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Novel Multifunctional Organic−Inorganic Hybrid Curing Agent with High Flame-Retardant Efficiency for Epoxy Resin

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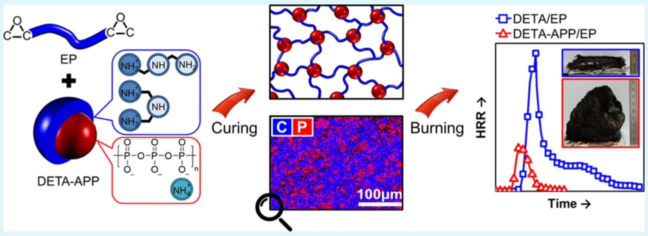

ABSTRACT: A novel multifunctional organic−inorganic hybrid was designed and prepared based on ammonium polyphosphate (APP) by cation exchange with diethylenetriamine (DETA), abbreviated as DETA-APP. Then DETA-APP was used as flame-retardant curing agent for epoxy resin (EP). Curing behavior, including the curing kinetic parameters, was investigated by differential scanning calorimetry (DSC) and X-ray photoelectron spectroscopy (XPS). The flame retardance and burning behavior of DETA-APP cured EP were also evaluated. The limiting oxygen index (LOI) value of DETA-APP/EP was enhanced to 30.5% with only 15 wt % of DETA-APP incorporated; and the UL-94 V-0 rating could be easily passed through with only 10 wt % of the hybrid. Compared with DETA/EP, the peak-heat release rate (PHRR), total heat release (THR), total smoke production (TSP), and peak-smoke production release (SPR) of DETA-APP/EP (15 wt % addition), obtained from cone calorimetry, were dropped by 68.3, 79.3, 79.0, and 30.0%, respectively, suggesting excellent flame-retardant and smoke suppression efficiency. The flame-retardant mechanism of DETA-APP/EP has been investigated comprehensively. The results of all the aforementioned studies distinctly confirmed that DETA-APP was an effective flame-retardant curing agent for EP.

KEYWORDS: *ammonium polyphosphate, hybrid, epoxy resin, curing, flame retardance*

1. INTRODUCTION

Epoxy resins (EP), also known as polyepoxides, are a class of reactive prepolymers or polymers with epoxide groups, which have long been considered as one of the most extensively applied thermosetting polymers standing out with many attractive properties, such as good heat and solvent resistance, satisfactory electrical and mechanical properties, remarkable adhesive strength, ease of curing and processing, etc.[1−3] Nevertheless, the flammability is one of the main drawbacks to restrict its applications in many areas involved in transportation, construction, and electric and electronic industries. As one of the important commercial flame retardants, halogen compounds have been widely used due to their high-efficiency and broad applicability in EP; however, the numerous toxic products and smoke produced during combustion are the main drawbacks of this kind of flame retardants.[4,5] Moreover, the harmfulness of these flame retardant additives to the natural ecosystem and human health should be the top priority in both research and industry application fields. Therefore, ever-increasing attention has been paid to the field of halogen-free flame retardants, where desired flame retardance and high thermal stability are needed.[6−10] In the last decades, plentiful efforts have been made to improve the flame retardance of EP, such as the development of flame-retardant monomers,[5,11−15] curing agents,[16−21] and additives.[22−27] Among them, intumescent flame retardants (IFRs) have drawn more attention, because of their unmatched low-toxicity, low-smoke, and high-efficiency.[28−31] A typical intumescent system should cover an acid source (the dehydration catalyst for char formation), a carbon source (the carbonization agent), and a gas source (the blowing agent).[4,32,33] The carbonization agent will be charred under the catalytic effect of the acid agent, and the carbon will be expanded by the blowing agent to develop a voluminous, stable carbonaceous layer on the surface of the material.[34] As a common IFR, APP can provide the acid source and the gas source simultaneously, making it a frequently studied flame retardant in recent years. Numerous researchers have applied it to an EP system.[35,36] Even though APP could bring satisfactory results on many substrates, it mostly was used as the additive into the materials. Under these conditions, the problem of compatibility between additive and materials matrix easily arose. Moreover, without a char-forming agent, APP could hardly perform well as a desirable IFR.[4,37,38] Herein, an attempt to introduce a carbon source into APP was carried out. Shao and Wang reported a series of modified APP by cation

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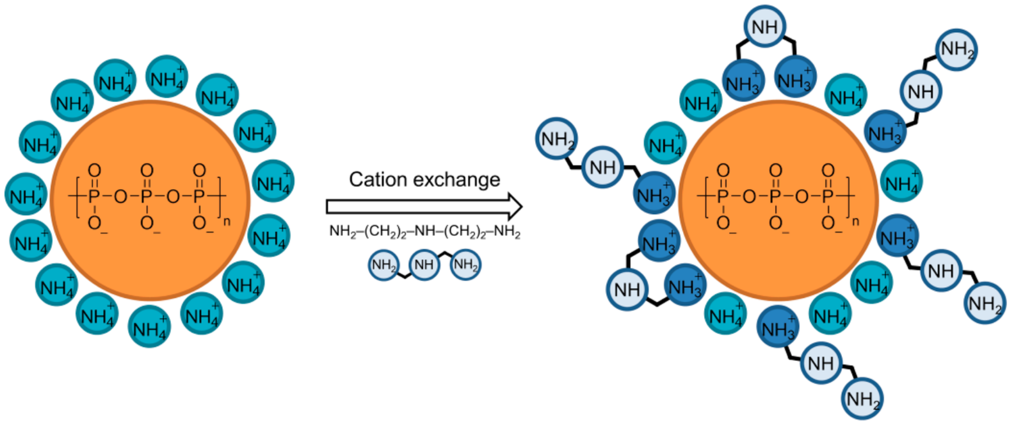
Scheme 1. Synthesis Route of DETA-APP



exchange with different alicyclic and aliphatic amines, and successfully applied them in polypropylene (PP) as the monocomponent polymeric intumescent flame retardant, resulting in desired flame retardance.[39−41] In addition, EP are almost useless in an uncured state. This indicated that the value of the curing agent to it is unambiguous. Moreover, amine hardeners were a kind of highly efficient and frequently researched curing agents. Considering the problems mentioned above, a special EP curing agent containing APP as the reactive flame-retardant unit was designed and synthesized through similar cation exchange.

In this manuscript, through the cation exchange reaction between APP and DETA, APP was modified successfully as an organic−inorganic hybrid flame retardant, named DETA-APP. In addition, unreacted primary amines, as well as the secondary amines, could act as the multireactive sites with the epoxy groups on the surface of DETA-APP, making it a multifunctional flame-retardant curing agent. The organic shell of the hybrid brings the curing ability, while the inorganic polyphosphates core endows the excellent flame retardance. Therefore, a series of flame-retardant EPs cured by DETA-APP were prepared and studied. The results of LOI, UL-94, Cone calorimetry, and thermogravimetry (TG) revealed that the DETA-APP could be a highly effective flame-retardant curing agent for EP. The flame retardance and smoke suppression of the cured EPs have been greatly enhanced. In conclusion, a plausible mechanism was also proposed.

2. EXPERIMENTAL SECTION

2.1. Materials. Commercial APP (form II) was supplied by Changfeng Fire Retardants Co., Ltd. (Sichuan, China) and used as received; diethylenetriamine (DETA, AR, 99.0%) and ethanol (AR, 99.7%) were purchased from Kelong (Sichuan, China); diglycidyl ether of biphenol A (E-44) was provided by Lanxing Resin Co., Ltd. (Lanzhou, China) and used as received.

2.2. Preparation of DETA-APP. The procedure for preparing DETA-APP was illustrated as Scheme 1, according to the previous literature.[39−41] The reaction occurred on the surface of APP, covering the APP core with an aliphatic multiamine shell. A certain ratio of ethanol and water (800:30 in volume) was transferred into a three-neck flask and stirred under nitrogen (N_2) atmosphere. Half an hour later, DETA (55 g) and APP (100 g) were added into the flask respectively with stirring. After 4 h of reaction at 90 °C in N_2 atmosphere, the mixture was cooled down to room temperature and filtrated to remove the solvent. Then, the white residues were dried overnight in a vacuum oven at 80 °C after washing with excessive ethanol (115 g, 74.2% yield).

2.3. Curing. The original EP sample was obtained by traditional thermal curing as reference. EP was steadily stirred at 100 °C in vacuum until no bubbles emerged. DETA (mass ratio, as shown in Table 1) was then added into it with discontinuous stirring. When the mixture became homogeneous, it was poured rapidly into a prepared mold. After turning gelatinous at room temperature, another 2 h of reaction at 100 °C was conducted for the curing of EP.

Table 1. Formulation of Cured Original and Flame-Retardant EP

Samples	E-44 (g)	DETA (g)	DETA-APP (g)	Content of P (%) calculated	Content of P (%) tested
DETA/EP	93.0	7.0			
DETA-APP 7.5/EP	92.5		7.5	1.78	1.71
DETA-APP 10/EP	90.0		10.0	2.38	2.39
DETA-APP 12.5/EP	87.5		12.5	2.98	2.74
DETA-APP 15/EP	85.0		15.0	3.57	3.44

A flame-retardant epoxy sample cured by DETA-APP was prepared in a similar procedure with a little modification, as follows. First, the prepared DETA-APP was dried in a vacuum oven at 80 °C for 10 h to remove trace water. A certain mass ratio of EP and DETA-APP, as listed in Table 1, was mixed in a one-neck flask. To obtain a homogeneous mixture, the blend was steadily stirred at 165 °C in vacuum until no bubbles emerged. Then the viscous liquid was transferred quickly into a preheated mold (165 °C) in an oven. After 20−30 h of curing at 165 °C, the flame-retardant samples were prepared. The phosphorus contents of each cured EP were obtained from inductively coupled plasma atomic emission spectroscopy (ICP-AES).

2.4. Characterization. Fourier transform infrared (FTIR) spectra were recorded between 400 and 4000 cm^{-1} (KBr pellets) at room temperature on a Nicolet FTIR 170SX infrared spectrophotometer (Nicolet, America).

^1H (400 MHz) and ^{13}C NMR (100.6 MHz) spectra were obtained with a Bruker AVANCE AV II-400 NMR instrument (Bruker, Germany), and D_2O was used as the solvent.

Scanning electronic microscopy (SEM, JEOL JSM 5900LV, Japan) was utilized to observe the surficial morphology of the testing samples at the accelerating voltage of 20 kV, including the surface of the DETA-APP hybrid and the burning residues of cured EP with or without DETA-APP after cone calorimetry. The energy dispersive X-ray spectrometer (EDX) was equipped for the elemental analysis in the surface scanning model.

The elemental contents of carbon (C), nitrogen (N), and hydrogen (H) in DETA-APP were measured by elemental analysis (EA) on a CARLO ERBA1106 instrument (Carlo Erba, Italy). The phosphorus (P) contents of APP, DETA-APP, and cured EPs were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, IRIS Advantage, TJA solution). The testing samples for APP and DETA-APP were prepared as follows: about 6 mg of the powder sample was dissolved into 10 mL of concentrated hydrochloric acid in a 100 mL flask for 48 h; then a certain amount of distilled water was added into the flask to a constant volume (100 mL). The testing samples for cured EPs were prepared through another method. About 15 mg of each polymer was completely combusted under sufficient oxygen atmosphere; then the volatiles were absorbed by 25 mL of 0.001 mol L^{-1} $KMnO_4$ aqueous solution and then diluted to 100 mL with deionized water.

The curing kinetics of DETA/EP and DETA-APP/EP was carried out on a TA Instruments Q200 differential scanning calorimeter (DSC) equipped with a thermal analysis data station, operating at a heating rate of 5, 10, and 20 °C min^{-1} under nitrogen atmosphere.

The flame retardance of the testing materials was evaluated by limited oxygen index (LOI) values and an Underwriter Laboratory 94 vertical burning test (UL-94 V). LOI values were measured on a HC-2C oxygen index meter (Jiangning, China) with a sheet dimension of 130 mm × 6.5 mm × 3.2 mm according to ASTM D2863-97. The UL-94 V burning rating was conducted on a CZF-2 instrument (Jiangning, China) according to ATSM D 3801 testing procedure. The samples were made with a size of 130 mm × 13 mm × 3.2 mm. The combustion behavior of the samples was measured with a cone calorimeter (Fire Testing Technology, U.K.). The samples with the dimension of 100 mm × 100 mm × 1.6 mm were exposed to a radiant cone at a heat flux of 35 kW m^{-2}.

Thermogravimetric analysis (TG) was obtained on TG 209 F1 (NETZSCH, Germany). The samples (about 5 mg) were heated from 40 to 700 °C at a rate of 10 °C min^{-1} under the nitrogen flow of 50 mL min^{-1}.

XPS spectra were recorded by a XSAM80 (Kratos Co, UK), using Al *Kα* excitation radiation (*hν*-1486.6 eV). The assigned spectral peaks were ascertained through the ThermoFisher scientific XPS database (http://www.lasurface.com/xps/index.php).

3. RESULTS AND DISCUSSION

3.1. Preparation of DETA-APP. *3.1.1. FTIR.* As shown in Figure 1, compared to the FTIR spectra of APP, some new absorption peaks at 2971 cm^{-1}, 2907 cm^{-1}, and 1533 cm^{-1} appeared after the cation exchange, which corresponded to the characteristic stretching absorption of $-CH_2-CH_2-$ and the bending absorption of $-NH_3^+$ respectively, revealing the formation of DETA salt ($R-NH_3^+$) instead of ammonium salt (NH_4^+).[41] The peaks located at 3400−3030 cm^{-1} were ascribed to the asymmetric stretching vibration of NH_4^+.

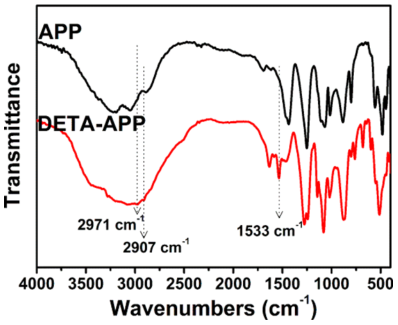


Figure 1. FTIR spectra of APP and DETA-APP.

3.1.2. ^1H and ^{13}C NMR. To further determine the structure of DETA-APP, ^1H and ^{13}C NMR measurements were performed and the results are shown in Figure 2. In the ^1H NMR spectra of APP, there was no other characteristic peak except the resonance peak at 4.8 ppm, corresponding to the absorbed water. Meanwhile there was no apparent peak of NH_4^+, which might be ascribed to the rapid alternation reaction between the deuterium (D_2O) and hydrogen in NH_4^+. After the cation exchange of APP, two new resonance peaks at 2.91 and 3.07 ppm appeared in the ^1H NMR spectra of DETA-APP, which were attributed to the protons of $-CH_2-$ next to $-NH_3^+$ and $-CH_2-$ next to -NH- in the DETA segment. However, compared with the spectra of DETA and its physical mixture with APP, there was an obvious shift of the characteristic peaks from 2.65 and 2.73 ppm of DETA to 2.91 and 3.07 ppm, respectively, meaning the existence of the $NH_3^+-CH_2-CH_2-NH-CH_2-CH_2-NH_3^+$ structure in DETA-APP.

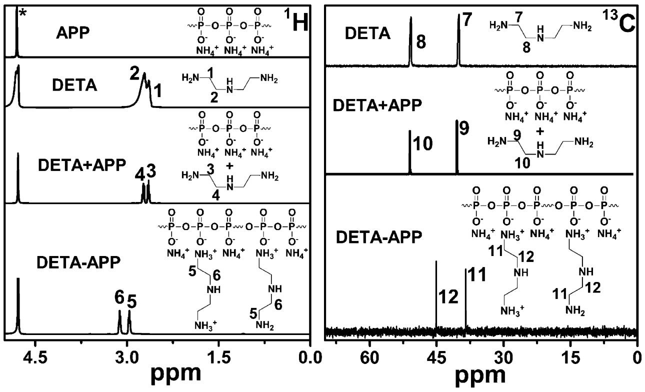


Figure 2. ^1H and ^{13}C NMR spectra of APP, DETA, and DETA-APP; for comparison, a physical mixture of DETA and APP (DETA+APP) was also recorded.

The corresponding ^{13}C NMR spectra were also obtained and displayed similar results, as illustrated in ^1H NMR spectra. All the aforementioned results demonstrated the successful synthesis of DETA-APP.

3.1.3. The surface morphologies. SEM testing was taken in microscale to ensure the success of the reaction. The surface morphologies of the original and modified APP were shown in Figure 3. An obvious change between APP and DETA-APP on the surfaces could be easily found. The commercial APP particles exhibited a smooth surface. After cation exchange by DETA, serious aggregation was generated. Because of the organic modification, intermolecular or interparticles interactions between DETA-APP were formed through H-bonding and ion-dipole forces, and then led to particles aggregation and fusion. It was also an intensive suggestion of the successful modification of APP by DETA.

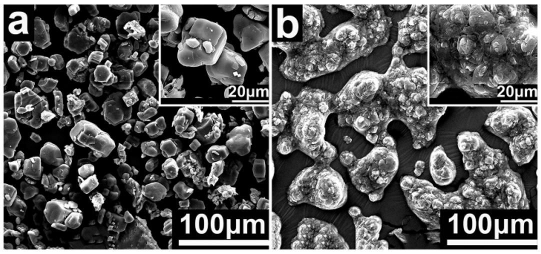


Figure 3. SEM images of II-APP (a) and DETA-APP (b).

3.1.4. The elemental contents. EA and the ICP testing are often applied to distinguish the element content changes of carbon (C), nitrogen (N), hydrogen (H), as well as phosphorus (P) in compounds. The corresponding data were listed in Table 2. After cation exchange with DETA, the elemental contents of C, N, and H in DETA-APP all increased more or

Table 2. Elemental Contents of APP and DETA-APP

	C (%)	N (%)	H (%)	P (%)
II-APP	0.1	13.0	4.2	28.9
DETA-APP	13.7	15.0	6.0	23.8

less. Particularly after the cation exchange, the content of C rose greatly from 0.1 to 13.7%, in which the trace content of C in original APP might be ascribed to the residual surfactants or absorbed CO_2. Conversely, P in DETA-APP was obviously decreased from 28.9 to 23.8% compared to APP. Both remarkably demonstrated the successful reaction between DETA and APP.

3.2. Curing process of DETA-APP/EP. Aiming to find the reason why the curing reaction of DETA-APP/EP was so difficult, compared with DETA/EP, the curing kinetics of each have been studied by nonisothermal DSC testing, as shown in Figure 4. The reaction activation energy (E_a), reaction order (n), and pre-exponential factor (A) were calculated by the Kissinger equation[42] combined with the Crane equation,[43] as shown in Table 3. E_a is a parameter denoting how difficult the curing reaction is. n indicates the influence of concentration on the reaction rate. A is a constant that depends only on the reaction nature, regardless of the reaction temperature and the concentration of substances in the system. The Flynn—Wall—Ozawa equation[44] was also applied to verify the E_a value. The three methods were applied to calculate the kinetic parameters without any assumption about a conversion-dependent equation.[11] Each curing process according to the n-order reaction was hypothesized. Through comparing the results calculated from both the Kissinger and Flynn—Wall—Ozawa methods, it could be found that the E_a values obtained from the two methods were much closer to each other, which supports the hypothesis of n-order reaction in the DETA/EP and DETA-APP/EP curing process. The curing reactions of DETA/EP as well as DETA-APP/EP were both consistent with the n-order kinetic model, where the n values were equal to 0.91 and 0.94, respectively. The n value of DETA-APP/EP was a little higher, consistent with its slower curing rate. Considering the E_a, the value of DETA-APP/EP was higher, and would decrease a little with the increased curing agent addition.

Table 3. Kinetic Parameters of the Curing Reaction with Different Additions of DETA-APP

		DETA/EP	DETA-APP 10/EP	DETA-APP 15/EP
Kissinger[d] and Crane eq[e]	E_a[a]	60.59	113.10	109.47
	ln A[b]	15.35	26.97	25.87
	n[c]	0.91	0.94	0.94
Flynn—Wall—Ozawa eq[f]	E_a[a]	63.39	114.41	110.95

[a] The reaction activation energy in kJ mol^{-1}. [b] Pre-exponential factor. [c] Reaction order. [d] Kissinger equation: $\ln(\beta/(Tp \times Tp)) = \ln((A \times R)/E_a) - (E_a/R) \times (1/Tp)$. [e] Crane equation: $\ln \beta = -(E_a/nR) \times (1/Tp) + C$. [f] Ozawa equation: $\ln \beta + 1.0516 \times (E_a/R) \times (1/Tp) = C'$.

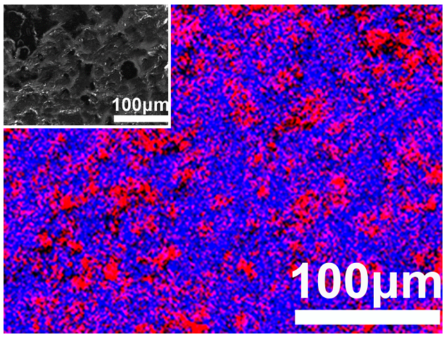


Figure 5. Merged EDX elements mapping image (P in red signal and C in blue signal) of DETA-APP 15/EP.

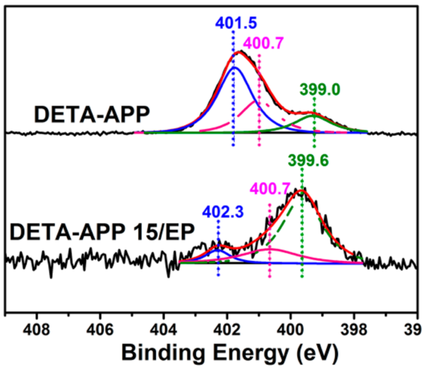


Figure 6. XPS spectra (N_{1s}) of DETA-APP and DETA-APP 15/EP.

As mentioned before, DETA-APP was an effective curing agent for EP. But as a solid additive in an epoxy resin matrix, the problem of dispersion is much more serious. Moreover, in this situation, how did it work? Therefore, EDX and XPS testing were conducted respectively, as shown in Figure 5 and Figure 6. EDX element mapping showed the spatial distribution of P and C in epoxy resin. The P signal in red represented the polyphosphate core, while the C signal in blue was the representation of epoxy chains and the DETA shell of the hybrid. It showed that the particle sizes were about 10—30 μm, indicating that DETA-APP was well-distributed in the epoxy

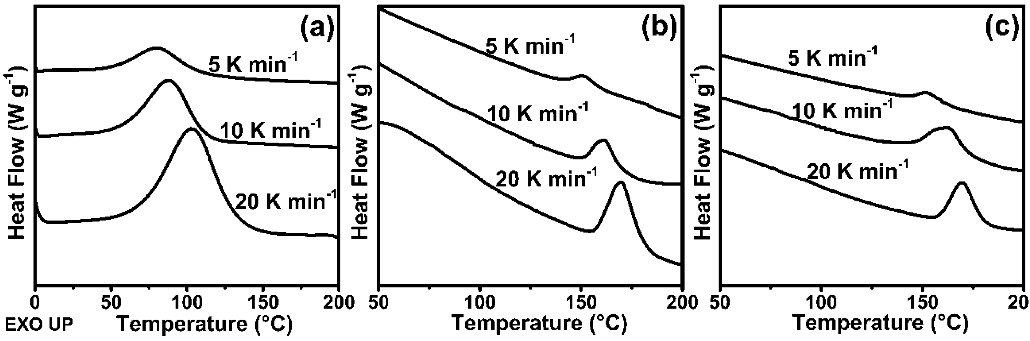
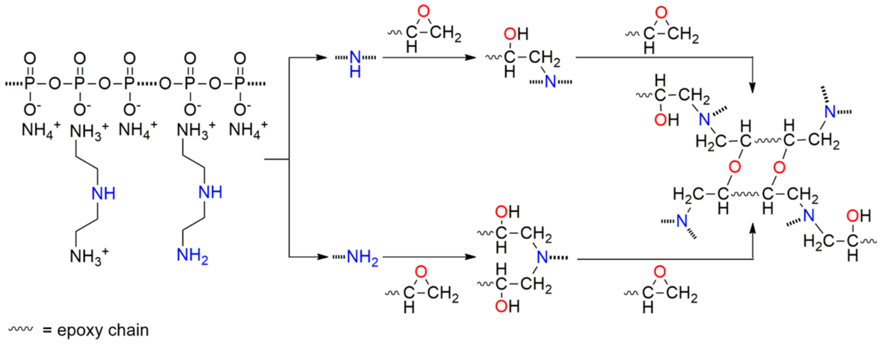


Figure 4. DSC curves of DETA/EP (a), DETA-APP 10/EP (b), and DETA-APP 15/EP (c) with different heating rates (5, 10, and 20 K min^{-1}).

Scheme 2. Curing Process of DETA-APP for EP



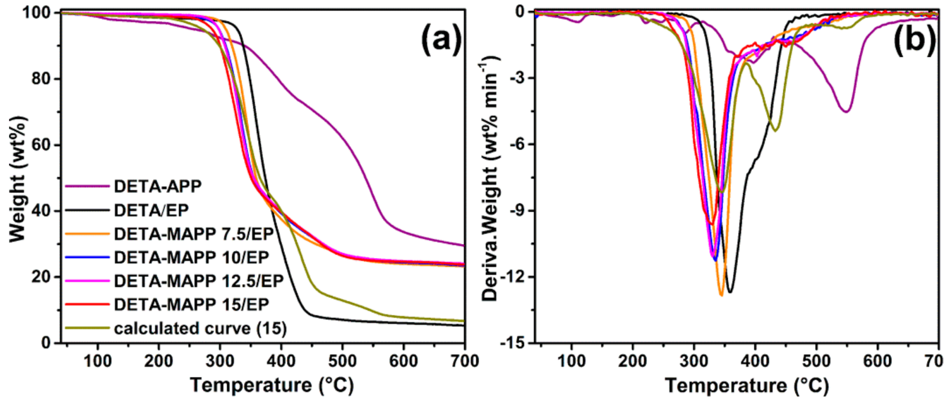


Figure 7. TG (a) and DTG (b) curves of DETA-APP, DETA/EP, DETA-APP 7.5/EP, DETA-APP 10/EP, DETA-APP 12.5/EP, and DETA-APP 15/EP and the calculated curve of DETA-APP 15/EP composites at a heating rate of 10 °C min^{-1} under N_2 atmosphere.

resin. Then, the corresponding N_{1s} spectra of DETA-APP and DETA-APP 15/EP, obtained from XPS testing, were shown in Figure 6. In the N_{1s} spectra of DETA-APP, the binding energies at 401.5 and 402.3 eV were both ascribed to the NH_4^+. Moreover, the characteristic binding energy of $-NH_3^+$ did not change (400.7 eV). But the binding energy peak of N in the $-NH_2$ and C−NH−C groups at 399.8 and 399.0 eV, respectively, almost disappeared after the curing reaction. Meanwhile, a new peak at 399.6 eV appeared, attributed to the binding energy of the N atom in the tertiary amino group. This indicated that, at a certain temperature, the epoxy group was opened by −NH− or $-NH_2$, resulting in the generation of a hydroxyl group and a tertiary amino group. The newly formed hydroxyl groups could further react with another epoxy group. Thus, cross-linked networks with both tertiary amino and ether linkages could be obtained from the surface of DETA-APP. The curing process was shown in Scheme 2.

3.3. Thermogravimetric analysis. Figure 7 showed the TG and derivative thermogravimetric analysis (DTG) curves of DETA-APP, DETA/EP, and DETA-APP/EP under the N_2 atmosphere, and the corresponding data were presented in Table 4. DETA-APP/EP exhibited two degradation processes ranging from 250 to 390 °C and from 390 to 520 °C, respectively. But there was only one degradation step for DETA/EP ranging from 350 to 450 °C. For DETA-APP, the thermal decomposition was more complex with several decomposition ranges. As shown in Figure 7(a), around 100 °C, a small weight loss appeared, corresponding to the vaporization of the moisture absorbed onto the salt surface. When the temperature increased to 200 °C, the DETA-APP began decomposition, where NH_3 and H_2O molecules released.

Table 4. Thermogravimetric Properties of Cured EPs

	$T_{5\%}$[a] (°C)	T_{max} (°C) 1	T_{max} (°C) 2	Residue (%)
DETA-APP	276.9	396.4	556.7	33.0
DETA/EP	328.0	358.7		5.3
DETA-APP 7.5/EP	309.5	344.4	443.9	23.2
DETA-APP 10/EP	298.3	334.7	449.0	23.5
DETA-APP 12.5/EP	297.9	329.4	456.7	24.1
DETA-APP 15/EP	287.2	329.1	459.7	23.8
calculated data	272.4	334.9	432.4	6.8

[a] The temperature where 5 wt % of weight was lost.

With the temperature rising, it was going to decompose with an increasing degradation rate, especially at 556.7 °C, where the rate reached the highest point.

As shown in Figure 7(a), the initial decomposition temperatures ($T_{5\%}$, defined as the temperature where 5 wt % of weight lost) of DETA-APP/EP samples were all lower than the neat EP, and it would continually decrease with the increasing of DETA-APP addition. Such a decrease of $T_{5\%}$ was a characteristic phenomenon of P-containing EP, which was due to the fact that both the C−N (305 kJ mol^{-1}) and P−O (335 kJ mol^{-1}) bonds are less stable than the C−C bond (347 kJ mol^{-1}).[21] It could be deduced that the C−N bond broke first; then the P−O and C−C bonds ruptured at a relatively higher temperature. The shift in degradation temperatures might be attributed to the fact that the cured EPs could form phosphoric and polyphosphoric acids at a relative lower temperature; then the produced acids accelerated the decomposition (dehydration and carbonization) of the EPs to form a stable char or aromatic precursors. So in the high temperature region, the second decomposition ranges of DETA-APP/EP samples were all higher than the calculated value.

For the DETA/EP, the only weight loss occurred in the region from 300 to 450 °C. The residue at 700 °C was only 5.3%, almost nothing left. Noticeably, the residues of DETA-APP/EP samples were 23−24%, much higher than the value of DETA/EP and calculated one. Generally, with increasing incorporation of DETA-APP into epoxy resin, the content of phosphorus in the cured epoxy systems increased. Interestingly, in this manuscript, the decomposition residue of all cured samples in Figure 7 and Table 4 was around 23%. This indicated that DETA-APP with only 7.5 wt % addition was enough to form the thermal stable residue during the degradation of the cured epoxy resin, which could play a positive role in flame retardance in the condensed phase. With further addition of DETA-APP, however, the increasing amount of DETA-APP might not be able to form the thermally stable residue effectively. Otherwise, the left DETA-APP would decompose easily during its combustion, making it have a negative role on the residual content increasing during the TG test.

Moreover, the factual decomposed rate was largely slower than the calculated rate at high temperature. These results illustrated that, during the thermal degradation of DETA-APP/EP, phosphorus groups decomposed at a relatively lower temperature, and then accelerated the decomposition and catalyzed carbonization of EP to form a heat-resistant char layer, retarding the mass loss rate of the EP at high temperatures. Nitrogen, serving as blowing agent and char-reinforcing component, could lead to the production of intumescent chars which would protect the underlying combustible substrate to get good flame retardance.[45]

3.4. Flame retardance.

Flame-retardant performances of cured EP were shown in Table 5. The LOI value of DETA/EP was 21.5%. However, when the curing agent was changed to DETA-APP, the LOI value of the flame-retardant EP improved. Furthermore, with increasing the DETA-APP content, the LOI value further increased gradually to 30.5% with 15 wt % of DETA-APP. However, the increase of LOI was nonlinear with the content of DETA-APP, which could be explained by the fact that 7.5 wt % DETA-APP as the flame retardant was already enough to form the cross-linking char as a protective layer during degradation. This also could be found from the TG results, in which the residues did not obviously change with the increasing addition. Moreover, with 10 wt % of DETA-APP, the corresponding materials could easily pass the V-0 rating, suggesting that the DETA-APP was a kind of highly efficient flame-retardant curing agent for EP.

Table 5. Flammability Tests of Cured EP with Different Contents of DETA-APP

		UL-94	
Samples	LOI (%)	Rating	Dripping
DETA/EP	21.5	NR	No
DETA-APP 7.5/EP	27.5	V-1	No
DETA-APP 10/EP	28.5	V-0	No
DETA-APP 15/EP	30.5	V-0	No

The Cone calorimeter is an effective method to study the materials' flammability. The corresponding data of the Cone calorimeter testing for a material were the important parameters to estimate its flame retardant performance.[46,47] As shown in Figure 7 and Table 6, the total heat releases (THRs) of DETA-APP cured EP were 12.7 MJ m^{-2} with 10 wt % DETA-APP addition and 11.4 MJ m^{-2} with 15 wt % addition. However, for DETA/EP, THR is much higher (55.2 MJ m^{-2}), more than 4 times of the former. Furthermore, the peak of the heat release rate (PHRR) of DETA-APP/EP was only 310.5 kW m^{-2} with just 15 wt % DETA-APP addition. Compared with DETA/EP (980.4 kW m^{-2}), there was a great dropping when DETA-APP was incorporated.

Table 6. Cone Calorimeter Data of DETA/EP and DETA-APP/EP

	DETA/EP	DETA-APP 10/EP	DETA-APP 15/EP
TTI (s)	40	35	32
THR (MJ m^{-2})	55.2	12.7	11.4
PHRR (kW m^{-2})	980.4	388.0	310.5
TTPHRR (s)	85	60	55
FIGRA (kW m^{-2} s^{-1})	11.5	6.5	5.6
TSR (m^2 m^{-2})	1894.7	586.9	397.9
TSP (m^2)	16.7	5.2	3.5
Peak SPR (m s^{-1})	0.203	0.196	0.142
Residue (%)	8.9	59.2	66.5

Based on the HRR curves, the fire growth rate (FIGRA) has been calculated to assess the fire hazard of the composite according to the following equation:[48,49]

$$\mathrm{FIGRA} = \mathrm{PHRR}/\mathrm{TTPHRR}$$

where TTPHRR denotes the time to PHRR. Generally, a lower FIGRA value indicates that the time to flashover is delayed, which means there is enough time to evacuate for people in distress and/or reach for the fire extinguishers.[48,50] For DETA/EP, the FIGRA was 11.5 kW m^{-2} s^{-1}. However, the FIGRA values of the DETA-APP cured EP were only 6.5 kW m^{-2} s^{-1} and 5.6 kW m^{-2} s^{-1} with the DETA-APP addition of 10 and 15 wt %, respectively, indicating that the introduction of DETA-APP increased the fire safety of the materials.

Smoke produced during fire has long been considered as the most important factor which directly puts people to death by suffocation and/or inhalation of the toxic gases on site. Thus, smoke suppression is very important for flame-retardant polymers. The curves of smoke production rate (SPR) and total smoke production (TSP) were shown in Figure 8(c) and (d), and the corresponding data were also listed in Table 6. Compared to DETA/EP, the TSPs of DETA-APP 10/EP and DETA-APP 15/EP had dropped from 16.7 m^2 to 5.2 m^2 and 3.5 m^2, respectively. Moreover, the SPR values of DETA-APP 15/EP decreased to 0.142 m^2 s^{-1} (only 70% of that of DETA/EP). Both results illustrated that DETA-APP played a positive role in restraining the production of smoke. It could be described as follows: during combustion, the phosphorus-containing curing agent facilitated the carbonization of EP, which would further promote the formation of char. The cross-linked carbonaceous shields were difficult to be taken away by the evolving gases and then form an intumescent barrier. As a consequence, the decrease of soot volatized during fire led to much more burning residues.

Compared to DETA/EP, both the time to ignition (TTI) and TTPHRR of DETA-APP/EP samples became much

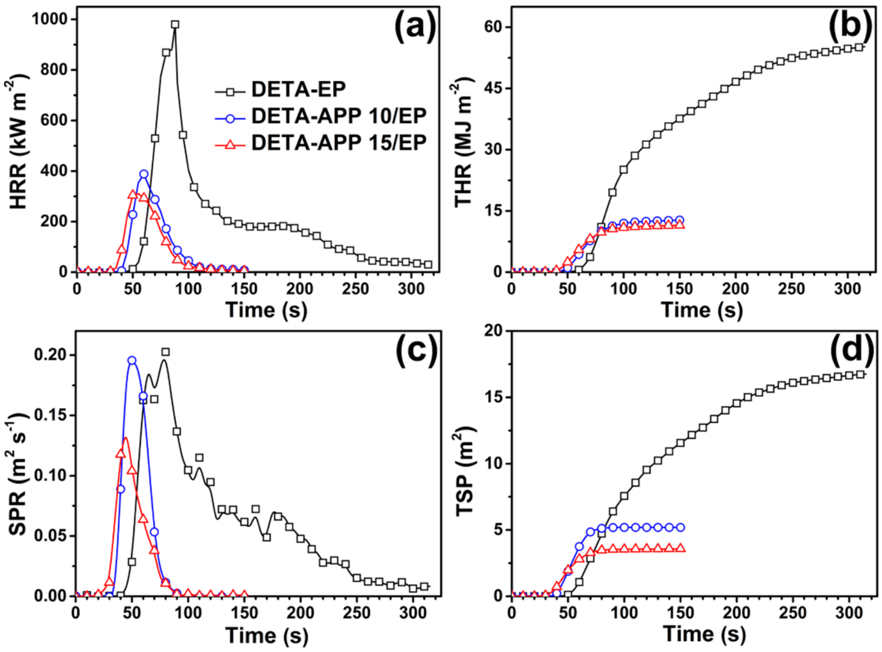


Figure 8. Total heat release (THR) (a), heat release rate (HRR) (b), total smoke production (TSP) (c), and smoke production rate (SPR) (d) plots of DETA/EP, DETA-APP 10/EP, and DETA-APP 15/EP.

shorter, which should be ascribed to the early decomposition of DETA-APP at the beginning of ignition, in accord with the results from TGA.

The digital photos and SEM images of the burning residues after Cone calorimetry were shown in Figure 9. For the DETA/EP sample, there was almost no residue left after combustion. On the contrary, an extremely intumescent char layer was formed for the DETA-APP cured samples after burning, which could prevent the underlying materials from heat and oxygen, and limit the volatilization of the combustible gases feeding back to the burning zone, thus weakening the flammability of the materials. Moreover, as observed from the SEM images of the samples, a more compact char layer would be formed with more incorporation of the hybrid curing agent.

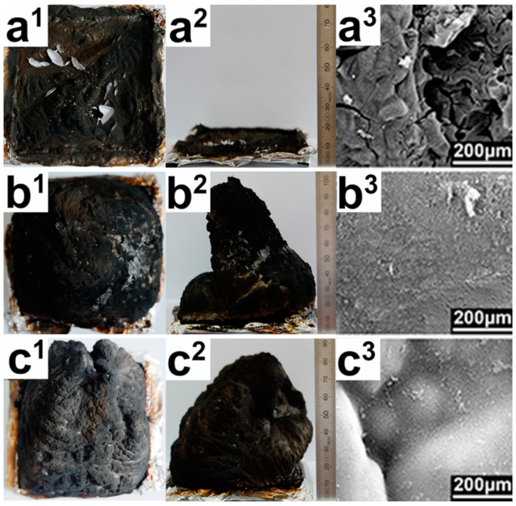


Figure 9. Digital photographs and SEM images of burning residues of DETA/EP (a), DETA-APP 10/EP (b), and DETA-APP 15/EP (c) obtained after Cone calorimetry; superscript 1 represents the top view, 2 denotes the side view of the residue, and 3 illustrates the SEM images (×500).

3.5. Flame-retardant mechanism. To understand how DETA-APP worked on enhancing the flame retardance of EP, the chemical constitutions of the charring residue after decomposition in nitrogen were investigated by XPS. Figure 10 illustrated the C_{1s}, N_{1s}, O_{1s}, and P_{2p} spectra of DETA-APP/EP, which were obtained at room temperature (RT), 330 °C (T_{max}), and 600 °C in a muffle for 3 min under N_2 atmosphere, respectively.

The binding energy for C_{1s} at around 284.5 eV, as shown in Figure 10(a), was attributed to the C−H and C−C bonds in aliphatic and aromatic groups, which could still be detected at 600 °C. When the temperature reached 330 °C, a new binding energy peak at 285.0 eV emerged, which corresponded to the C=C carbon bond formed via dehydration and further carbonization. The binding energy peak at 286.2 eV was ascribed to the C−O−C, C−OH, and C−N groups, which disappeared at 600 °C consequently.

As revealed in Figure 10(b), the changes of N_{1s} were also obvious. With the temperature increasing to 330 °C, the characteristic binding energy peaks at 399.6, 401.5, and 402.3 eV disappeared, which should be ascribed to tertiary amino and NH_4^+ groups, respectively, resulting in the release of NH_3, H_2O, and volatiles containing a C−N structure. These nonflammable gases could act as the blowing agents for the intumescent char and dilute the flammable gases as well as oxygen. However, the $-NH_3^+$ group located at 400.7 eV showed better thermal stability than the NH_4^+ group and still existed at 330 °C. Another noticeable new peak at 399.7 eV was formed, which was assigned to the P−N−P group, indicating the synergistic effect between N and P in DETA-APP. Figure 10(c) is the related O_{1s} spectra. Two peaks at 532.2 and 533.1 eV were ascribed to −O− in C−O−C, C−O−P, P−O−P, and/or C−OH groups, existing all along the decomposition process. A new peak at 531.1 eV appeared with the increasing temperature and was assigned to P=O in phosphoric and

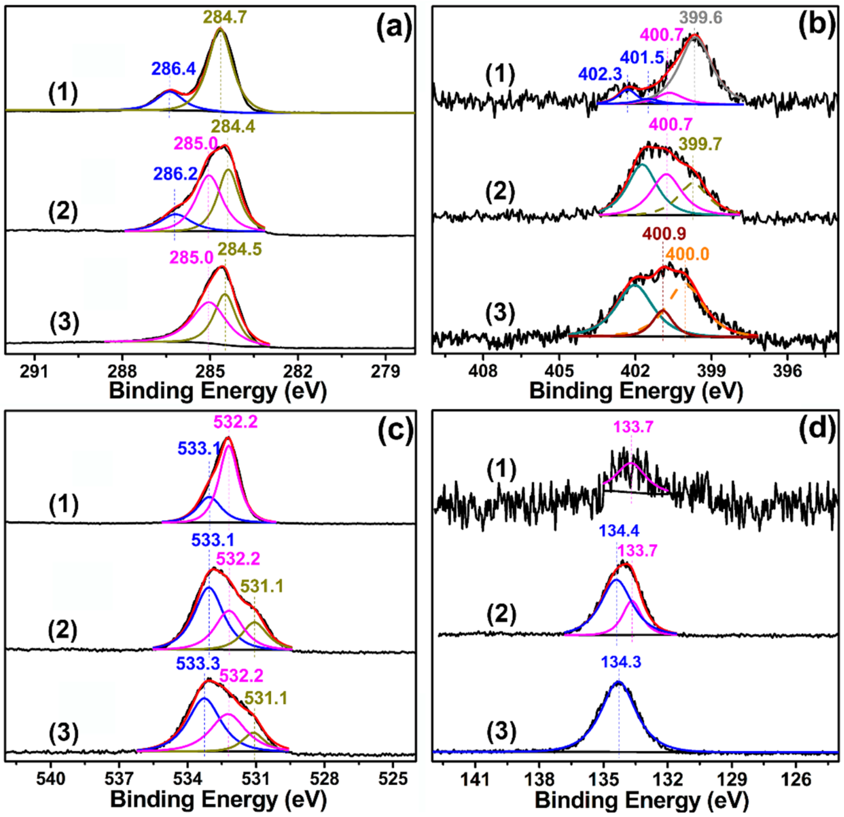


Figure 10. C_{1s} (a), N_{1s} (b), O_{1s} (c), and P_{2p} (d) spectra of DETA-APP/EP at RT (1), 330 °C (2), and 600 °C (3) in a muffle for 3 min in N_2 atmosphere.

poly/pyro/ultraphosphoric acids, which could catalyze decomposition and carbonization of EP to form a heat-resistant char.[51,52]

Figure 10(d) shows the P_{2p} spectra of DETA-APP/EP at different temperatures. At RT, the peak at 133.7 eV was assigned to a P−O−P and/or PO_3^- group in phosphate. However, with increasing temperature, the P_{2p} binding energy became higher and gradually shifted to 134.3 eV, resulting from the further cross-linking of the phosphoric acid to poly/pyro- and ultraphosphoric acids.

All above discussion indicated that phosphorus groups would decompose at relatively low temperature to form a heat-resistant char, to retard the mass loss rate of the polymers at high temperatures. Nitrogen-containing compounds could produce some noncombustible gases when degraded, beneficial for the formation of an intumescent char layer. The swollen char could isolate the transfer of mass and heat between the materials and the flame in a fire, and then protect the unburned materials. Condensed-phase and gas-phase effects both played critical roles in the flame-retarding of DETA-APP/EP.[51,53]

4. CONCLUSION

Aiming to develop a multifunctional flame retardant for epoxy resins, an APP-based organic−inorganic hybrid named DETA-APP was successfully prepared via cation exchange with diethylenetriamine, which could be used as the flame-retardant curing agent for EP. Curing kinetics calculation suggested that DETA-APP was an effective curing agent for EP. At a certain temperature, the epoxy group was opened by −NH− or $-NH_2$ in DETA-APP, resulting in the generation of hydroxyl and tertiary amino groups. The new formed hydroxyl groups could further react with another epoxy group. Thus, cross-linked networks with both tertiary amino and ether linkages could be obtained. The flame retardance and combustion behavior of DETA-APP/EP were comprehensively investigated. With just 15 wt % addition, the LOI value of DETA-APP cured EP was increased to 30.5%, and the sample could easily pass through the V-0 rating with only 10 wt % DETA-APP. Cone calorimetric results displayed that the DETA-APP/EP has an outstanding flame-retardant property and a sharply ameliorated smoke suppression. Moreover, SEM micrographs and digital photos directly illustrated that a more compact and stable intumescent char barrier could be formed after combustion. The results from TGA and XPS indicated that there were two thermal degradation stages of DETA-APP/EP. First, the compounds of phosphoric and poly/pyro/ultraphosphoric acid were generated, resulting in the formation of a phosphorus rich layer under higher temperature by dehydration and carbonization of EP. Then, this unstable layer decomposed further and yielded a compact and intumescent char covering onto the surface of the samples, which could effectively prevent the combustible compounds from transferring between the heat source and the substrate. Therefore, it is a significant and fruitful attempt to improve the flame retardance of EP by using this functionalized flame-retardant curing agent.

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Notes

The authors declare no competing financial interest.

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