Inclusion complex between beta-cyclodextrin and phenylphosphonicdiamide as novel bio-based flame retardant to epoxy: Inclusion behavior, characterization and flammability

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highlights

- A bio based flame retardant (IC) was synthesized via inclusion behavior
- Impact of IC on thermal stability and flame retardancy of EP was investigated
- Flame retardant mechanism of EP/IC was proposed

graphical abstract

abstract

The aim of this work was to study the impact of inclusion complex (IC) between β cyclodextrin (β CD) and N, N' diamyl p phenylphosphonicdiamide (P MA) on the thermal stability and flame retardancy of epoxy resin (EP) IC was synthesized via inclusion process and characterized by ¹H nuclear magnetic resonance (NMR), X ray dif fraction (XRD), differential scanning calorimeter (DSC) and scanning electron microscopy with X ray microanal ysis (SEM EDS) ¹H NMR was used to identify the mole ratio of β CD/P MA in IC, shown that their mole ratio was 1:0.5 The inclusion complex (IC) was proposed to be a char promoter in EP via a combination of the properties of β CD and P MA during the combustion. By incorporating the IC, the flame retardancy of EP was expected to be improved Thermal gravimetric analysis (TGA) showed that the thermal stability of IC was better than those of P MA and physical mixture of β CD and P MA (PM) The impact of IC and PM on thermal stability and flame retardancy in EP were studied by TGA, limiting oxygen index (LOI), UL94 and cone calorimeter tests The heat and smoke releases of EP/IC were suppressed compared with those of EP and EP/PM

1. Introduction

Thermoset polymer, epoxy resin is applied in numerous fields such as transportation, aircraft and electronic&electrical industrials (EE)

owing to its high performances on mechanical, electrical and chemical resistance [1,2]. However, the intrinsic flammable property of epoxy resin brings fire hazard to these applications [3]. In last 10 years, the development of halogen free eco friendly flame retardant polymer composite from bio based compounds is becoming a new trend [4]. Many bio based compounds were used to develop novel flame retardant for polymers, such as phytic acid [5], natural polysaccharide [6], cyclodextrin [7–9], deoxyribonucleic acid (DNA) [10] from animal and protein [11].

Cyclodextrins (CDs) are synthetic substances obtained from the enzymatic degradation of polysaccharides (starch) [12]. The structures of CDs are truncated cone shaped with a hollow cone cavity. The hydrophobic cavity of CDs is able to form non covalent host guest inclusion complex that has been widely used in diverse research fields such as pharmacology, food and agriculture [13–16]. The size and dimension of the cavity differed with the number of glucose unit. α , β and γ CD are the well known members of CDs, which have 6, 7 and 8 glucose unit, respectively [17]. Among these CDs, β CD is the most frequently studied in order to form host guest inclusion complex [16,18]. In recent reports, β CD and its derivatives were applied in flame retardant thermoplastic polymer materials [4]. For instance, intumescent flame retardant grouped by ammonium polyphosphate, melamine and β CD increased LOI value of poly (lactic acid) (PLA) from 19.8% to 34.2% with 20 wt% loading [19]. The residue of β CD was increased by > 10 wt% at 400 °C after the inclusion behavior with triphenyl phosphite (TPP) [20]. J. Alongi et al. reported flame retardants containing cyclodextrin nanosponges and phosphorus compounds. These flame retardant showed high yield of char residue under nitrogen (N_2), whereas the initial thermal decomposition occurred at low temperature (< 200 °C) [21]. In the above studies, β CD exhibited high charring ability in polymer materials under acid condition.

In current researches, halogen free flame retardants are widely developed to replace some halogenated flame retardants to epoxy resin [22,23]. Many researchers, such as Döring [24–26], Scharrel [27–30], Yang [31–33], Hu [34–37] and Toldy [38–40], have reported numerous types of phosphorous nitrogen containing flame retardants to epoxy resin. 9,10 dihydro 9 oxa 10 phosphaphenanthrene 10 oxide (DOPO) and its derivatives are the most reported flame retardants in epoxy resin. Döring et al. [24] reported five novel rod shape DOPO derivatives to D.E.N. 438™ epoxy resin. A good flame retardant epoxy system was shown as phosphorous percentage reached 1 wt%. DOPO based aminic hardeners were reported to epoxy resin by Thompson [41] and Yao [42]. Scharrel et al. [30] linked DOPO structure to a star shaped aliphatic molecule to synthesize novel flame retardant named as DOPP and DOPI. LOI of carbon fiber reinforced RTM 6/DOPI was increased evidently from 33.2% to 47.7% compared with reference sample. Both Bourbigot [43] and Yang [33] reported a good synergistic effect between polyhedral oligomeric silsesquioxanes (POSS) based structures and phosphorous containing flame retardants in epoxy resins. Wang et al. [44] reported a series of phenylphosphonate based flame retardants which endowed epoxy resin with V 0 rating in UL 94 test at 5 wt% flame retardant loading. N, N' diamyl p phenylphosphonicdiamide (P MA) was one phenylphosphonate based flame retardant which was reported in our previous report [45]. The flammability of bi functional diglycidyl ester of bisphenol A based epoxy (EP) was reduced after the addition of P MA. 5 wt% loading of P MA increased LOI of EP from 22% to 32% and remarkably decreased peak of heat release rate (pHRR) of EP from 1079 kW/m² to 469 kW/m². However, the thermal stability of EP/P MA was lowered compared with EP due to the low thermal stability of P MA.

Under the consideration that β CD acted as nature charring precursor and P MA acted as acid source, the aim of this work was to study the impact of inclusion complex (IC) between β CD and P MA on flame retardancy of EP compared with that of PM in EP. Moreover, the inclusion behavior was expected to improve thermal stability of P MA. The inclusion behavior was characterized by diverse methods: ¹H NMR, XRD, DSC and SEM EDS. TGA was used to study the impact of inclusion

behavior on thermal properties of β CD and P MA. Meanwhile, the impact of PM and IC on thermal properties of EP was also studied. The flammability of EP, EP/PM and EP/IC was investigated by limiting oxygen index (LOI), UL 94 and cone calorimeter tests. The flame retardant mechanism was proposed to explain the results of flame retardancy in this work.

2. Experimental

2.1. Materials

Phenylphosphonic dichloride (PPDCI, 90%), amylamine (MA, 98%), β CD, diethyl ether and triethylamine (TEA) were purchased from Sigma Aldrich Corporation and used without any further purification. All the chemical reagents used in this work were anhydrous. Deionized water was obtained from IMDEA materials laboratory. Epoxy resin (Brand name, EPC) was purchased from Faserverbundwerkstoffe® composite technology. Epoxy equivalent of EPC was 0.54. The curing agent, 4,4 diaminodiphenylsulfone (DDS) was supplied by Sigma Aldrich Corporation.

2.2. Synthesis of flame retardant P MA (N, N' diamyl p phenylphosphonicdiamide)

The synthesis of P MA was synthesized according to our previous work [45] the structure of P MA was showed in Fig. 1c. MA (0.21 mol) and TEA (0.2 mol) were dissolved in 200 ml diethyl ether at 0–5 °C in three neck flask. Then into the flask was added dropwise the mixture of PPDCI (0.1 mol) and diethyl ether (100 ml). The whole mixture reacted at 0–5 °C for 2 h and then the reaction continued at room temperature (RT) for 5 h. After the reaction finished, the solid liquid mixture was filtered off to remove triethylamine hydrochloride salt and the filtrate was evaporated under vacuum to obtain the crude product of P MA. The product was purified by washing with deionized water for three times. P MA: yellow liquid at 25 °C; yield, 90%; ¹H NMR (DMSO *d*₆): δ (ppm), 7.8–7.4 (Ar H, 5H); 5.8 (=CH, 2H); 5.1–4.9 (=CH₂, 4H); 3.4 (—CH₂—, 4H); ¹³C NMR (DMSO *d*₆): δ (ppm), 137.8, 135.5, 134.3, 131.2, 130.6, 127.8, 114.2, 42.4; ³¹P NMR (DMSO *d*₆): δ (ppm), 19.8.

2.3. Preparation of inclusion complex (IC) of β CD and P MA

β CD (11.35 g, 0.01 mol) was dissolved into 115 ml deionized water to form β CD aqueous solution at 65 °C. Then P MA (2.96 g, 0.01 mol) was added dropwise into the prepared aqueous solution at 65 °C and stirred for 2 h. After cooling for 24 h at room temperature, the rough product of IC was obtained after the filtration of the solid liquid mixture. Finally, IC was obtained after washing the rough product by acetone for three times. The yield of IC was 85%. In order to compare with IC, the physical mixture (PM) of β CD and P MA was prepared. β CD and P MA was mixed with molar ratio: 1:0.5 though solving the two chemicals in dimethylsulfoxide (DMSO) at room temperature. Then DMSO was evaporated by rotating evaporating machine to get PM.

2.4. Preparation of epoxy composites of EP, EP/PM and EP/IC

Reference epoxy (EP) was prepared as below: curing agent DDS was dissolved into EPC at 130 °C with stirring; the mixture of EPC/DDS was poured into pre heated polytetrafluoroethylene (PTFE) molds. The curing temperature profile was set as 180 °C for 2 h and 200 °C for 1 h.

The preparations of EP/PM and EP/IC followed the same procedure as below. Firstly certain amounts (2, 4 and 6 wt%) of PM or IC were dispersed into EPC at 170 °C. Then the curing agent DDS was dissolved into EPC/PM and EPC/IC mixture at 130 °C. After DDS was totally dissolved by EPC, the final mixture was poured into pre heated polytetrafluoroethylene (PTFE)

Fig. 1. ^1H NMR spectra of β -CD (a), IC (b) and P-MA(c); enlarged ^1H NMR spectra of a, b and c; f, the structure of β -CD.

molds. The curing temperature profile was the same with that of EP. The formula of EP, EP/PM and EP/IC were listed in Table 1.

2.5. Characterization

2.5.1. Nuclear magnetic resonance (NMR)

NMR measurements were carried on Varian Mercury AS400 spectrometer which was operated at 400 MHz. ^1H NMR spectra was collected at room temperature by using tetramethylsilane (TMS) as internal standard and DMSO as the solvent.

2.5.2. Fourier transform infrared spectrum (FTIR)

The FTIR spectra of β CD, P MA, PM of them and IC were measured with Nicolet iS50 infrared spectrometer. KBr pellet pressing method was used to prepare the samples. The scanning number and resolution of setting up were 16 and 4 cm^{-1} .

2.5.3. Wide angle X ray diffraction (WAXD)

PANalytical X ray diffractometer was employed to perform WAXD measurements. The specific parameters for the measurements were as below: Ni filtered Cu K α radiation source with $\lambda = 1.544\text{ \AA}$; scanning

range of $3^\circ/2\theta$ with a step size of 0.017° ; 45 kV and 40 mA of the voltage and current respectively.

2.5.4. Differential scanning calorimeter (DSC)

DSC (TA, Q200) measured the heat flow thermograms of β CD, PM, IC and P MA under nitrogen atmosphere. The solid sample pan was in use. 4–6 mg of samples was examined at a heating rate of $10^\circ\text{C}/\text{min}$ during temperature range of $25\text{--}350^\circ\text{C}$.

2.5.5. Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis (TA, Q50) was performed under nitrogen atmosphere. The sample gas purge flow was $90\text{ mL}/\text{min}$. $7.5 \pm 0.5\text{ mg}$ of samples was tested over a temperature range from room temperature to 700°C at heating rate of $10^\circ\text{C}/\text{min}$.

2.5.6. Scanning electron microscopy with X ray microanalysis (SEM EDS)

SEM EDS (Zeiss, EVO MA15) measurement was conducted to analyze the morphology and distribution of element of β CD and IC. The samples were coated with a fine gold layer under 20 kV condition.

2.5.7. Limiting oxygen index (LOI)

LOI tested on oxygen index meter (FTT) according to ASTM D2863 97. The precision of LOI test was $\pm 0.2\%$. The sample size was $130 \times 6.5 \times 3.2\text{ mm}^3$.

2.5.8. UL 94 test

The Vertical burning tests were carried on a UL 94 Horizontal/Vertical Flame Chamber (FTT, UK) and sheet dimensions of the samples were $130 \times 13 \times 3.2\text{ mm}^3$ according to ASTM D3801.

2.5.9. Cone calorimeter test

Cone calorimeter tests were carried out according to the ISO 5660 1 standard with a cone calorimeter (FTT). Square specimens ($100 \times 100 \times 4\text{ mm}^3$) were irradiated at a heat flux of $50\text{ kW}/\text{m}^2$.

Table 1

The formulations, Tg and results of LOI of EP, EP/PM and EP/IC.

Sample	EPC/DDS (wt%)	PM (wt%)	IC (wt%)	Tg ($^\circ\text{C}$)	LOI (%)
EP	100	–	–	195	22.0
EP/PM(2 wt%)	98	2	–	194	24.5
EP/PM (4 wt%)	96	4	–	190	24.8
EP/PM (6 wt%)	94	6	–	189	25.5
EP/IC (2 wt%)	98	–	2	194	26.5
EP/IC (4 wt%)	96	–	4	190	26.8
EP/IC (6 wt%)	94	–	6	190	26.8

Table 2

Chemical shifts and its variations for the protons of β -CD, P-MA in the free state and in the inclusion complex.

Proton	σ (ppm)			
	β -CD	P-MA	IC	$\Delta\sigma$ ($\sigma_{\text{complex}} - \sigma_{\text{free}}$)
H-3	3.642	–	3.644	0.002
H-5	3.566	–	3.568	0.002
H-6	3.666	–	3.667	0.001
H'-1	–	0.790	0.809	0.019
H'-(2,3)	–	1.171	1.195	0.024
H'-4	–	1.351	1.362	0.011
H'-5	–	2.686	2.712	0.026
H'-6	–	7.703	7.708	0.005
H'-7,8	–	7.431	7.427	0.004

3. Results and discussion

3.1. Characterization of IC

3.1.1. ^1H NMR analysis

As one of the frequently used tools to characterize the structure of inclusion complex, ^1H NMR spectroscopy is insightful to show the changes of chemical shift (σ) of H protons on host and guest structures caused by the inclusion behavior [46–49]. The chemical shifts of H 3, H 5 and H 6 protons inside the β CD cavity (Fig. 1f) would show changes when P MA is embedded into the cavity. Fig. 1 showed the ^1H NMR spectra of β CD(a), IC(b) and P MA(c). Table 2 listed the σ of β CD, IC and P MA. $\Delta\sigma$ were calculated as the differences between σ of IC (σ_{complex}) and σ of β CD or IC (σ_{free}).

After the inclusion behavior, σ of H 3, H 5 and H 6 protons inside the β CD cavity shifted to upfield by 0.002, 0.002 and 0.001 ppm, respectively. All σ of H protons of P MA showed upfield shifts. The $\Delta\sigma$ of β CD and P MA in Table 2 indicated that P MA was evidently embedded into the cavity of β CD. Furthermore, $\Delta\sigma$ of H' 1, H' (2, 3), H' 4 and H' 5 on alkyl chain of P MA were 0.019, 0.024, 0.011, 0.026 ppm respectively, which were much further than $\Delta\sigma$ of H' 6 and H' (7, 8) on benzene ring

of P MA. It indicated that inclusion behavior might occur mainly between the alkyl chains of P MA and β CD cavity.

In addition, the integral area ratios of H 1 of β CD (A_1), H' benzene ring (A_2) and H' (1, 2, 3 and 4) (A_3) was 7:9:2.5, indicating that one P MA molecule was included with two β CD molecules. It meant the molar ratio between β CD and P MA was 1:0.5 in IC. The possible IC structures were showed in Fig. 2a and b. The inclusion behavior occurred between alkyl chain and β CD was considered to start from the wide side of β CD owing to the higher σ of H 3 and H 5 than that of H 6.

3.1.2. FTIR analysis

FTIR spectroscopy is a common measurement to characterize the molecular structure due to the infrared vibrations of functional groups. In this study, FTIR was used to show the inclusion behavior between β CD and P MA. Fig. 3 showed the FTIR spectra of β CD, IC, PM and P MA.

The assignments of main IR peaks of β CD were: 3380 cm^{-1} ($-\text{OH}$); 2828 cm^{-1} ($\text{C}-\text{H}$ of $-\text{CH}_2$ and $-\text{CH}$); $1080, 1028\text{ cm}^{-1}$ ($\text{C}-\text{O}-\text{C}$); 1159 cm^{-1} ($\text{C}-\text{C}$); $756, 707\text{ cm}^{-1}$ (skeleton of β CD). The assignments of main IR peaks of P MA were: 3200 cm^{-1} ($\text{N}-\text{H}$); 3055 cm^{-1} ($\text{C}-\text{H}$ of benzene ring); $2956, 2863\text{ cm}^{-1}$ ($\text{C}-\text{H}$ of $-\text{CH}_3$); $2932, 2875\text{ cm}^{-1}$ ($\text{C}-\text{H}$ of $-\text{CH}_2$); $1627, 1542, 1469$ and 1436 cm^{-1} ($\text{C}-\text{C}$ of benzene ring); 1180 cm^{-1} ($\text{P}=\text{O}$); 1129 cm^{-1} ($\text{C}-\text{N}$); $1025, 730\text{ cm}^{-1}$ ($\text{P}-\text{N}$); 924 cm^{-1} ($\text{P}-\text{N}-\text{C}$); $752, 696\text{ cm}^{-1}$ (benzene ring). Compared with the spectra of β CD and P MA, both the spectra of PM and IC showed the similar outline with the spectrum of β CD rather than that of P MA. The reasons were that the molar ratio of IR groups of β CD was much higher than that of IR groups of P MA and the IR peaks of β CD overlapped with most of IR peaks of P MA.

Nevertheless, the spectra of PM and IC showed specific differences. The frequency ranges of $3100\text{--}2700\text{ cm}^{-1}$, $1550\text{--}1350\text{ cm}^{-1}$ and $810\text{--}660\text{ cm}^{-1}$ were enlarged and shown as a, b and c, respectively in Fig. 3. In Fig. 3a, the peaks at 2863 and 2875 cm^{-1} of P MA showed at the same peak position in spectra of PM, while these two peaks were very weak and almost did not show in spectra of IC. In Fig. 3b, the peak at 1436 cm^{-1} in spectra of P MA did not shift in the spectra of

Fig. 2. The possible structures of IC (a and b).

Fig. 3. FTIR spectra of β -CD, IC, PM and P-MA.

PM, while it shifted to 1442 cm^{-1} in spectra of IC. In addition, the peak of P MA at 696 cm^{-1} simply combined with the peak of β CD at 707 cm^{-1} in spectra of PM, showing as a broad peak in Fig. 3c. These two peaks merged to be one at 703 cm^{-1} in the spectrum of IC. Fig. 3a indicated the change of chemical environment of alkyl chain of P MA. Meanwhile, Fig. 3b and c showed the changes of chemical environment of benzene ring of P MA. All the above changes indicated that P MA was successfully embedded into the cavity of β CD.

3.1.3. XRD analysis

X ray diffraction (XRD) is a widely used method to study the inclusion complex. In general, the diffraction peaks of host and guest molecules are changed after the inclusion behavior [49–51]. In this study, the comparison of XRD spectra as shown in Fig. 4(a) was done between

β CD and IC. Fig. 4(a) showed the XRD spectra of β CD under two conditions: one was the spectra after treated by inclusion procedure with out P MA; the other one was the spectra without any treatment. The diffraction spectra of β CD before and after treatment showed that the crystalline phase of β CD was changed due to the re crystallization. The main peak at 12.3° was getting sharper and the intensities of peaks at 8.8 and 10.5° were higher, indicating that the crystal of β CD was changed after the treatment. In comparison with the above two XRD spectra of β CD, IC showed a totally different spectra. The diffraction peaks was broader and the number of peaks was less than those of β CD before and after the treatment. Three main peaks were at 5.8 , 11.6 and 18.1° . These differences indicated that new compound formed during inclusion procedure. It was another evidence to verify the success of inclusion behavior.

Fig. 4. a XRD spectra of β -CD and IC; b, DSC curves of β -CD, IC, PM and P-MA under N_2 .

Fig. 5. SEM and element distribution mapping images of β -CD (a, c) and IC (b, d).

3.1.4. DSC analysis

Seen from the heat flow curves in Fig. 4(b), β -CD showed a broad endothermic peak around 125 °C caused by the dehydration reaction. There was no other peak appeared before 300 °C. As to P MA, there was no significant peak showed before 180 °C. Compared with β -CD and P MA, the physical mixture (PM) of them showed a different DSC curve. The dehydration peak of β -CD was still existed, while the decomposition temperature shifted to the low temperature around 253 °C. The reason was that the acid compounds formed during thermal decomposition of P MA were able to accelerate the decomposition of β -CD. In contrast, IC showed totally different curve compared with the above three samples. Firstly, the endothermic peak around 125 °C was weakened remarkably, indicating the dehydration effect of IC was weaker than those of β -CD and PM. The decomposition of IC occurred at around 280 °C, which was higher than that of PM, but lower than that of β -CD. This information showed that IC was not physically mixed during the inclusion procedure, indicating that the inclusion behavior between β -CD and P MA was succeeded.

3.1.5. Morphological analysis

SEM EDS is a useful tool to characterize the morphology and detect the element types on the sample surface [52]. After the inclusion behavior, the morphologies of β -CD and IC are supposed to be different with each other. In addition, phosphorous element should be detected only in IC.

Fig. 5a and b were SEM images of β -CD and IC, respectively. Compared with the large particle size and shape of β -CD, IC showed small and irregular lamella particles. Fig. 5c and d were the element

distribution mapping of C, O and P of β -CD and IC respectively. The mapping areas of β -CD and IC were marked respectively in the SEM images with white frame. From Fig. 5, there was no detection of phosphorous element in β -CD, while phosphorous element was obviously showed in IC and the distribution was kept the same state with those of C and O elements. These results further indicated the inclusion behavior between β -CD and P MA was succeeded.

Fig. 6. TGA and DTG curves of β -CD, IC, PM and P-MA under N_2 .

Fig. 7. TGA and DTG curves of EP, EP/PM (6 wt%) and EP/IC (6 wt%) under N₂ (a) and under air (b).

3.2. Impact of IC on thermal stability of EP

The thermal stability of β CD, P MA, PM and IC were compared by TGA under nitrogen (N₂). Fig. 6 showed the TGA curves of β CD, P MA, PM and IC under N₂. The thermal and thermo oxidative stability of EP, EP/PM and EP/IC were studied by TGA under N₂ and air respectively. Fig. 7 showed TGA and DTG curves of EP, EP/PM (6 wt%) and EP/IC (6 wt%) under N₂ (a) and under air (b). The TGA data of EP, EP/PM (2, 4 and 6 wt%) and EP/IC (2, 4 and 6 wt%) were shown in Table 3.

In Fig. 6, the initial decomposition temperature of β CD was around 270 °C, while flame retardant P MA showed remarkable weight loss from 100 °C to 200 °C. On DTG curve, β CD showed one peak around 320 °C. P MA showed a broad low decomposition peak on DTG curve. PM started to decompose since around 220 °C, while the initial thermal decomposition of IC occurred above 250 °C. Compared with β CD, thermal decomposition of PM showed two peaks on DTG curves. One peak was at 257 °C, the other peak was at 320 °C. The first peak was caused by the decomposition of P MA and then the decomposition of β CD was induced. In contrast, IC showed one step decomposition. The decomposing peak appeared at 270 °C which was also different with that of β CD. Both PM and IC showed higher char residue amounts compared with β CD and P MA at 600 °C. The residue of PM was 16.8%, while those of β CD and P MA were 8.1 and 2.2%, respectively. The increase of residue amount for PM and IC was due to the catalytic effect of acid compounds produced from the thermal decomposition of P MA. IC showed a higher residue amount (25.9%) than that of PM, indicating that the catalytic effect of P MA was enhanced via inclusion behavior. Above analysis illustrated that IC showed enhanced thermal stability compared with PM and P MA; IC showed better charring ability compared with β CD, PM and P MA.

Table 3

TGA data of EP, EP/PM and EP/IC under N₂ and air.

Samples	T _{d5%} ^a (°C)		T _{max1} ^b (°C)		T _{max2} ^c (°C)		T _{max3} ^d (°C)		Residue (700 °C, %)	
	N ₂	Air	N ₂	Air	N ₂	Air	Air		N ₂	Air
EP	394	392	427	412	–	580	–	–	14.4	0
EP/PM (2 wt%)	386	378	328	333	418	411	573	–	17.9	0
EP/PM (4 wt%)	370	362	330	329	414	406	570	–	19.9	0
EP/PM (6 wt%)	344	327	322	323	408	405	559	–	21.6	0
EP/IC (2 wt%)	390	386	423	411	–	573	–	–	17.8	0
EP/IC (4 wt%)	380	376	415	406	–	570	–	–	21.5	0
EP/IC (6 wt%)	380	366	412	406	–	560	–	–	21.5	0

^a T_{d5%} meant the temperature when the weight loss was 5%.

^b T_{max1} meant the first peak T at maximum decomposition rate.

^c T_{max2} meant the second peak T at maximum decomposition rate.

^d T_{max3} meant the third peak T at maximum decomposition rate.

In Fig. 7(a), the thermal decomposition of EP went through one stage decomposition. T_{d5%} and T_{max} of EP were at 394 °C and at 427 °C respectively. The residue amount was 14.4% at 700 °C. With regard to EP/PM, PM showed significant impact on thermal decomposition of EP. T_{d5%} was lowered greatly along with the rising of PM loading in EP. For instance, T_{d5%} of EP/PM (6 wt%) was at 344 °C which was 50 °C lower than that of EP. From 300 °C to 550 °C, EP/PM went through two stage decomposition. The first DTG peak was considered to be induced by thermal decomposition of P MA in EP. T_{max1}s of EP/PM (2, 4 and 6 wt%) were at 328, 330 and 322 °C respectively. The second DTG peaks of EP/PM were the main decomposition peak. T_{max2}s of EP/PM were at lower temperature than T_{max1} of EP, showing that the addition of PM accelerated the decomposition of EP. T_{max2} of EP/PM (6 wt%) was at 408 °C which was 19 °C lower than T_{max1} of EP. The residue amounts were increased from 14.4% to 17.9, 19.9 and 21.6% at 2, 4 and 6 wt% loading of PM in EP. Compared with PM, the impact of IC was not as significant as that of PM on thermal decomposition of EP. T_{d5%}s of EP/IC (2, 4 and 6 wt%) were at 390, 380 and 380 °C respectively, which were higher than those of EP/PM at the same loading. DTG curves of EP/IC showed one peak as well as that of EP. T_{max1}s of EP/IC were between those of EP and EP/PM at the same loading. T_{max2} of EP/IC (6 wt%) was at 412 °C. The residue amounts of EP/IC (2, 4 and 6 wt%) were 17.8, 21.5 and 21.5% at 700 °C which were close to that of EP/PM with the same loading. Above all, the thermal stability of EP/IC was between those of EP/PM and EP. The residue amounts of EP/IC were close to EP/PM.

In Fig. 7(b), thermal oxidative behavior of EP showed a two stage TGA curve under air. T_{d5%} of EP was at 392 °C. T_{max1} and T_{max2} of EP were at 412 and 580 °C, respectively. There were almost no residues remained at 700 °C for all samples. EP/IC showed two stage TGA curves under air as well as EP. T_{d5%}s of EP/IC (2, 4 and 6 wt%) were at 386, 376 and 366 °C, respectively, which were lower than that of EP. This result was induced by the thermal oxidation of IC. T_{max1} and T_{max2} of EP/IC shifted to lower temperatures. The maximum mass loss rate of the first peak on DTG curve of EP/IC was lower than that of EP. With regard to the second DTG peak, the maximum mass loss rate of EP/IC was higher than that of EP as shown in Fig. 7(b). It showed that the residues of EP/IC were not as stable as those of EP which were formed. At 700 °C, no residue was left to EP/IC. Unlike EP and EP/IC, EP/PM showed three stage TGA curves as shown in Fig. 7(b). T_{d5%} of EP/PM showed at lower temperatures in comparison with EP/IC. This trend increased as the PM loading was increased in EP. For example, T_{d5%} of EP/PM (6 wt%) was 327 °C which was 39 °C lower than that of EP/IC (6 wt%). T_{max1} of EP/PM (2, 4 and 6 wt%) showed at relatively low temperatures (333, 329 and 323 °C respectively) as well, caused by the thermal oxidation of P MA in EP. The acidic compounds from P MA were able to accelerate the thermal oxidation of EP matrix. The second and third peaks on

DTG curves of EP/PM were quite similar with those peaks on DTG curves of EP/IC as shown in Fig. 7(b). Above all, TGA results under air mainly showed that IC and PM showed a different impact on the thermal oxidative behavior of EP at the initial stage.

Overall, the thermal stability of P MA was improved and the residue amount of β CD was increased via inclusion process according to the comparison between IC and PM. The thermal stability of EP/IC was improved compared with EP/PM with the same loading. Both EP/IC and EP/PM showed a higher residue amount compared with EP under N_2 , but no residue was kept at 700 °C under air as well as EP.

3.3. Impact of IC on flame retardancy of EP

3.3.1. LOI and UL 94 tests

LOI and UL 94 tests were two typical small scale tests to evaluate the flammability of polymer materials. LOI test measured the minimum concentration of oxygen in a flowing mixture of oxygen and nitrogen that can support flaming combustion of polymer materials. Table 1 showed LOI results of EP, EP/PM and EP/IC. The addition of PM increased LOI of EP from 22% to 24.5% at 2 wt% loading. When the loading rose to 6 wt%, LOI of EP/PM was 25.5%. The results showed that PM reduced the flammability of EP and this impact was proportional with the loading of PM. LOI of EP/IC (2 wt%) was 26.5% which was 2 units higher than that of EP/PM (2 wt%). The increase of LOI was not proportional with the IC loading in EP. LOI of EP/IC (4 and 6 wt%) were 26.8% respectively which was very close to that of EP/IC (2 wt%). The flammability of EP/IC was lower compared with those of EP and EP/PM in LOI test. UL 94

test was used to determine the fire performance for the samples. As well as EP, both EP/PM and EP/IC showed no rating in UL 94 test. The results showed that PM and IC did not show a direct impact on the improvement of self extinguishing ability of EP at a loading range from 2 to 6 wt%. The possible reason might be corresponding to the mass loading of P MA used in epoxy matrix that was too low to reduce fire propagation ability of EP. Since the mass loading of P MA in PM and/or IC was 11.5 wt%, at the loading range from 2 to 6 wt% of PM or IC in EP, the mass loading of P MA in EP was only ranged from 0.23 to 0.69 wt%. Such loadings of P MA may be too low for EP to pass some classification in UL94 test.

3.3.2. Cone calorimeter test

By using heat release equipment, as the cone calorimeter, the different parameters (such as material ignitability, heat release and smoke production) can be measured in the same instrument, in a manner generally relevant to real fires [53]. Fig. 8 illustrated the characteristic curves of EP, EP/PM (6 wt%) and EP/IC (6 wt%) under 50 kW/m² from cone calorimeter test: a, HRR vs time; b, weight vs time; c, THR (total heat release) vs time and d, TSP (total smoke production) vs time. The related data from this test were collected in Table 4. TTI meant time to ignition and pHRR meant peak of HRR. Fig. 9 showed the carbon monoxide (CO)/carbon dioxide (CO₂) ratio curves of releasing rate of EP, EP/PM (6 wt%) and EP/IC (6 wt%).

Compared with TTI of EP (at 59 ± 5 s), TTIs of EP/PM and EP/IC were at earlier time. For instance, TTIs of EP/PM (6 wt%) and EP/IC (6 wt%) were at 54 ± 3 s and 50 ± 2 s respectively. In the condition of same

Fig. 8. a, HRR vs time; b, mass loss vs time; c, THR (total heat release) vs time and d, TSP (total smoke production) vs time curves of EP, EP/PM and EP/IC from cone calorimeter test.

Table 4

The data from cone calorimeter test of EP, EP/PM and EP/IC at a heat flux of 50 kW/m².

Sample	TTI ^a (s)	pHRR ^b (kW/m ²)	THR ^c (MJ/m ²)	EHC ^d (kJ/kg)	TSP ^e (m ²)	Residue (wt%)
EP	57 ± 5	1108 ± 155	96.2 ± 1.3	22.0 ± 0.5	31.9 ± 3.1	12.1 ± 3
EP/PM (2 wt%)	56 ± 2	970 ± 100	84.2 ± 0.5	21.8 ± 0.3	27.1 ± 1.8	14.5 ± 3
EP/PM (6 wt%)	54 ± 3	840 ± 63	78.5 ± 6.4	20.8 ± 0.4	24.6 ± 0.5	17.6 ± 2
EP/IC (2 wt%)	55 ± 2	905 ± 65	73.0 ± 3.5	21.0 ± 0.3	21.0 ± 1.6	17.1 ± 2
EP/IC (6 wt%)	50 ± 2	541 ± 50	68.8 ± 3.0	19.8 ± 0.3	21.2 ± 0.2	19.2 ± 3

^a TTI was time to ignition.

^b pHRR was peak of heat release rate.

^c THR was total heat release.

^d EHC meant effective heat of combustion.

^e TSP meant the total smoke production.

loading of IC or PM in EP, TTI of EP/IC showed at earlier time than that of EP/PM. A shift of TTI to the earlier time in EP/PM and EP/IC would be related to the thermal decomposition of PM and IC in EP.

HRR curves of EP, EP/PM (6 wt%) and EP/IC (6 wt%) were shown in Fig. 8(a). Compared with EP and EP/PM, a clear shoulder peak appeared on the main HRR peak of EP/IC (6 wt%). The shoulder peak was at 64 ± 5 s with a HRR value of 350 ± 50 kW/m². Both pHRRs of EP/IC and EP/PM were lower than that of EP. EP/IC (2 and 6 wt%) showed pHRR values of 905 ± 65 and 541 ± 50 kW/m², respectively. The pHRR of EP/IC (6 wt%) showed 51% reduction compared with that of EP. pHRRs of EP/PM (2 and 6 wt%) were 970 ± 100 and 840 ± 63 kW/m², respectively, showing 12% and 24% reduction compared with that of EP. Clearly, the reductions of EP/IC were higher than that of EP/PM at the same loading. THR of EP was reduced after the addition of PM or IC. THR of EP/PM (6 wt%) decreased to 78.5 ± 6.4 MJ/m², while that of EP/IC (6 wt%) decreased to 68.8 ± 3.0 MJ/m². EHC is the heat of combustion which would be expected in a fire where incomplete combustion takes place [54]. From Table 4, EHC values of EP/IC (2 and 6 wt%) were 21.0 ± 0.3 and 19.8 ± 0.3 MJ/kg, respectively. Compared with EP and EP/PM, EP/IC showed a relatively lower EHC value in this test. The reduction of EHC indicated that a possible flame retardant mechanism occurred in the gas phase. In Fig. 8(b), the mass loss rates of EP/PM (6 wt%) and EP/IC (6 wt%) were lower compared with that of EP. The residue amounts of EP/IC (2 and 6 wt%) were 17.1 ± 2 and 19.2 ± 3 wt% which were higher than those of EP and EP/PM.

In addition, both the addition of IC and PM decreased TSP of EP, as shown in Fig. 8(d). TSP of EP/IC was lower than that of EP/PM. TSP of EP/PM (2 and 6 wt%) were 27.1 ± 1.8 m² and 24.6 ± 0.5 m², respectively, which were lower than that of EP (31.9 ± 3.1 m²). EP/IC (2 wt%) showed TSP of 21.0 ± 1.6 m² which was 6.1 m² lower than that of EP/PM (2 wt%). In Fig. 9, CO/CO₂ release ratio of EP/IC and EP/PM were

Fig. 9. The CO/CO₂ ratio curves of release rate of EP, EP/PM (6 wt%) and EP/IC (6 wt%).

higher than that of EP, indicating incomplete combustion behavior occurred during the combustion of EP/IC.

Overall, IC showed better effect on improving the flame retardancy of EP compared with PM. The LOI of EP was increased from 22.0% to 26.8% after the addition of IC. In cone calorimeter test, the heat release and smoke production of EP/IC were evidently suppressed compared with EP and EP/PM. However, the CO/CO₂ release ratio of EP/PM and EP/IC was higher than that of EP, indicated a possible flame retardant mechanism occurred in the gas phase by adding PM and IC in EP.

3.4. Flame retardant mechanism

On the base of the results in Section 3.3, clearly the IC showed better flame retardancy to EP compared with PM; moreover, possible flame retardant mechanism was proposed as follows. On the one side, the residue amount of EP/IC (6 wt%) was 7.1% which was higher than that of EP in cone calorimeter test; the char residue of EP/IC was intumescence. This type of char residue was able to interrupt the gaseous (e.g. volatiles, air, etc.) and heat transfer during the combustion. These results indicated a flame retardant mechanism occurred in the condensed phase by incorporating the IC into EP. Possibly, when IC thermal decomposed, the host molecule (β CD) acted as char precursor due to the polyol structure; the guest structure (P MA) acted as acid source which were able to accelerate the char formation. On the other side, the fact that is the decreased EHC values of EP/IC (6 wt%) and its increased ratio of CO/CO₂ compared with those EP indicated IC acted in the gas phase to reduce the flammability of EP. Based upon the conclusions in the previous report [44,45], phenylphosphonate based flame retardant showed effectively flame inhibition during the combustion of EP. However, such mechanism might not be the dominant flame retardant mechanism in EP/IC due to the fact that the weight percent of P MA in EP/IC (6 wt%) was only 0.69 wt%.

4. Conclusions

In this work, IC was synthesized via the inclusion behavior between β CD and P MA and characterized by ¹H NMR, FTIR, XRD, DSC, and SEM EDS methods. The inclusion ratio of β CD and P MA was 2:1 and possible inclusion structures were proposed according to the results of ¹H NMR spectra. The results of TGA under N₂ showed that the charring ability of IC was higher than those of PM. The char residue of PM was 16.8%, while that of IC was 25.9% at 600 °C. The initial thermal decomposing temperature of IC was increased remarkably above 250 °C which was improved compared with PM.

The flame retardancy of EP/IC was lower compared with that of EP and EP/PM. LOI of EP/PM (2 wt%) was 24.5%, whereas that of EP/IC (2 wt%) was 26.5%. In cone calorimeter test, pHRR of EP/IC (6 wt%) were 541 kW/m² which was lower by 36% compared with EP/PM (6 wt%). In addition, TSP of EP/IC was 6.1 m² lower than that of EP/PM at 2 wt% loading. The reduction of EHC values and increased CO/CO₂ release rate ratio showed that IC acted in the gas phase during the

burning of EP/IC. Flame retardant mechanism of IC in EP was proposed in both condensed and gas phases.

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