29.8 wt%. The IFR-PE was prepared by using a counter-rotation twin-screw extruder under the following standard condition: average residence time: 25 s; rotation of screw: 80 rpm; mixing temperature: 150°C. The extrudate was cut into pellets and then extruded again.

All the metal chelates (CuSAO, CoSAO and NiSAO) were introduced into the IFR-PE at a concentration of 0.2 wt%. One sample of 29.8 wt% IFR-PE had 0.2 wt% of IFR added as a control sample. All the samples were prepared by mixing all the constituents on a two-roll mill at a roller temperature of 150–160 ^{o}C. After mixing, the samples were hot-pressed under 10 MPa for 5 min at 120 ^{o}C into a sheet of suitable thickness and size as required for the corresponding test standard.

2.3. Characterization

2.3.1. LOI test

The LOI values were measured on a JF-3 oxygen index meter (Jiangning, China) using sheet dimensions of 130×6.5×3 mm^3 according to ASTM D2863-97.

2.3.2. UL-94 test

Vertical burning tests were conducted on a vertical burning test instrument (CZF-2-type) (Jiangning, China) using sheet dimensions of $130\times13\times3$ mm^3 according to ASTM D3801.

2.3.3. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed on a DuPont 1090B thermogravimetric analyzer at a heating rate of 10 ^{o}C/min. 7 mg of samples were examined under flowing air (80ml/min) over a temperature range from room temperature to 600 ^{o}C. Each determination was carried out in duplicate.

2.3.4. Scanning electron microscopy (SEM)

A HITACHI MODEL: S-450 scanning electronic microscopy (SEM) was used to investigate the outer surface of residues of PE-IFR and PE-IFR-CuSAO. The residue samples for SEM were obtained after two samples were burnt directly in air. The micrographs of the residual char samples were recorded after surface treatment using a sputtered deposition of gold.

2.3.5. Cone calorimeter

The cone calorimeter tests were carried out following the procedures indicated in the ISO 5660 standard with a FTT cone calorimeter. Square specimens ($100\times100\times6$ mm) were irradiated at a heat flux of 25 kW/m^2.

3. Results and discussion

3.1. LOI and UL-94 test

As is well known, LOI measurement and UL-94 test are widely used to evaluate the fire retardant properties of materials. In this paper, all the samples have been tested using LOI and UL-94 measurement according to ASTM D2863-97 and ASTM D380, respectively. The LOI values, UL-94 rating and dripping behaviour of all the specimens is shown in table 1.

Composition of Fire-Retardant PE				LOI values	UL-94 Rating	Drip
PE(wt%)	IFR(wt%)	Metal chelate	Conc (wt %)	%		
100	0	--	--	18	No Rating	Heavily
70	30	--	--	27	V-0	No
70	29.8	CuSAO	0.2	29	V-0	No
70	29.8	CoSAO	0.2	28	V-0	No
70	29.8	NiSAO	0.2	28	V-0	No

Table 1 Effect of the composition of IFR–metal chelate on fire retardancy of PE with 30 wt% total loading level of additives.

From table 1, it can be observed that the LOI values of PE increased from 18 to 27 when 30 wt% IFR is added to PE, simultaneously, the UL-94 reached V-0 rating showing both reduced flame spread and no dripping during burning. More interestingly, it was observed that the LOI values increased modestly from 27 to 29, 28 and 28 respectively with the addition to the fire retardant PE of only 0.2 wt% metal chelate (CuSAO, CoSAO and NiSAO), while maintaining 30 wt% loading of fire retardant.

3.2. Thermogravimetric analysis (TGA)

In order to understand the effects of metal chelate (CuSAO, CoSAO and NiSAO) for intumescent fire retardant PE, we compared the thermal degradation behaviour and the mass of residue obtained for the various samples. TGA testing of PE, PE-IFR, PE-IFR-CuSAO, PE-IFR-CoSAO and PE-IFR-NiSAO was carried out in air at a heating rate 10 ^{o}C /min. TG and DTG curves are presented in figure 1 and figure 2, respectively, and some detailed data shown in table 2.
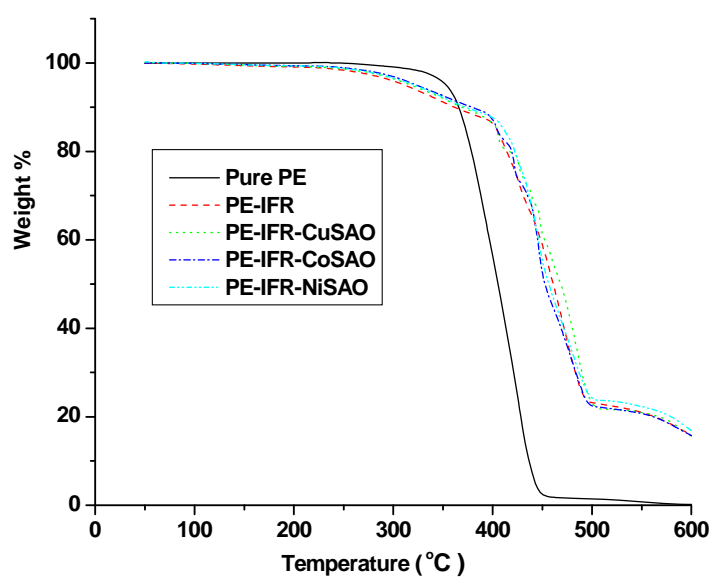

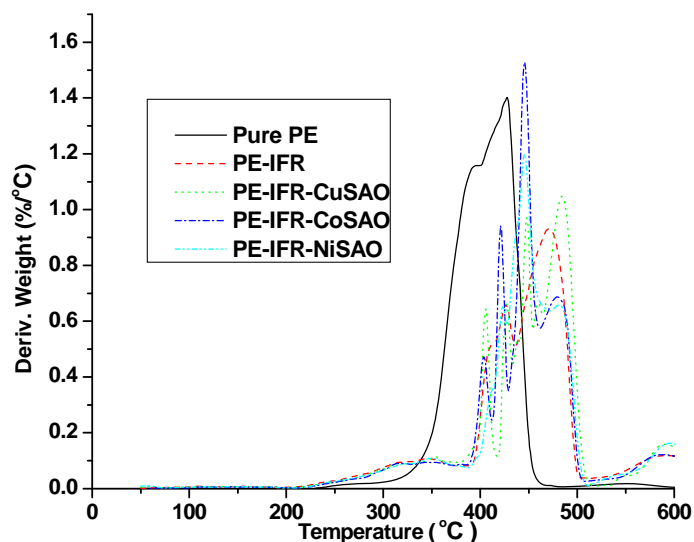Fig. 1. TG curves of PE, PE-IFR, and PE-IFR–metal chelate systems in air.

Fig. 2. DTG curves of PE, PE-IFR, and PE-IFR–metal chelate systems in air.

It is as expected that PE-IFR and PE-IFR-Metal chelates (CuSAO, CoSAO and NiSAO) increase the residue yield significantly by comparison with pure PE. However, it is more interesting to look at the difference in the thermal degradation behaviour of intumescent fire retardant PE based upon the addition of only 0.2 wt % metal chelates. It can be observed from table 2 that T_{onset} of PE-IFR-metal chelate (CuSAO, CoSAO and NiSAO) are modestly enhanced compared with that of PE-IFR, while comparison of T_{max} and $T_{50\%}$ shows no clear pattern. Even so, it is worth noticing that the T_{max} and $T_{50\%}$ of all samples are between 400 and 500 ^{o}C. Meanwhile from figure 2, it can be observed that DTG curves of fire retardants containing metal chelates are significantly more complex than that without metal chelate over the temperature range. For PE-IFR, DTG curve shows only two peaks between 400-500 ^{o}C, while over the same temperature range, the number of peaks in DTG curves is four, four and three for PE-IFR-CuSAO, PE-IFR-CoSAO, PE-IFR-NiSAO, respectively. This suggests that when subjected to heating or burning the addition of the metal chelate correspondingly complicates the reactions taking place. When the residue yields at 600 ^{o}C are compared, it is found that although PE-IFR, PE-IFR-CuSAO

and PE-IFR-CoSAO are similar at about 15.8 %, the yield from PE-IFR-NiSAO is somewhat greater at

about 16.9 %. This implies a greater degree of carbonisation under TGA condition. The TGA data

combined with the LOI data suggest that the metal chelate can enhance the intumescent fire retardant in

PE.

sample	T_{onset}[a](℃)	$T_{50\%}$[b](℃)	T_{max}[c](℃)	Y[d](%)
PE	353	405	428	0.1
PE-IFR	311	461	471	15.9
PE-IFR-CuSAO	317	469	484	15.7
PE-IFR-CoSAO	323	453	446	15.7
PE-IFR-NiSAO	321	457	446	16.9

a):T_{onset} the on-set degradation temperature (temperature at 5% weight loss). **b):**$T_{50\%}$ the half degradation temperature (temperature at the half amount of the initial weight loss). **c):**T_{max} the maximum-rate degradation temperature. **d):** Y the residue at 600 ℃

Table 2 Calculated results from TG curves of various samples (heating rate: 10 °C/min).

3.3. Scanning electron microscopy (SEM)

In order to investigate the relationship between the structure of intumescent chars formed and the

fire-resistant properties of the polymer compositions, the char residues left after burning in air were

examined by SEM. Figure 3 presents the SEM micrographs of intumescent chars obtained from PE-IFR

and PE-IFR-CuSAO at different magnifications. Significant differences between the SEM micrographs

can be observed. From figure 3 (a) and (c), the char layer from PE-IFR shows a open porous char

structure. Whereas the char structure obtained from PE-IFR-CuSAO shown in figure 3 (b) and (d) is more

compact and appears to have a composed of platelets structure, which would be a more effective harrier.

Generally the speed of formation of the protective char layer and the performance of char layer are highly

dependant upon factors such as fire retardant, fire temperature and the viscosity of the molten polymer.

Comparing the char layers of PE-IFR and PE-IFR-CuSAO, suggests that the addition of small amounts of

CuSAO induces processes, such as crosslinking or dehydration, and changes the morphology of the carbonization compounds formed during burning, so that a char layer with improved performance is formed. Furthermore, it is likely that this is related to the increase in the viscosity of the molten mixture resulting from early catalytic oxidation. This is in accord with the results from TG analysis. It is well known that the intumescent char structure acts as an insulating barrier, can prevent heat and fuel transfer between the flame zone and the underlying substrate, and thus protect the substrate from heat and fire. It is apparent that the fire-resistant performance of these materials is directly connected with the quality of this barrier. SEM analysis demonstrates that the intumescent fire retardant with small amounts of metal chelate produces a more closed char and as a consequence has potentially better fire-retardant properties than that without metal chelate. This is in line with the LOI results.

(a) PE-IFR (1000×)

(b) PE-IFR-CuSAO (1000×)

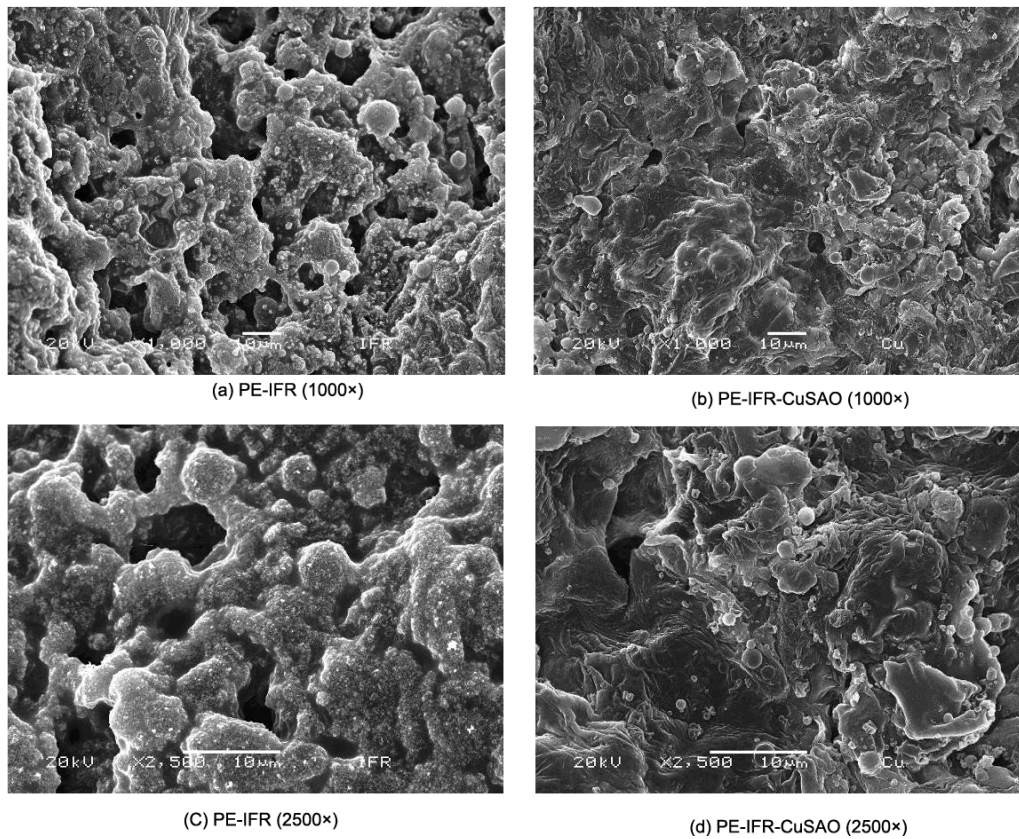(C) PE-IFR (2500×)

(d) PE-IFR-CuSAO (2500×)

Fig. 3. SEM images of char layer from PE-IFR and PE-IFR–CuSAO after burning in air: (a) PE-IFR (1000×); (b) PE-IFR–CuSAO (1000×); (c) PE-IFR (2500×) and (d) PE-IFR–CuSAO (2500×).

3.4. Cone calorimeter results

The cone calorimeter is a performance based bench scale fire testing apparatus and provides a wealth of information on combustion behaviour [20]. Some cone calorimeter results have been found to correlate well with those obtained from large scale fire tests, so that it can be used to predict the behaviour of materials in a real fire [21]. Furthermore, it provides comprehensive insight into fire risk via parameters such as heat release rate (HRR), total heat release (THR) and time to ignition (TTI). Thus the cone calorimeter is a useful tool for the evaluation of fire retardant materials. Figure 4 shows curves of the heat release rate (HRR) of pure PE, PE-IFR, PE-IFR-CuSAO, PE-IFR-CoSAO and PE-IFR-NiSAO. Pure PE burns very rapidly after ignition and a sharp HRR peak appears with a peak heat release rate (PHRR) of 734 kW/m^2. Of more interest is the difference in HRR between materials with and without metal chelate. The PHRR of PE-IFR is 278 kW/m^2, while PE-IFR-CuSAO, PE-IFR-CoSAO and PE-IFR-NiSAO show a lower burning rate with the peak reduced to 166, 169, 147 kW/m^2 respectively, only 60 %, 61 % and 53 % of that of PE-IFR and only 23 % , 23 % and 20 % of that of pure PE, the detailed data is shown in table 3. The results suggest that the addition of only small amounts of metal chelate shows a considerable effect on the IFR system.
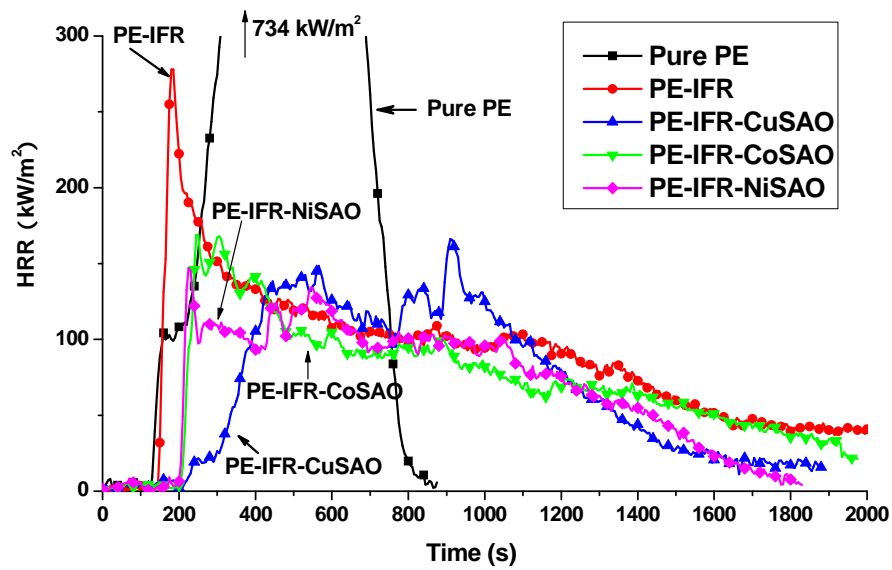
Fig. 4. Comparison of heat release rate curves of studied samples.

Sample	TTI (s)	Av-RHR (kW/m^2)	PHRR (kW/m^2)	THR (MJ/m^2)	Residual Mass (%)
PE	132	352	806	239	0.9
PE-IFR	166	71	278	173	31.6
PE-IFR-CuSAO	268	67	166	127	46.2
PE-IFR-CoSAO	218	70	169	137	46.0
PE-IFR-NiSAO	217	67	147	125	46.8

TTI: time to ignition

Av: average

Residual Mass%: mass percentage left when testing finished

Table 3. Combustion parameters obtained from cone calorimeter.

However, the most notable difference in the experiments using the cone calorimeter comes from time

to ignition (TTI). The TTI of pure PE and PE-IFR are 132 s and 166 s, respectively. However, the TTI of

PE-IFR-CuSAO, PE-IFR-CoSAO and PE-IFR-NiSAO are 268 s, 218 s and 217 s, respectively, which is

much longer than those of pure PE and PE-IFR. We believe that this result from improvements in the performance of the protective char layer formed prior to ignition. It indicates that an ignition resistant protective char layer was formed after addition of small quantities of metal chelate. This is in accord with the results from SEM. The samples studied showed considerable differences in the Total Heat Release (THR/Time) curves presented in figure 5.
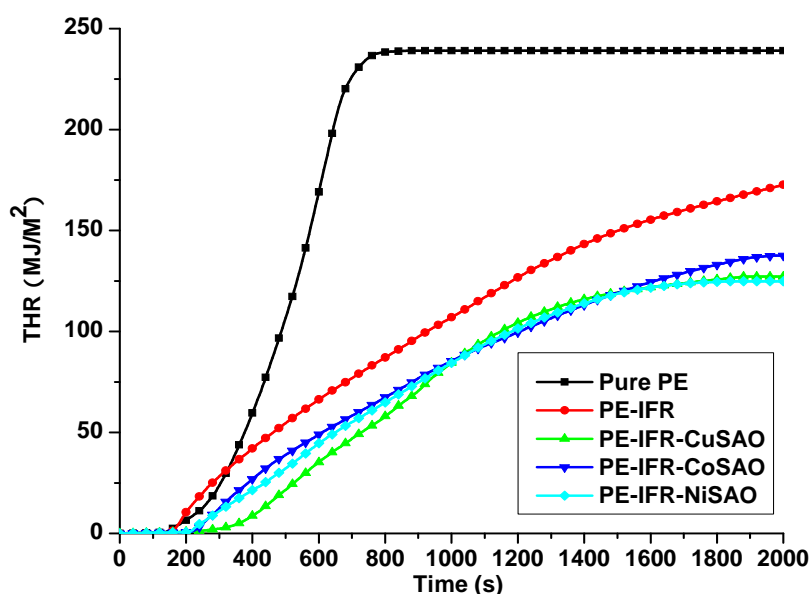

Fig. 5. Comparison of total release rate curves of studied samples.

At the end of burning, pure PE has released a total heat of 239 MJ/m^2, the PE-IFR has released is 173 MJ/m^2, whereas PEIFR-Metal chelates, only released 127 MJ/m^2, 137 MJ/m^2, and 125 MJ/m^2, respectively, for PE-IFR-CuSAO, PE-IFR-CoSA and PE-IFR-NiSAO. This lower THR value indicates that a part of the PE-IFR-Metal chelate has not completely combusted, probably undergoing a carbonization process. This is in accord with the mass loss, and the formation of residues, which are also presented in figure 6, 7, respectively.
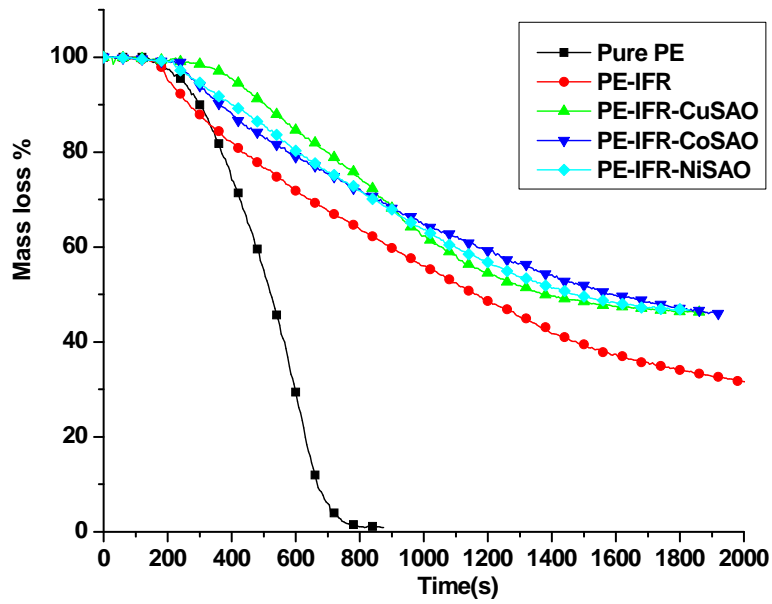
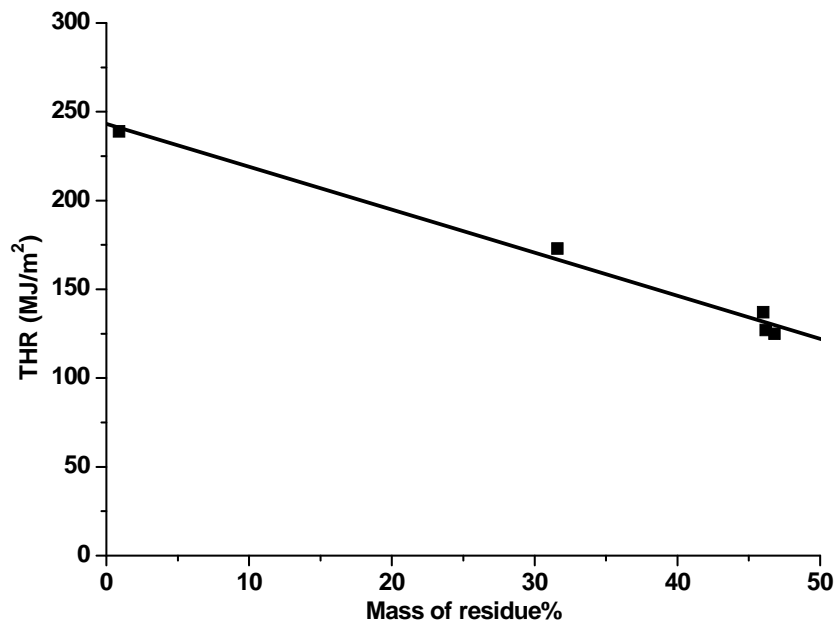Fig. 6. Comparison of mass loss curves of studied samples.

Fig. 7. Relationship of residual mass and THR of studied samples.

Figure 6 shows weight loss as a function of combustion time for pure PE and PE-IFR in comparison

with PE-IFR-Metal chelates (PE-IFR-CuSAO, PE-IFR-CoSAO and PE-IFR-NiSAO). It can be seen that

the PE-IFR-Metal chelates present a significantly lower mass loss (ML). Meanwhile, the relationship of

residual mass and THR of studied samples has presented in figure 7.

The figure 7 shows that the mass of residue is in proportion to the THR. This confirms the proposed mechanism of increased char yield as a means of reducing the heat release, for the early flaming condition of 25 kW/m^2. However, the availability of cone plaques for this work was limited. When tested at 35 kW/m^2 and 50 kW/m^2, the difference in THR were not observed between the metal chelate sample and the PE-IFR. However, at 35 kW/m^2, the CuSAO sample showed a significantly greater ignition delay time than the other samples.

Observation of the burning process and the residues remaining after the cone calorimeter test showed pure PE burns rapidly after ignition with almost no residue left. By comparison PE-IFR and PE-IFR-Metal chelate all show an obvious intumescent char layer. However, there are significant differences in the burning behaviour and the performance both the inner and outer char materials. In the initial stages, the flaming of PE-IFR is more intense than that of PE-IFR-Metal chelate, particularly the PE-IFR-CuSAO and PE-IFR-NiSAO. The latter show candle-like burning from fuel evolved through small hole in the protective layer. The PE-IFR-Metal chelate residues showed an obviously metallic lustre on their surface, suggesting more complete graphitization. The residue on the PE-IFR surface was quite loose and friable by comparison with the residues from the PE-IFR-Metal chelates. The tougher outer layer produce by the metal chelate IFR systems would prevent the effective transfer of gas and volatiles through the surface, so preventing burning. The presence of the metal chelate seems to inhibit significantly the decomposition process. It was observed that there were significant differences between the materials with respect to the inner layer of the residues. It was observed that the residue from PE-IFR-Metal chelate had a lower liquid layer (probably olefinic) arising from the incomplete combustion of the inner layer. The presence of this residence was not observed with the PE-IFR system. After cooling

down, the thickness of the protective layers was measured using callipers. The average thickness of the

layers for different samples is shown in table 4. It is known that the thicker the layer, the more difficult

transfer of gas and volatile will be, and assuming comparable densities, the greater the amount of fuel

retained in the char. From the results of table 4, it can be observed that the residue layers from the system

containing metal chelate are thicker than from PE-IFR. Thus they can offer a more effective protection

and prevent the transfer of the gas, volatiles and heat. The result is in accord with the results from SEM.

So it is concluded that there is an important role for low concentration of metal chelate in the

improvement of the performance of a char layer during burning.

sample	PE	PE-IFR	PE-IFR-CuSAO	PE-IFR-Co SAO	PE-IFR-NiSAO
Thickness of Residue Layer (mm)	0	2.0	2.6	2.3	2.5

Table 4. The average thickness of residues layers for samples.

4. Conclusions

In this study, PE was treated with various formulations containing an IFR and different

metal-chelates (CuSAO, CoSAO and NiSAO). The effect of very small amounts of the metal chelates on

the thermal stabilization and burning behaviour is apparent, showing inhibition of thermal decomposition.

By cone calorimetry, PE-IFR-metal chelate (PE-IFR-CuSAO, PE-IFR-CoSAO and PE-IFR-NiSAO)

shows very significant decrease in HRR, PHRR, ML, THR and very considerable improvement in TTI

compared to materials without metal chelate. Furthermore, it is significant to observe from SEM and

observation of the char layer that PE-IFR-metal chelate system produces a compact and tough char

structure compared to a loose porous char layer formed without metal chelate. The reason may be related to the catalysis (such as crosslinking or dehydration) leading to enhanced graphitization, but this is not yet clear. Further work will be needed to study and understand the fire retardant mechanism and obtain more direct evidence.

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