

A Novel Intumescent Flame Retardant: Synthesis and Its Application for Linear Low-Density Polyethylene

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Received: 26 April 2016 / Accepted: 19 January 2017 / Published online: 7 February 2017
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Abstract A novel intumescent flame retardant, melamine salt of pentaerythritol phosphate montmorillonite (MPPM), was synthesized and characterized by ¹H NMR, FTIR, and XRD. Its effect on the thermal stability and flammability properties of linear low-density polyethylene (LLDPE) was investigated. The thermogravimetric analysis data exhibited that MPPM enhanced the char formation and the thermal stability of LLDPE at high temperatures. The cone calorimeter results showed that addition of MPPM to LLDPE reduced greatly the peak of heat release rate, total heat release, mean mass loss rate, and fire growth rate index in all LLDPE composites. Moreover, MPPM increased the fire performance index of LLDPE and led to achieve V-0 rating in UL-94V test. The morphology, FTIR, and EDXS analysis for char residue after cone calorimeter test showed the formation of thermally stable char containing Al, Si, -CH₂-, P-O, P-O-C, C-N, and C=N. This meant that MPPM was efficient in reducing the fire hazardous of LLDPE.

Keywords Intumescent · Montmorillonite · LLDPE · Melamine · Pentaerythritol phosphate

1 Introduction

Polyethylene (PE), as one of most common polymeric materials, has been used in many fields such as household goods, packaging, furniture, and electrical industries due to its good electric insulation, low density, good chemical resistance, ease of processing, and low cost [1,2]. Unfortunately, PE is highly flammable and has dripping tendency during combustion due to its chemical structure. This problem restricts greatly its application in many fields. So, it is important to improve the flame retardancy of PE [1]. Adding flame retardants into PE is a main and simple method to prepare flame retardant PE. The more effective flame retardants for PE are halogen-based flame retardants, mineral fillers, and intumescent flame retardants [1–4]. Halogen-based flame retardants are environmentally forbidden as these materials are highly toxic, although having excellent flame retardant performance. Mineral fillers, like magnesium and aluminum hydroxides, are not toxic flame retardant additives. However, they achieve flame retardancy in PE at high loading levels, and this lead to deterioration for the mechanical properties of PE [4,5]. Among all flame retardants, intumescent flame retardants (IFRs) have been deeply researched because of their excellent advantages like low smoke and toxicity, halogen free, and little corrosive gases production. So, IFRs can be chosen as fillers for PE to replace halogen-based flame retardants and mineral fillers. IFR systems are usually consisting of three components which include char forming agent, acid source, and blowing agent. The traditional IFR system, ammonium polyphosphate/pentaerythritol/melamine system, is widely used in

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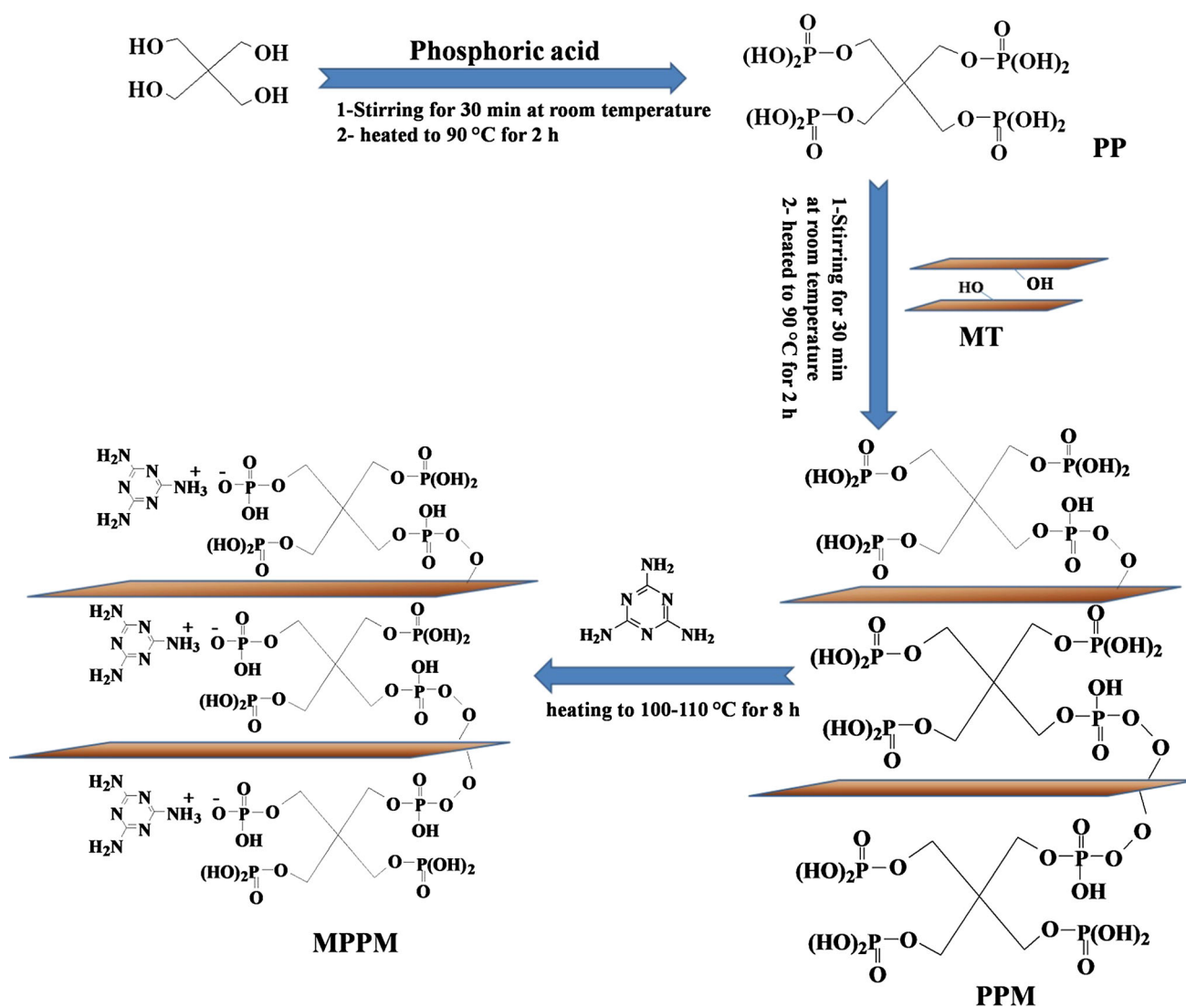


Fig. 1 A schematic representation for synthesis of MPPM

polyolefins [4–20]. However, it has some disadvantages such as high loading levels are required to achieve good flame retardancy, water leaching, lower thermal stability, highly polar system, and low compatibility with polyolefins [21]. To overcome these problems, a single-molecule IFR, melamine salt of pentaerythritol phosphate (MPP), was prepared by reactive extrusion method. This process has been reported for preparing IFR and their master batch by reacting melamine phosphate and pentaerythritol. MPP can overcome the previous drawbacks by reducing the polarity of IFR and increasing the compatibility with polyolefins [21].

In this paper, a novel intumescent flame retardant, MPPM, was synthesized and characterized by 1H NMR, FTIR, and XRD. MPPM was incorporated into LLDPE at different ratios to form LLDPE/MPPM composites. The thermal stability and flammability properties of the prepared composites

were studied. The fire performance of the different composites was evaluated.

2 Experimental

2.1 Materials

LLDPE was produced by Sabik Company, Saudi Arabia. Melamine with purity 99%, pentaerythritol with purity 98%, and montmorillonite k10 (MT) were purchased from Alfa Aesar Company, Germany. Phosphoric acid and methanol HPLC were obtained from Sigma-Aldrich Company, Germany.

2.2 Preparation of MPPM

MPPM was synthesized by adding 115.29 g of phosphoric acid and 40 g of pentaerythritol in a 400-ml beaker fitted

Table 1 Formulations and UL-94V rating of LLDPE and its composites

Sample code	LLDPE%	MPPM%	UL-94V rating
LLDPE	100	–	No rating
PE/25	75	25	V-2
PE/30	70	30	V-2
PE/35	65	35	V-0

by stirrer. The mixture was stirred for 30 min at room temperature and heated to 90 °C for 2 h to form pentaerythritol phosphate (PP). Then, 20 g of MT was added to previous reaction, and the mixture was stirred for 24 h at room temperature and then heated to 100 °C for 1 h. Pentaerythritol phosphate montmorillonite (PPM) was obtained as intermediate. In three-necked flask, 73 g of melamine was dispersed into 500 ml methanol. The synthesized PPM was added into the flask slowly at 100–110 °C and the reaction continued for 8 h. The solution was filtered, washed three times with methanol, and dried at room temperature. The final product (MPPM) was 244 g in pale white color and was grinded to be fine powder. A schematic representation for synthesis of MPPM is shown in Fig. 1.

2.3 Preparation of Flame Retarded LLDPE Composites

LLDPE composites were prepared using twin screw extruder (manufactured by Newplast Company, India) with three heating zones which were adjusted at 170 °C. The twin screw speed was maintained at 25 rpm. MPPM with desired amounts was first mixed with LLDPE pellets and then added to the extruder. The formulations of the prepared samples are presented in Table 1. The polymer composite samples were pressed under 15 MPa for 10 min at 160 °C into sheets with suitable thickness and size for UL-94V and cone calorimeter tests.

2.4 Measurements

¹H NMR spectra were recorded on a Varian Mercury VX-300 NMR spectrometer which run at 300 MHz in dimethyl sulphoxide (DMSO-d₆). Chemical shifts were quoted in (δ) and were related to that of the solvents. FTIR analysis was performed by a Nicolet 380 spectrophotometer. Each sample was mixed with KBr powder and then pressed into a tablet. The measurements were taken in the optical range of 4000–400 cm⁻¹. The XRD experiments were performed on Empyrean diffractometer from Panalytical Co. (The Netherland) using Cu K α radiation corresponding to a wavelength of 0.1542 nm. The scanning speed of the detector was 0.055°/s. Thermogravimetric analysis (TGA) was conducted on a Shimadzu DTG-60 with a linear heating rate 10 °C/min. The temperature range started from room temperature to 750 °C under nitrogen atmosphere with flow

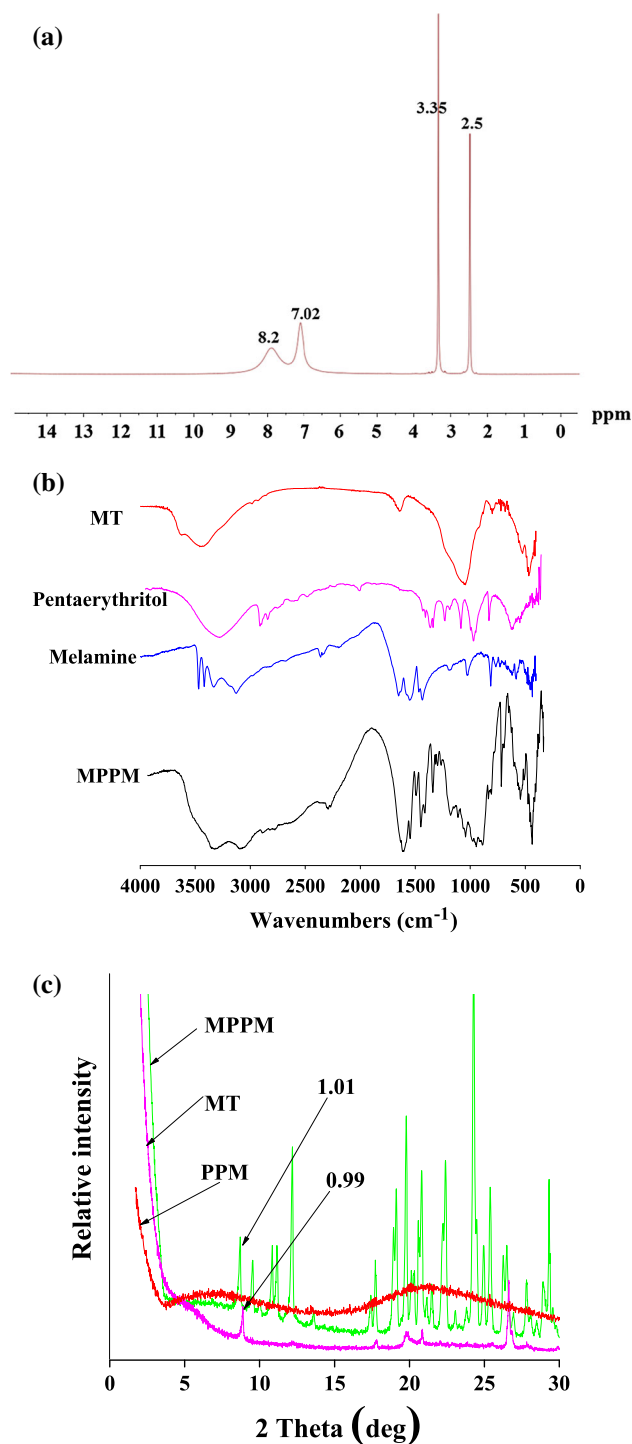


Fig. 2 a ¹H NMR spectrum, b FTIR spectrum for MT, pentaerythritol, melamine, and MPPM, and c XRD for MT, PPM, and MPPM

rate 300 mL/min. Each sample was placed in a platinum crucible, and the samples' weights were about 7–7.5 mg. The vertical burning test was carried out by UL-94 flame chamber manufactured by Stanton Redcroft Ltd, UK, according to ASTM D 3801–2010. The specimen dimensions were

Table 2 FTIR of melamine, pentaerythritol, MT, and MPPM

Compound	Wave number (cm ⁻¹)	Functional group	References
Melamine	3469, 3419, 3329, 3128	Primary amine	[15]
	1652, 1551, 813	Triazin ring	[15]
	1028	C–N of primary amine	[15]
Pentaerythritol	3339	OH of alcohol	[23]
	2944, 2889	–CH ₂ – groups	[23]
MT	3626, 3450	OH stretching	[24]
	1637	OH deformation of water	[24]
	1085, 787	Si–O stretching	[24]
	620	Coupled Al–O and Si–O, out of plane	[24]
MPPM	505	Si–O–Al	[15,24]
	3160	+NH ₃	
	1246, 1180, 1110	P=O, P–O, P–O–C	[15]
	505	Si–O–Al	[15,24]

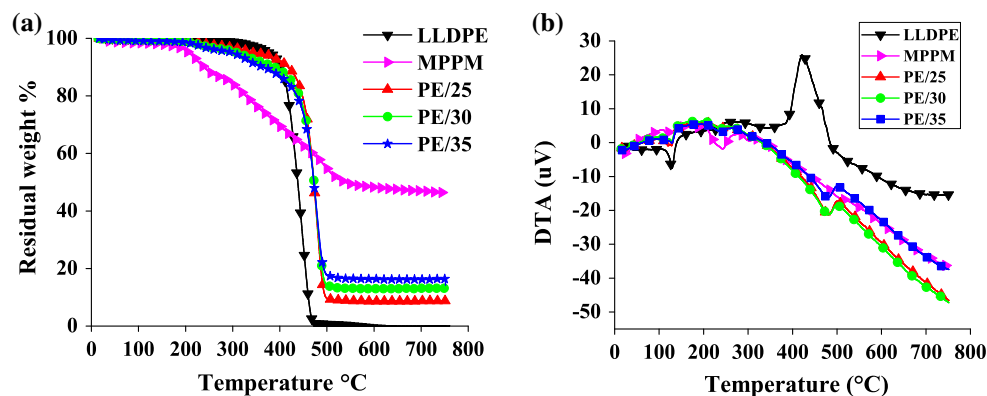
Table 3 TGA data of LLDPE and its composites

Sample code	$T_{10\%}$ (°C) ^a	$T_{50\%}$ (°C) ^b	T_{\max} (°C) ^c	Char at 750 °C (wt%)
MPPM	239	540	496	53.4
LLDPE	402	439	445	—
PE/25	417	471	479	8.7
PE/30	389	472	479	13.2
PE/35	362	472	480	16.3

^a $T_{10\%}$ defined as the temperature at which 10 wt% weight loss occurred

^b $T_{50\%}$ defined as the temperature at which 50 wt% weight loss occurred

^c T_{\max} defined as the temperature at which maximum weight loss rate occurred

**Fig. 3** a TGA and b DTA curves of MPPM, LLDPE, and its composites

130 mm × 10 mm × 3 mm and fixed vertically above a cotton patch during tests. The combustion tests were performed in a cone calorimeter (manufactured by Fire Testing Technology Company, UK) according to ISO 5660 standard procedures. The specimen dimensions were 50 mm × 50 mm × 4 mm. Each sample was wrapped in aluminum foil and exposed horizontally to 35 kW/m² external heat flux. Scanning electron microscope (SEM) images were observed by using Quanta 250 FEG (Field Emission Gun) manufactured by FEI Company, the Netherlands. The SEM was connected with

EDXS unit (energy-dispersive X-ray spectrometry), which has accelerating voltage 30 kV.

3 Results and Discussion

3.1 Characterization of MPPM

The ¹H NMR spectrum for MPPM is presented in Fig. 2a. It is clearly seen that the proton for CH₂–O located at $\delta = 3.3$ ppm, the proton for NH₂ presented at $\delta = 2.5$ ppm, and

Table 4 Flammability properties of LLDPE and its composites

Parameters	Samples			
	LLDPE	PE/25	PE/30	PE/35
pHRR (kW/m ²)	1318	653	471	319
tp-HRR (s)	285	220	275	270
mHRR (kW/m ²)	897	295	197	142
THR (MJ/m ²)	229	158	149	127
TTi (s)	112	51	53	51
mEHC (MJ/Kg)	42	31	32	27
mMLR (g/s)	0.052	0.014	0.015	0.012
MARHE (kW/m ²)	625	392	303	208
FPI (m ² s/kW)	0.084	0.078	0.112	0.159
FGI (kW/m ² s)	4.6	2.9	1.7	1.1

the proton peak of (⁺NH₃⁺O–P=O) appeared at $\delta = 7$ ppm [22].

The FTIR spectra for melamine, pentaerythritol, MT, and MPPM are presented in Fig. 2b. In addition, the main absorption peaks for reactants and MPPM are shown in Table 2, and it shows good agreement with absorption peaks in the literature. The FTIR spectrum for MPPM, Fig. 2b, shows the absence of MT characteristic OH peak at 3626 cm⁻¹, the presence of peak at 3160 cm⁻¹ for ⁺NH₃, the appearance of peaks at 1246, 1180, and 1110v cm⁻¹ for P=O, P–O, and P–O–C. The presence of peak at 505 cm⁻¹ for Si–O–Al [15,23,24]. The ¹H NMR spectrum and FTIR results confirmed the interaction between reactants to form MPPM.

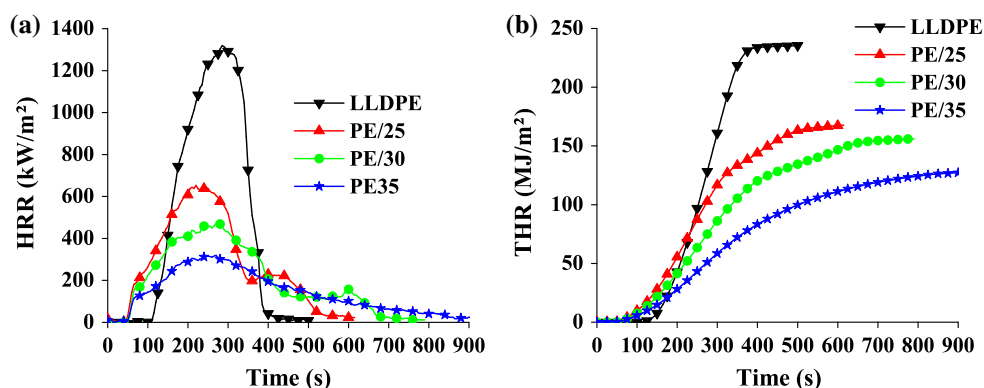
Figure 2c shows the XRD pattern of MT, PPM, and MPPM samples. In general, the increase in the basal spacing of MPPM comparing with MT indicates that the interaction between reactants occurred between clay layers [15]. The XRD pattern of MT, Fig. 2c, shows four main peaks at $2\theta = (8.9, 19.8, 20.9, \text{ and } 26.5)$ and the d-space at $2\theta = 8.9$ is 0.99 nm. The XRD for PPM (intermediate) shows two broad peaks at $2\theta = (6.9 \text{ and } 21.4)$. The results for MPPM, Fig. 2c, show

many clear diffraction peaks in the range $2\theta = 2.5\text{--}30$. The first diffraction peak appears at $2\theta = 8.6$ with d-space 1.01 nm and confirms the presence of reactants between clay layers. Moreover, the great change in the XRD pattern of MPPM comparing with MT indicates that the reactions occurred on the surface and inner layers of clay.

3.2 Thermal Degradation Behavior of LLDPE and Its Composites

The TGA is widely used technique for identifying the thermal stability of polymer composites. The TGA and DTA data are presented in Table 3 and Fig. 3a, b. The data obtained from TGA are $T_{10\%}$, $T_{50\%}$, T_{\max} , and the char yield at 750 °C. From Table 3 and Fig. 3a, it is clearly seen that MPPM decomposed in three steps with 53.4% char residue at 750 °C. The three decomposition steps for MPPM started and ended at the temperature ranges 150–250, 250–530, and 530–750 °C, respectively. MPPM attained $T_{10\%}$, $T_{50\%}$, and T_{\max} at 239, 540, and 496 °C, respectively. Moreover, it lost 1.9% in the temperature range 600–750 °C which indicated the formation of thermally stable char in this range.

LLDPE decomposed completely without nearly any char residue at 750 °C and achieved $T_{10\%}$, $T_{50\%}$, and T_{\max} at 402, 439, and 445 °C, respectively. The addition of MPPM to LLDPE improved $T_{10\%}$ by 15 °C in PE/25 composite. This may be attributed to that MPPM decomposition led to the formation of certain radicals (mainly PO[·]) and inert gases which were able to quench and interact with $\cdot\text{H}$ and $\cdot\text{OH}$ radicals that were produced from LLDPE decomposition [25]. Meanwhile, $T_{10\%}$ of PE/30 and PE/35 samples were decreased by 13 and 40 °C comparing with LLDPE. This can be referred to that a greater decomposition took place in the bonds (such as P–O and C–N) which were less thermally stable than C–C bonds in LLDPE [25]. In contrast, $T_{50\%}$ and T_{\max} of PE/25, PE/30, and PE/35 composites increased by 33 and 34 °C relative to LLDPE. The char residue at 750 °C improved from

**Fig. 4** a HRR curves and b THR curves of LLDPE and its composites

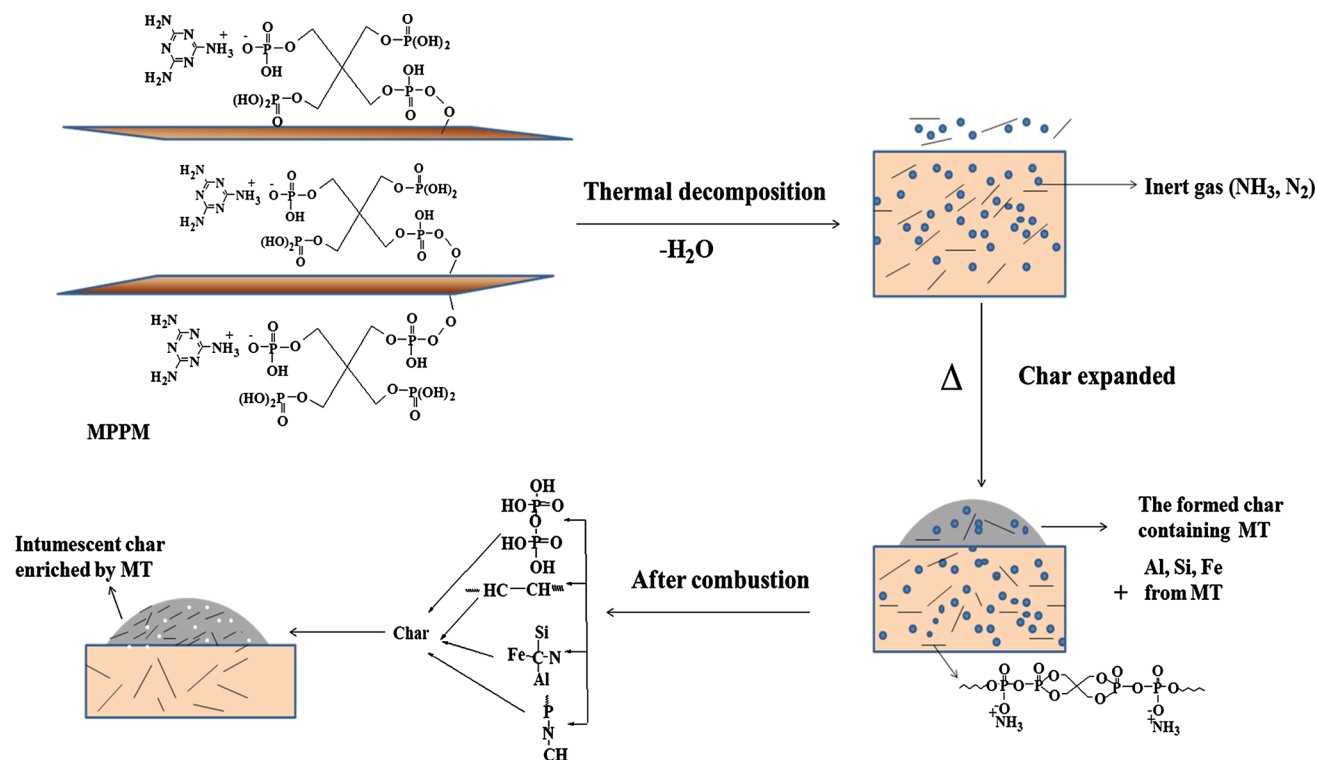


Fig. 5 A schematic representation of LLDPE/MPPM composites combustion and char formation mechanism

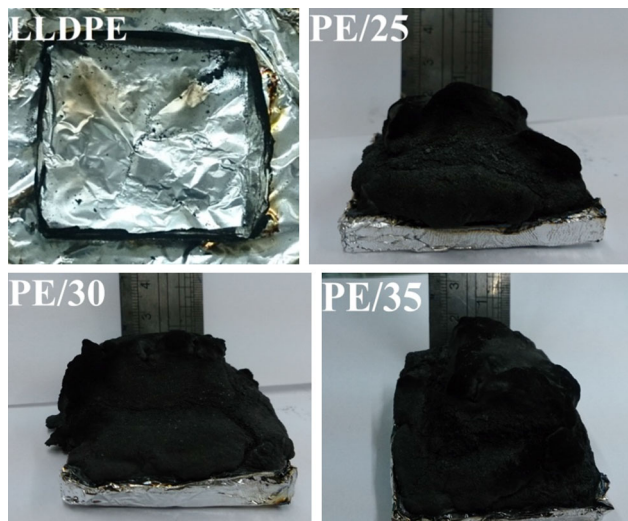


Fig. 6 Digital photographs for the char residues of LLDPE and its composites after cone calorimeter test

nearly 0% in the neat polymer to 8, 13, and 16% in PE/25, PE/30, and PE/35 composites.

The DTA curves of LLDPE/MPPM composites, Fig. 3b, showed decomposition peak at 129 °C which was attributed to the melting point of LLDPE. In addition, the DTA curves presented a decomposition peak at 240 °C which may be due to losing certain small molecules like water vapor and starting formation of phosphate ester. The DTA of LLDPE

showed exothermic decomposition peak in the temperature range 384–488 °C. In contrast, DTA of LLDPE/MPPM composites showed an endothermic peak in the temperature range (450–505 °C). This endothermic decomposition may be the reason for positive shifts that were occurred in $T_{50\%}$ and T_{max} values of LLDPE composites comparing with pure polymer. The TGA and DTA data indicated that the maximum weight loss in LLDPE composites was found in the temperature range 400–500 °C. This was attributed to that LLDPE/MPPM systems decomposed to give NH_3 , CO_2 , H_2O , cross-linking structure containing P–N, P–O–C, C=N, and lower hydrocarbon chains [25,26]. Moreover, MT in MPPM base structure decomposed to give Al, Si, and Fe which were interacted with the other degradation products to form thermally stable char layer. In the temperature range 600–750 °C, it is noticed that the weight loss in PE/25, PE/30, and PE/35 composites was small and this confirmed the formation of thermally stable char [25,26]. The improvement in the thermal stability properties of LLDPE composites indicated that MPPM has good flame retardant action on LLDPE.

3.3 Flame Retardancy of LLDPE and Its Composites

3.3.1 UL-94V Rating

The results of UL-94V test are presented in Table 1, and it shows that LLDPE is highly flammable polymer and has

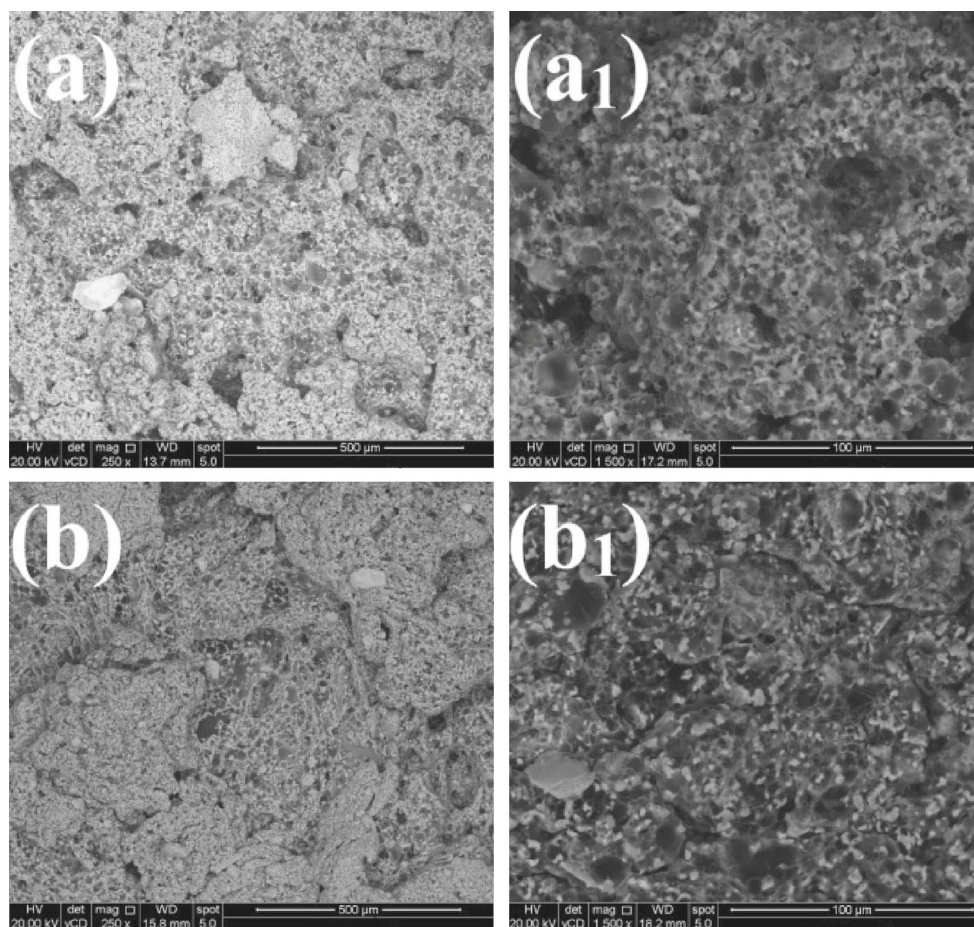


Fig. 7 SEM images of PE/30 and PE/35 char after cone calorimeter test: **a, b** at magnification power 250 \times , and **a₁, b₁** at magnification power 1500 \times

great tendency to form flammable driplets. The addition of MPPM to LLDPE at 25 and 30 % loading levels (PE/25 and PE/30) led to achieving V-2 class. Failure in achieving V-0 at 25 and 30% MPPM loadings was due to the formation of flammable driplets. LLDPE achieved V-0 rating at 35% MPPM loading level (PE/35).

3.3.2 Cone Calorimeter Results

Cone calorimeter test is widely used for evaluating the flammability properties of polymer composites. In general, the data obtained from cone test are time to ignition (TTi), peak of heat release rate (pHRR), time to reach peak of heat release rate (tp-HRR), mean heat release rate (mHRR), mean effective heat of combustion (mEHC), mean mass loss rate (mMLR), and maximum average rate of heat emission (MARHE). pHRR values take great interest from fire science researchers because it can reflect the intensity of fire. The cone calorimeter test results are shown in Table 4 and Fig. 4a, b. The data in Table 4 show that LLDPE burnt rapidly

after ignition and a sharp pHRR appeared at 1318 kW/m². The addition of MPPM to LLDPE decreased the pHRR by 50, 64, and 75% in PE/25, PE/30, and PE/35 composites, respectively (see Fig. 4a). The value of mHRR for LLDPE was minimized by 67, 78, and 84% in PE/25, PE/30, and PE/35 samples, respectively. THR of LLDPE was 229 MJ/m², and it reduced to 158, 149, 127 MJ/m² in PE/25, PE/30, and PE/35 samples (see Fig. 4b). TTi values indicated that LLDPE composites started ignition earlier than pure polymer. This was attributed to the presence of MPPM which started degradation early and activated the formation of intumescent, compact, and thermal stable char layer [25]. The results of mMLR decreased from 0.025 g/s in virgin polymer to 0.014 g/s, 0.015 g/s, 0.012 g/s in PE/25, PE30, and PE/35 composites. This indicated that MPPM decreased effectively the thermal degradation of LLDPE, and this agreed with the data obtained from TGA. The mEHC value of LLDPE was minimized by the addition of MPPM, as it is shown in Table 4, and the maximum reduction was 35% and obtained at 35% MPPM loading level (PE/35).

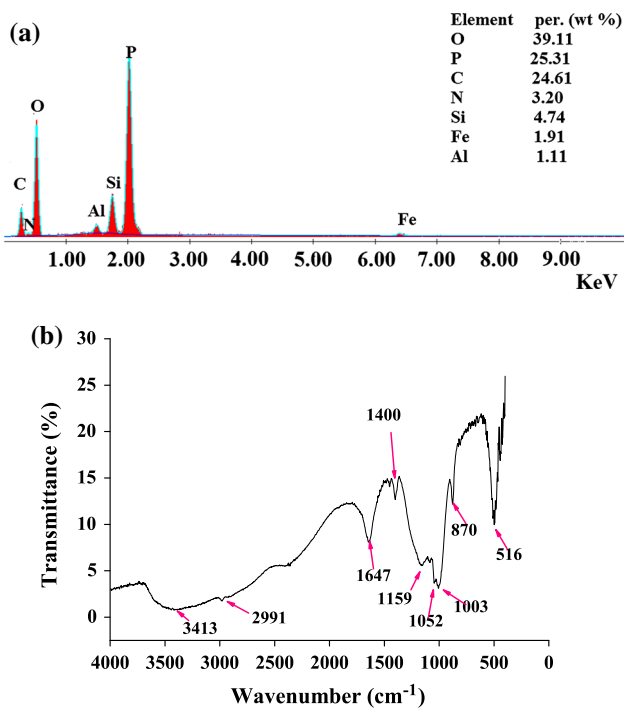


Fig. 8 **a** EDXS spectrum and **b** FTIR spectrum for PE/35 residual char after cone calorimeter test

3.4 Mechanism of Flame Retardation and Char Morphology

Figure 5 shows a schematic representation for LLDPE composites combustion and char formation mechanism. The cone calorimeter data indicated that during combustion process, LLDPE/MPPM composites decomposed to give inert gases like NH_3 , CO_2 , and water vapors. These gases helped in reducing oxygen concentration (from air) in the combustion zone. In addition, LLDPE/MPPM degradation process produced cross-linking structure containing P–O–C, C–N, C=N, and lower carbon hydrogen chains. Moreover, MT in the base structure of MPPM produced Al, Si, and Fe which promoted the formation of intumescent, thermally stable, compact, coherent, and continuous char layer on the polymer composites surfaces [27]. The presence of pentaerythritol in MPPM structure and NH_3 molecules (which produced during combustion) assisted in char swelling. The char was effective in protecting the underlying polymer from the effect of heat, oxygen, and flammable gases [28]. As a result, LLDPE/MPPM composites showed high flame retardancy comparing with pure polymer.

The morphology of the char formed after cone calorimeter is a useful tool for characterizing the flame retardation mechanism. The digital photographs and SEM images were used for studying the morphology of the char residue. Figure 6 shows digital photographs for the char residue of LLDPE, PE/25, PE/30, and PE/35 composites. It is clearly shown

in Fig. 6 that LLDPE burnt completely without nearly any char residue after cone test. In contrast, PE/25, PE/30, and PE/35 samples showed the formation of intumescent, compact, coherent, and continuous char layer on the polymer composites surfaces. The char formed protected the underlying polymer from the effect of heat, oxygen, and flammable gases.

Figure 7a, b, a₁, b₁ show SEM images for char residue of PE/30 and PE/35 composites at magnification power $250\times$ ($500\mu\text{m}$) and $1500\times$ ($100\mu\text{m}$), respectively. In Fig. 7a, b, where magnification power is $250\times$, it is clearly seen compact, continuous, and coherent char. Fig. 7a₁, b₁, where magnification power is $1500\times$, shows coherent char and certain large bubbles which confirmed the formation of swelling char.

In order to identify the main compositions of the char residue after cone calorimeter test, EDXS and FTIR analysis were performed for the char of PE/35 composite. Figure 8a shows the EDXS analysis for the char residue of PE/35 composite. According to the results in Fig. 8a, the chemical compositions of char contained oxygen (39.11%), phosphorus (25.31%), carbon (24.61%), silicon (4.74%), nitrogen (3.20%), aluminum (1.11%), and iron (1.91%) which interacted during combustion to form the char layer. The FTIR spectrum for PE/35 composite char is presented in Fig. 8b. The FTIR spectrum showed peak at 3413 cm^{-1} which was attributed to OH group from adsorbed water. The peak at 2991 cm^{-1} was referred to CH_2 group which indicated the presence of some carbon hydrogen chains in the char. The peak at 1647 and 1402 cm^{-1} was attributed to C=N and C–N. The peaks at 1159 and 1047 cm^{-1} were referred to P–O and P–O–C. The peak at 1003 cm^{-1} may be attributed to Si–O–C. The peak at 827 cm^{-1} was attributed to substituted alkene. The peak at 516 cm^{-1} was referred to the clay minerals [15, 24]. The digital photographs, SEM images, EDXS analysis, and FTIR spectrum for the char residue after cone test confirmed that the LLDPE/MPPM composites decomposed to give products like Al, Si, P–O–C, C=N, C–N, and substituted alkene which were interacted to form compact and swelling char. The residual char protected the underlying polymer from the effect of heat, oxygen, and combustible gases [15].

3.5 Fire Safety Rating Parameters

The parameters which are selected to evaluate the fire performance of LLDPE, and its composites are the maximum average rate of heat emission (MARHE), fire growth rate index (FGI), fire performance index (FPI), pHRR, and THR.

The average rate of heat emission (ARHE) is the ratio of the cumulative heat emission to time and its peak value is MARHE. The results of MARHE can reflect the tendency for fire development under real scale conditions [29, 30]. The

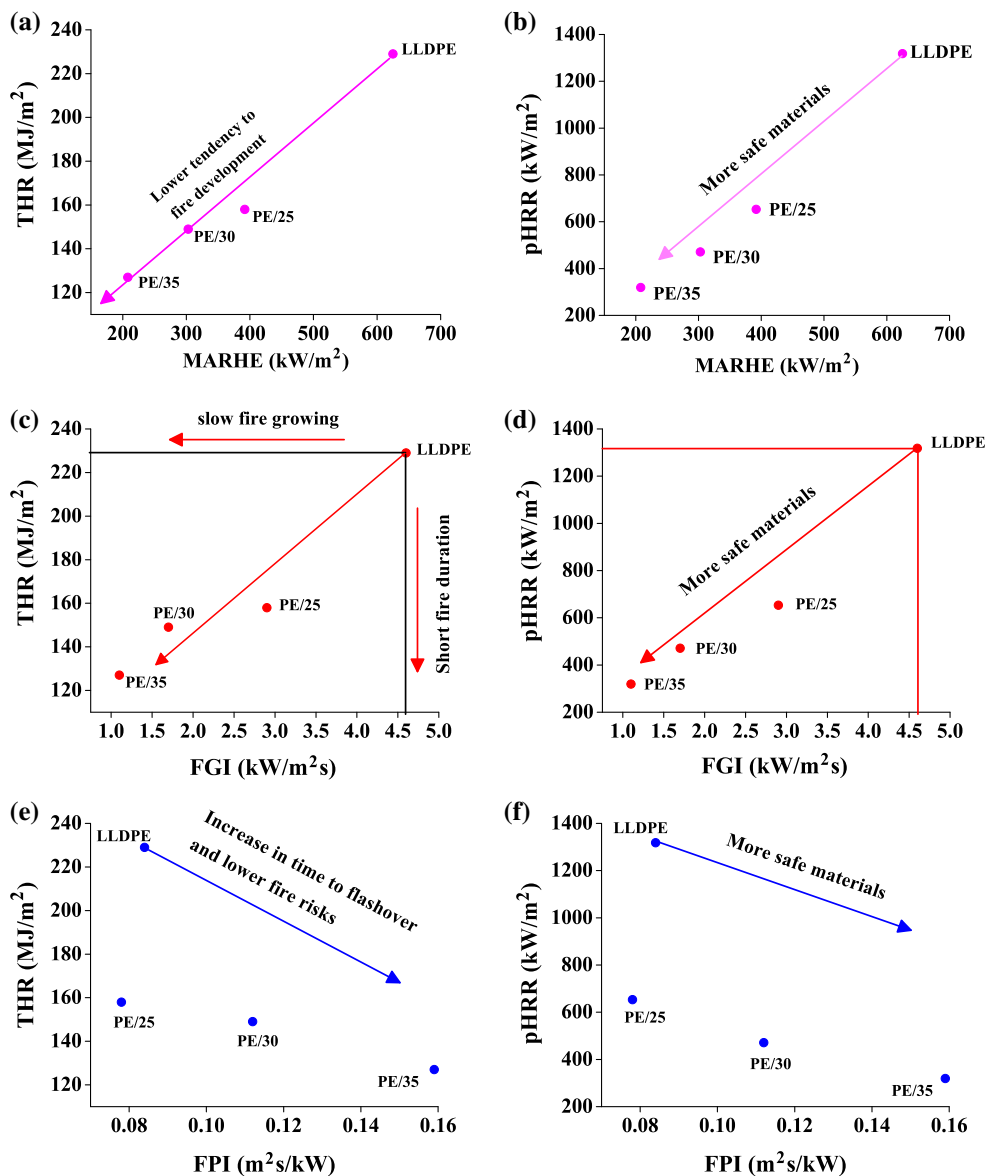


Fig. 9 Fire safety rating for LLDPE and its composites

data in Table 4 show that MARHE value of LLDPE decreased with increasing MPPM loading level in the prepared composites. Based on the data in Table 4, the tendency for fire development under real scale conditions has the following order: LLDPE > PE/25 > PE/30 > PE/35.

Fire growth rate index (FGI) is defined as the ratio of peak of heat release rate (pHRR) to time to reach peak of heat release rate (tp-HRR), and it is an indicator on the burning tendency of different materials. The decreasing in FGI values means lower fire growth in material and lower fire risks [29, 30]. According to FGI values in Table 4, MPPM addition to LLDPE decreased the FGI value of LLDPE. The maximum amount of reduction in FGI values was 76% and achieved in PE/35 composite. Based on FGI results in Table 4, the fire

safety of the prepared composites has the following order: PE/35 > PE/30 > PE/25 > LLDPE.

Fire performance index (FPI) is explained as the time to ignition (TTi) divided by the peak heat release rate (pHRR). FPI is usually connected with time to flashover where the lower values of FPI propose accelerated flashover event [29,30]. Therefore, polymer composites with low FPI values demonstrate higher fire risks. From the data in Table 4, PE/25 composite showed lower FPI value comparing with pure polymer and the amount of reduction was 7%. In contrast, PE/30 and PE/35 composites showed higher FPI value relative to LLDPE. The amount of improvement in FPI values was 33 and 89% in PE/30 and PE/35 composites, respectively. Based on FPI values in Table 4, the fire safety in the

prepared composites can be ordered as follows: PE/35 > PE/30 > LLDPE > PE/25

Although PE/25 composite had lower FPI comparing with LLDPE, the addition of 25% MPPM to LLDPE formed intumescent char layer on the polymer surface and decreased the pHRR and THR of pure polymer by 50.4 and 31%, respectively.

The relative overall fire performance of LLDPE composites can be estimated, as it is shown in Fig. 9a–f, by plotting the THR and pHRR against MARHE, FGI, and FPI values on Cartesian coordinate systems [30]. Fire safe composites should have lower THR, pHRR, MARHE, and FGI comparing with pure polymer. As a result, these composites should locate close to the coordinates (0;0) on Cartesian plot. In addition, fire safe composites should have FPI values > 0.085 (FPI of LLDPE) on (*x*) axis of Cartesian plot while pHRR and THR values are lower than pure polymer. According to Fig. 9a–f, nearly all LLDPE composites were more safe than neat polymer and the most safe composite was PE/35. The only exception was PE/25 composite which may has accelerated flash over event (or it has earlier time to flash over) comparing with LLDPE.

4 Conclusions

A novel multifunctional intumescent flame retardant, MPPM, was synthesized by the reaction of pentaerythritol phosphate with montmorillonite and melamine to improve the thermal stability and flame retardancy of LLDPE. The ¹H NMR, FTIR, and XRD analysis confirmed the interaction between the reactants to form MPPM.

The TGA and DTA results showed that addition of MPPM to LLDPE improved thermal stability of pure polymer at high temperatures where it increased $T_{50\%}$ and T_{max} by 33 and 34 °C, respectively. Moreover, it enhanced the char residues at 750 °C for all samples.

The vertical burning rate (UL-94V) test showed that addition of 25 and 30% of MPPM to LLDPE led to achieve V-2 rating. However, LLDPE/35% MPPM system achieved V-0 rating and prevented the problem of forming flammable driplets which appeared in PE/25 and PE/30.

Cone calorimeter test results indicated that LLDPE/MPPM systems showed great reduction in the pHRR, THR, mHRR, mEHC, and mMLR comparing with LLDPE alone. The maximum reductions in these parameters were 75, 44, 84, 35, and 76%, respectively, and obtained at 35% MPPM loading level.

The digital photographs, SEM images, EDXS analysis, and FTIR spectrum of char residue after cone calorimeter test showed that MPPM led to the formation of high quality and thermally stable intumescent char which protected the underlying polymer from heat, oxygen, and flammable gases during combustion. The char structure contained mainly Al,

Si, Fe, P–O, P–O–C, C–N, C=N, and certain carbon hydrogen chains.

The fire safety rating parameters, which included MARHE, FGI, FPI, pHRR, and THR, indicated that LLDPE/MPPM composites were safer than pure polymer. The only exception was LLDPE/25% MPPM which showed accelerated time to flash over comparing with pure polymer.

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