Synthesis of a Novel Flame Retardant Containing Phosphorus, Nitrogen, and Silicon and Its Application in Epoxy Resin

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ABSTRACT: A novel flame retardant (TDA) containing phosphorus, nitrogen, and silicon was synthesized successfully via a controllable ring-opening addition reaction between 1,3,5-triglycidyl isocyanurate, 9,10-dihydro-9-oxa-10-phosphaphenan-threne-10-oxide, and 3-aminopropyltriethoxysilane, and TDA was then blended with diglycidyl ether of bisphenol A to prepare flame-retardant epoxy resins (EPs). The chemical structure and components of TDA were confirmed by Fourier transform infrared (FTIR) spectra, ^{31}P nuclear magnetic resonance, and X-ray photoelectron spectroscopy. Thermogravimetric analysis results indicated that after the introduction of TDA, cured EP maintained good thermal stability with a minimum initial decomposition temperature of 337.6 °C, and the char yields of a EP/TDA-5 sample significantly increased by 76.2% compared with that of the neat EP thermoset. Additionally, with the addition of 25.0 wt % TDA (1.05 wt % phosphorus loading), the limited oxygen index value of cured EP increased from 22.5% of pure EP to 33.4%, and vertical burning V-0 rating was easily achieved. Meanwhile, after the incorporation of TDA, the total heat release and total smoke production of the EP/TDA-5 sample obviously reduced by 28.9 and 27.7% in the cone calorimeter test, respectively. Flame-retardant performances and flame-retardant mechanisms were further analyzed by scanning electron microscopy, FTIR, energy-dispersive spectrometry, and pyrolysis gas chromatography/mass spectrometry. The results reveal that the synergistic effect of phosphorus, nitrogen, and silicon plays an excellent flame-retardant role in both gaseous and condensed phases. In addition, the mechanical and dynamic mechanical properties of cured EP thermosets are well maintained rather than destroyed. All the results demonstrate that TDA endows epoxy resin with excellent flame retardancy and possesses great promise in the industrial field.
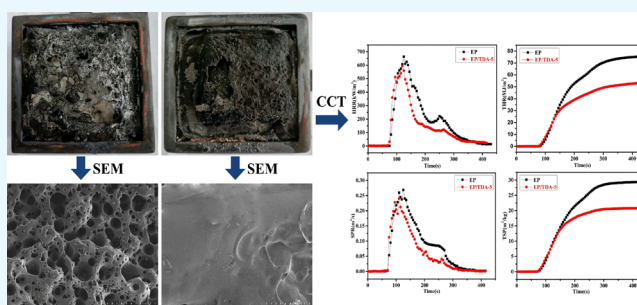
INTRODUCTION

Epoxy resin (EP), as one of the most representative thermosetting polymers, has motivated a worldwide interest due to its outstanding advantages such as excellent chemical corrosion resistance, remarkable dimensional stability and good adhesion, excellent electric insulating property, and low manufacturing cost; therefore, it has been extensively employed in various fields such as aerospace, laminates, coatings, adhesives, and encapsulations.[1−6] However, just like most of the polymer materials, unmodified epoxy resins are classified as combustible materials, and one of the main drawbacks is their intrinsic inflammability, which severely restricts their further application in the fields with high flame retardant requirements.[7−9] Consequently, to broaden their application in this field, it is particularly significant to enhance the flame retardancy of epoxy resin without sacrificing other properties.[10,11]

Over the past few decades, halogenated flame retardants have been widely employed to obtain flame-retardant epoxy resins owing to their low dosage and high flame retardant efficiency.[12] However, halogen-containing flame retardants may generate large amounts of toxic smoke and corrosive

gases during combustion, which will pose a great threat to the natural ecosystem and human health.[13] Consequently, halogenated flame retardants have been widely restrained in industrial fields.

In recent years, under the urgent requirement of environmental protection, the research on alternative halogen-free flame retardants, which generally includes organophosphorus compounds, nitrogen-containing compounds, and organosilicon compounds, has attracted extensive attention of researchers.[14,15] Phosphorus-containing compounds are regarded as one of the most effective flame retardants, which can capture active radicals in the gas phase to block the combustion reaction and release less toxic substances in the meanwhile.[16,17] In addition, many studies[18,19] have demon-
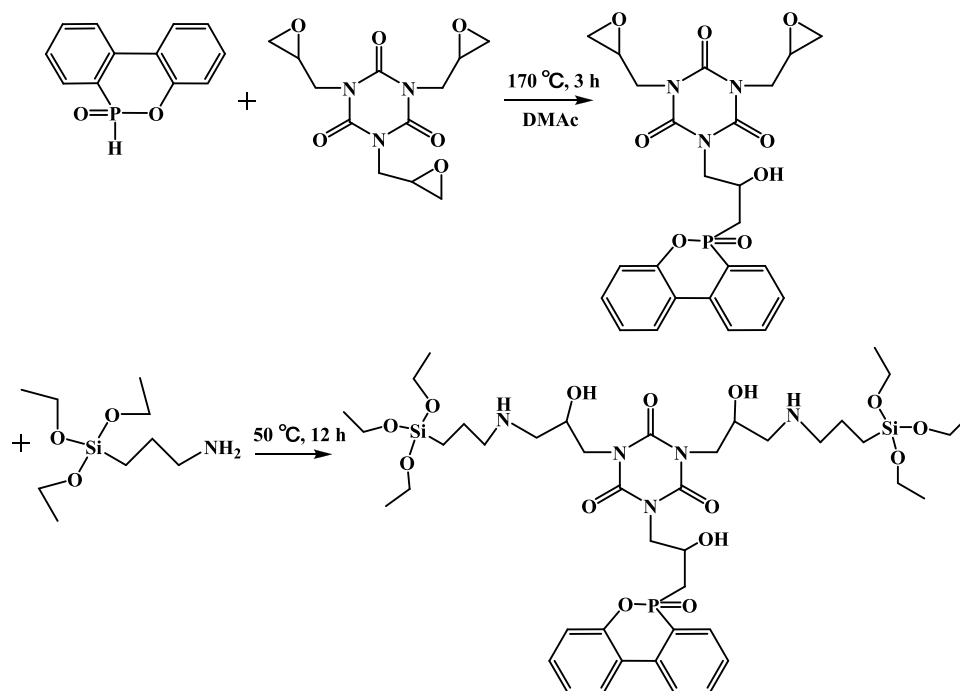
Scheme 1. Synthesis Route of TDA

strated that pyrolysis products of organophosphorus flame retardants will help to catalyze the formation of a char residue layer, which can effectively block the combustion process through separating combustible gases. 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and its derivatives are considered as the most promising phosphorus-containing flame retardants due to their high thermal stability, good flame retardancy, and compatibility in epoxy resin.[20,21] Whereas, it is too difficult for a single element to meet the requirements of efficient flame retardancy, and then integrating multiple elements into a one flame-retardant system has gradually become a popular research trend, which exactly meets the development requirements of novel high-efficiency flame retardants.[22-24] So, the flame retardancy of flame retardants based on DOPO can be significantly enhanced with the synergistic effect of other elements such as nitrogen and silicon.[25,26] Phosphorus-containing flame retardants are usually used as acid sources, while nitrogen-containing flame retardants can be used as blowing agents.[27] Nitrogen-based flame retardants can decompose to incombustible gases such as nitrogen oxide or ammonia without toxic gases and smoke, which can not only dilute the concentration of oxygen near the flame but also promote the formation of a foamy carbon barrier with the synergistic effect of phosphorus.[17,28] Therefore, integrating components containing phosphorus and nitrogen into the flame-retardant system is an efficacious way to obtain a high-efficiency flame retardant.[29] In addition, it is well known that silicon-containing flame retardants are among the best modifiers for epoxy resins, which can produce a Si—O—Si structure and form a protective silica layer to enhance the thermal stability and flame retardancy of materials.[30,31] Moreover, several silicon-containing compounds exhibit good compatibility with epoxy resins, for instance, γ-aminopropyl-triethoxysilane (APTES), which contains the reactive group —NH$_2$ can be well used as the curing agent for epoxy resin, contains both nitrogen and silicon and can work with DOPO to prepare flame retardants with an excellent performance.[25]

APTES was also used in our previous work to successfully make an efficient flame-retardant curing agent containing silicon and titanium for epoxy resins.[9]

An efficient DOPO-based flame retardant containing phosphorus, nitrogen, and sulfur was prepared by Wang et al.,[32] and the research shows that the synergistic effect of diverse inorganic elements is of great help for the matrix to produce more char residues and achieve higher thermal stability. Chao et al.[33] synthesized two P/N/Si-containing flame retardants, which exhibited good flame retardancy and compatibility with epoxy matrix. Consequently, the flame retardants containing diverse elements can achieve high flame-retardant properties, low toxic gas release, and smoke suppression under the synergistic effect of multiple elements.[34,35]

In our work, we designed and synthesized a novel synergistic flame retardant (TDA) containing phosphorus, nitrogen, and silicon through the ring-opening addition reaction between TGIC, DOPO, and APTES. The epoxy matrix was then cured by the flame retardant obtained to prepare flame-retardant epoxy resins (FREPs). The chemical structure and components of TDA were characterized by FTIR, ^{31}P NMR, and XPS. The thermal property, flame retardancy, and combustion behavior of the cured EP specimens were evaluated by thermogravimetric analysis (TGA), the limiting oxygen index (LOI), UL-94, and cone calorimeter (CC) tests. Meanwhile, the residual chars and gaseous pyrolysis products were investigated by Fourier transform infrared (FTIR), scanning electron microscopy (SEM), energy-dispersive spectrometry (EDS), and pyrolysis gas chromatography/mass spectrometry (Py-GC/MS) in order to reveal the flame-retardant mechanism of the prepared flame retardant in epoxy resins. Additionally, the mechanical properties of epoxy thermosets were analyzed by dynamic mechanical analysis (DMA) and tensile test.

RESULTS AND DISCUSSION

Synthesis and Characterization of TDA. TDA was synthesized via ring-opening addition between TGIC, DOPO, and APTES, and the synthetic route of TDA is shown in Scheme 1. FTIR and ^{31}P NMR were employed to characterize the chemical structure of TDA. As shown by FTIR spectrum in Figure 1, the broad absorption band at about 3454 cm^{-1}
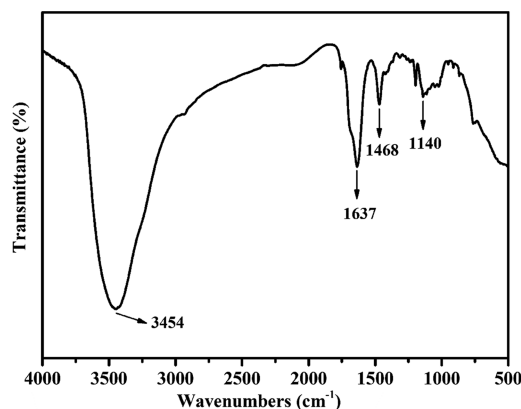

Figure 1. FTIR spectra of TDA.

indicates the presence of hydroxyl. The disappearance of a typical absorption peak at 3061 cm^{-1} of bond P–H in DOPO demonstrates that DOPO reacted with TGIC successfully.[36] Furthermore, the absorption peaks at 1637 and 1468 cm^{-1} can be respectively attributed to the stretching vibrations of C=C and C–N; and the absorption peak at around 1140 cm^{-1} is assigned to the stretching vibration of a Si–O–C structure.[20] The characteristic absorption peak of the epoxy functional group at around 850 cm^{-1} disappeared, indicating that the intermediate reacted successfully with APTES.

The ^{31}P NMR spectra of TDA are shown in Figure 2. As shown in Figure 2, the chemical shift of the ^{31}P NMR spectrum
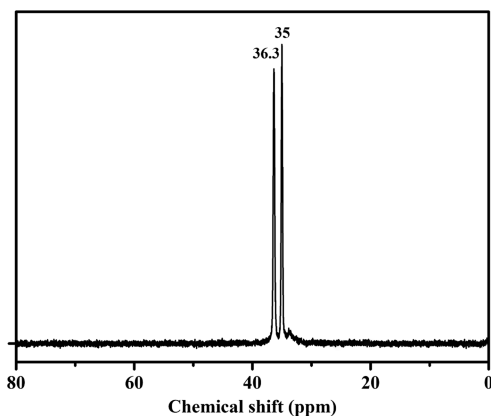

Figure 2. ^{31}P NMR spectra of TDA.

of TDA is very similar to that of TGIC-DOPO (35.9 ppm),[37] but the ^{31}P NMR spectrum of TDA showed two adjoining peaks at 36.3 ppm and 35 ppm. Because the two chemical shifts of the ^{31}P NMR spectrum of TDA were very close, we concluded that the steric effect may be the reason for the two chemical shifts of ^{31}P NMR spectrum of TDA.[38] The above results further confirm that TDA was synthesized successfully.

The chemical components of TDA were explored by X-ray photoelectron spectroscopy (XPS). As shown in Figure 3, the XPS spectrum reveals that the product TDA contains C, O, N, P, and Si elements. In the C_{1s} spectra, the peak at around 284.6 eV is attributed to the C–C and C–H bonds, and the peak at around 286.0 eV belongs to C–OH, C–O–P, and C–N.[32,34] In addition, the peaks at around 288.9 and 283.8 eV were due to the C–Si bonds and the carbonyl groups in polyaromatic structures, respectively. In the N_{1s} spectra, two peaks at around 400.2 and 398.6 eV are present, which may be corresponding to pyrrolic N and pyridinic N. In the Si_{2p} spectra, the peaks at 101.6and 102.2 eV are assigned to Si–C and Si–O bonds, respectively. The above results further demonstrate that the expected product TDA was successfully synthesized.

Thermal Properties. *Thermogravimetric Analysis.* The thermal degradation behaviors of EP and FREPs were evaluated by TGA under a nitrogen atmosphere. The TGA and derivative thermogravimetry (DTG) curves are shown in Figure 4. The corresponding characteristic thermal decomposition parameters are summarized in Table 2, including the initial decomposition temperature ($T_{5\%}$), temperature at maximum weight loss rate (T_{max}), and the char yields at 800 °C. As clearly shown in Figure 4a, all the samples exhibited only one stage in the thermal decomposition process, $T_{5\%}$ of FREPs gradually decreased with the increasing mass fraction of TDA, and many studies[39,40] have suggested that the $T_{5\%}$ of DOPO-based flame-retardant systems decreased with the incorporation of DOPO-based compounds, which can be explained by the catalytic decomposition effect of the phosphaphenanthrene group. On that basis, it can be inferred that the phosphaphenanthrene group of TDA decomposed to generate phosphorus-containing compounds, which could promote the EP matrix to decompose in advance, leading to the decrease in $T_{5\%}$ of FREPs. The catalytic decomposition effect was further enhanced with the increasing mass fraction of TDA, resulting in the minimum $T_{5\%}$ of EP/TDA-5. Similarly, as shown in Figure 4, with the increasing content of TDA, T_{max} of FREPs had a small decrease (from 411.4 to 394.6 °C), suggesting the earlier degradation of FREPs, which may be attributed to the lower stability of the P–O–C group from TDA compared with the C–C bond.[41] But in general, the thermal stability of matrix is not greatly affected. Furthermore, with the increasing mass fraction of TDA, the residual char yields at 800 °C of the samples indicate that the incorporation of TDA can gradually increase the char yields of the matrix. The char yields of cured EP increased from 15.07% of pure EP to 26.55% of EP/TDA-5, with a 76.2% relative increment, indicating that the incorporation of TDA enhanced the char yields significantly, which can prevent the inner material from further decomposition. All these results prove that TDA has little influence on the thermal stability of EP and exhibits efficient char-forming ability. The residual chars would also be further studied in the subsequent sections.

Flame-Retardant Performances. *LOI and UL-94 Tests.* The flame retardancy of the prepared EP thermosets was measured by limited oxygen index (LOI) and UL-94 vertical burning tests. The corresponding results are exhibited in Table 3. The LOI value of the neat EP sample is only 22.5%.[42] As presented in Table 3, the LOI value was gradually improved with the increasing content of TDA, and the LOI value of EP/TDA-1 sample loaded with only 5.0 wt % TDA increased to 25.6%; nevertheless, the EP/TDA-1 sample failed to pass the UL-94 burning test. When the TDA content increased to 10.0
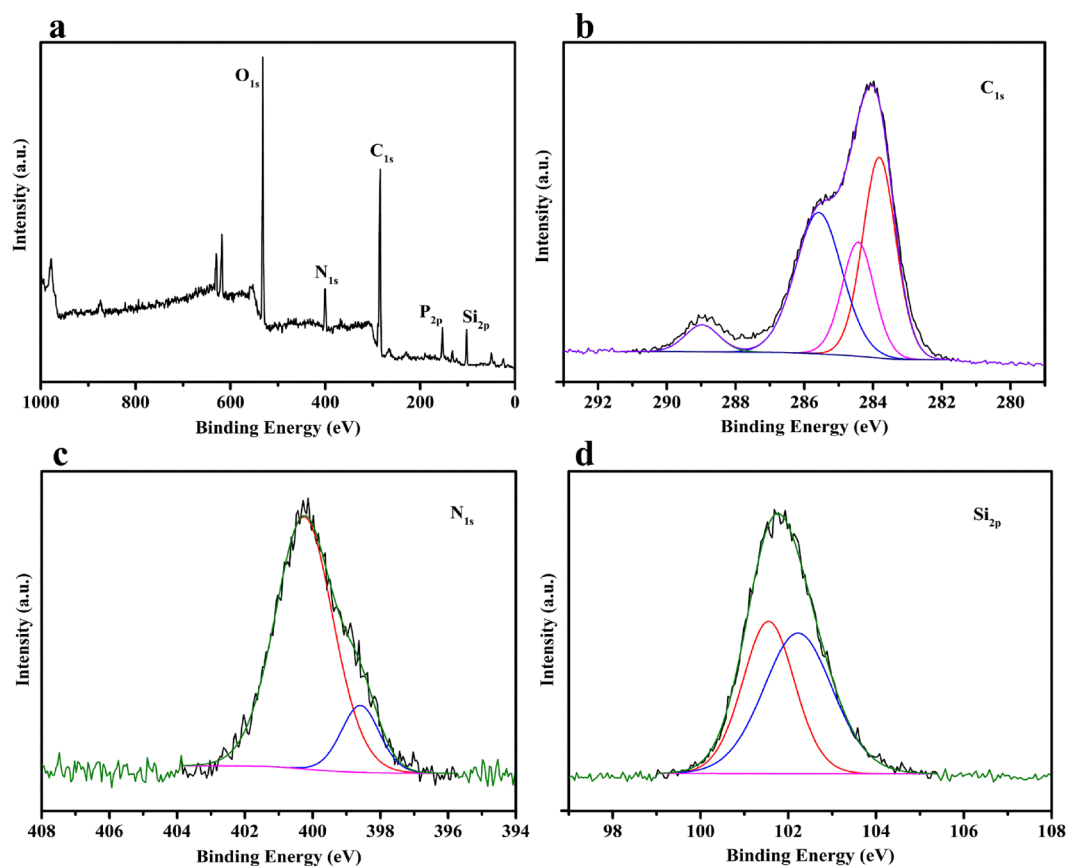
Figure 3. XPS spectra of TDA (a) and high-resolution XPS spectra of TDA (b) C_{1s}, (c) N_{1s}, and (d) Si_{2p}.

Table 1. Formulas of the Cured Epoxy Resins

sample	DGEBA (g)	DDS (g)	TDA (g)	TDA content (wt %)	phosphorus content (wt %)
EP	100	35.0	0	0	0
EP/TDA-1	100	35.0	7.1	5	0.21
EP/TDA-2	100	35.0	15.0	10	0.42
EP/TDA-3	100	35.0	23.8	15	0.63
EP/TDA-4	100	35.0	33.8	20	0.84
EP/TDA-5	100	35.0	45.0	25	1.05

Table 2. Thermogravimetric Data of the EP and FREPs

sample	$T_{5\%}$ (°C)	T_{max} (°C)	char residue at 800 °C (%)
EP	376.4	411.4	15.07
EP/TDA-1	359.2	405.5	19.52
EP/TDA-2	352.5	399.7	21.78
EP/TDA-3	348.5	398.3	23.24
EP/TDA-4	341.2	396.8	24.98
EP/TDA-5	337.6	394.6	26.55

wt %, the LOI value of the EP/TDA-2 sample rose to 28.3%, and it passed the UL-94 V-1 rating. The LOI value of the samples can be further improved by increasing the mass fraction of TDA in the matrix, such as the EP/TDA-5 sample
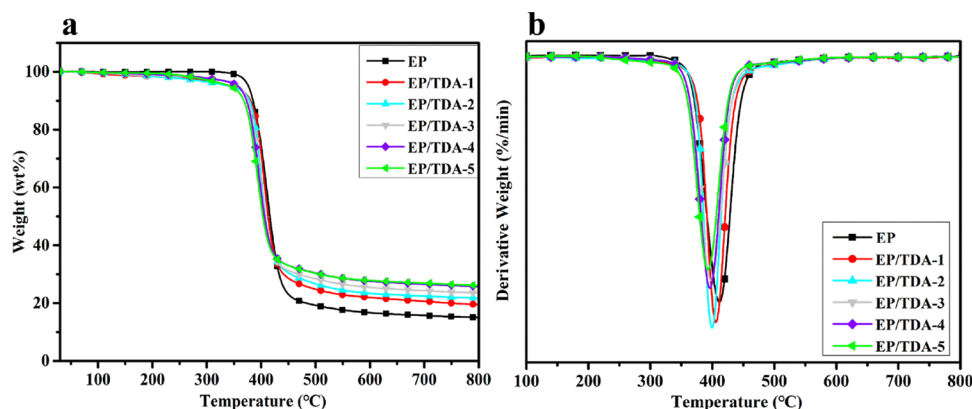

Figure 4. (a) TGA and (b) DTG curves of EP and FREPs.

Table 3. LOI and UL-94 Test Results of the Cured Epoxy Resins

sample	LOI (vol %)	UL-94 (3 mm) rating	dripping
EP	22.5	NR	yes
EP/TDA-1	25.6	NR	no
EP/TDA-2	28.3	V-1	no
EP/TDA-3	30.7	V-1	no
EP/TDA-4	31.9	V-0	no
EP/TDA-5	33.4	V-0	no

(25 wt % TDA loading) could achieve the maximum LOI value of 33.4%, and UL-94 rating could acquire the highest level of V-0 easily in the meantime. The results of UL-94 vertical burning test indicate that the UL-94 ratings of the EP thermosets were obviously enhanced with the increase of the TDA content. Apart from this, thermosets modified by TDA had no dripping phenomenon during the UL-94 vertical burning test compared with pure EP, implying the significant improvement of flame-retardant properties of the EP matrix. Therefore, it can be concluded that TDA is an efficient flame retardant with a multielement synergistic effect for EP.

Cone Calorimeter (CC) Test. The cone calorimeter (CC) test, which could provide useful references on the real fire condition, has been widely conducted to evaluate the flame-retardant behaviors of polymeric materials. The characteristic parameters of the CC test, such as the time to ignition (TTI), heat release rate (HRR), peak heat release rate (pHRR), time of peak heat release rate (t_{pHRR}), total heat release (THR), smoke production rate (SPR), total smoke production (TSP), CO production (COP), CO_2 production (CO_2P), effective

heat of combustion (EHC), and the corresponding data are shown in Figure 5 and Table 4.

Table 4. CC Test Results of EP and EP/TDA-5

sample	pure EP	EP/TDA-5
TTI (s)	28	25
p1HRR (kW/m^2)	676	509
t_{p1HRR} (s)	125	95
p2HRR (kW/m^2)	624	591
t_{p2HRR} (s)	135	120
THR (MJ/m^2)	75.36	53.58
p1SPR (m^2/s)	0.26	0.21
p2SPR (m^2/s)	0.27	0.23
TSP (m/kg)	29.49	21.32
av-COP (kg/kg)	0.07	0.11
av-CO$_2$P (kg/kg)	1.33	1.08
mean SEA (m^2/kg)	949.12	802.73
TOC (g)	49.03	32.36
av-EHC (MJ/kg)	20.60	14.34

TTI is often used as a critical indicator to evaluate the effect of flame retardants on combustibility of cured EP thermosets.[43] As summarized in Table 4, The TTI value of EP/TDA-5 thermoset was lower than that of pure EP thermoset, which is in accordance with the $T_{5\%}$ results as discussed above. The reason is that the catalytic decomposition effect of TDA weakened the ignition resistance of EP thermosets.[44−46]

The HRR and THR are also considered as the important parameters to evaluate the rate of flame growth and the fire size during combustion.[47] The HRR and THR curves of pure
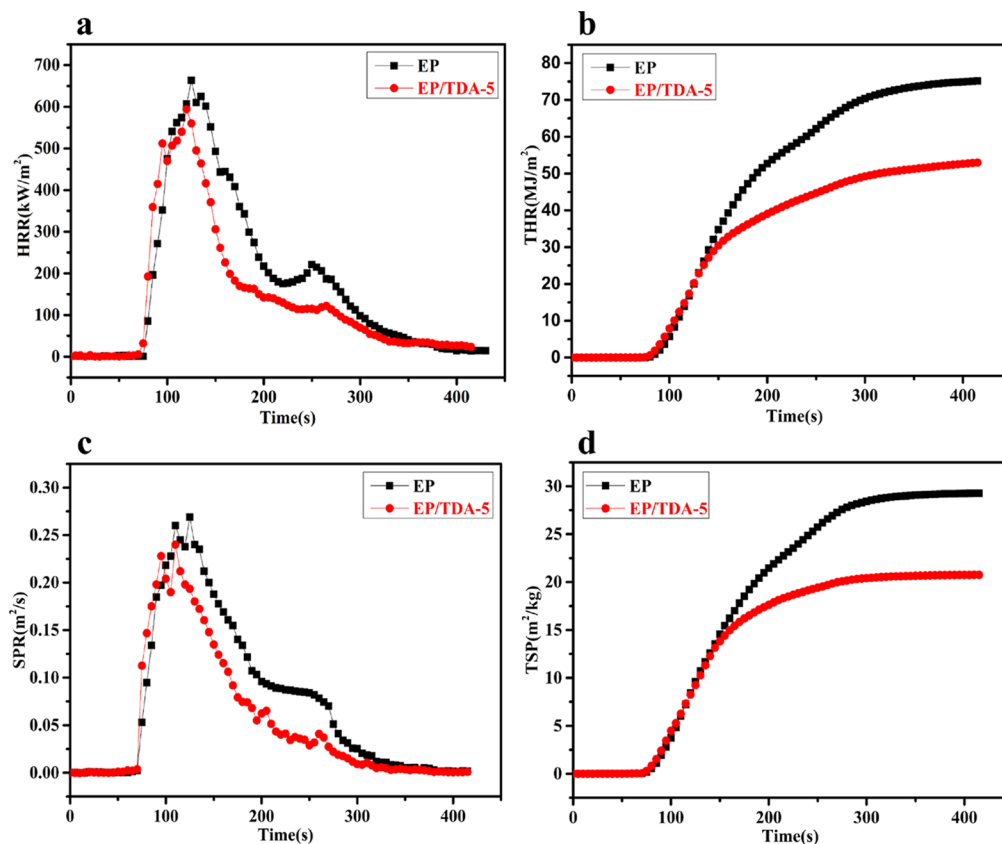
Figure 5. (a) HRR, (b) THR, (c) SPR, and (d) TSP curves of EP and EP/TDA-5.

EP and EP/TDA-5 are shown in Figure 5a,b, where we can see that pure EP burned fast after ignition, and the HRR of it reached the first peak point with a maximum value of 676 kW/m^2 at 125 s, and it is found that after the incorporation of TDA, the HRR of the EP/TDA-5 sample decreased to a peak value of 509 kW/m^2 at 95 s, corresponding to a 24.7% reduction. Therefore, it can be inferred that TDA decomposed to form a dense char residue layer on the surface of the sample during combustion, which can act as an effective barrier to keep the heat and combustible gases from entering into the interior matrix.

It has been reported that the gradient of the THR curve can be used to represent flame spread.[48] As shown in Figure 5b, it can be observed that the THR decreased from 75.36 MJ/m^2 of pure EP to 53.58 MJ/m^2 of EP/TDA-5 at the end of combustion. Compared with the neat EP thermoset, the THR of the EP/TDA-5 sample decreased by 28.9%. The results indicate that the flame spread rate slowed down obviously after adding TDA into the matrix. The main reason is that the introduction of phosphorus, nitrogen, and silicon elements into the system can prompt to form a synergistic phosphorus/nitrogen/silicon-rich char layer during combustion, which would effectively restrict the spread of the flames.

Becayse toxic gases and smoke in a real fire will pose a major threat to human life, the smoke performance of flame-retardant materials is considered as a significant parameter as well.[48] It can be seen from Figure 5c that the SPR curve of pure EP presented two obvious peak points, and the value was higher than that of EP/TDA-5. The first peak SPR value of pure EP was 0.26 m^2/s at 110 s during the combustion process. By contrast, the first peak SPR value of EP/TDA-5 was 0.21 m^2/s at 95 s, which was much lower than that of pure EP. Consequently, introducing TDA into the EP matrix can effectively reduce the generation of smoke in the combustion process.

As can be seen from Figure 5d, the TSR value obviously decreased with the addition of TDA. The EP/TDA-5 sample produced more smoke than the neat EP thermoset in the early stage, which is related to the higher combustion intensity of EP/TDA-5 thermoset during this stage. After that, the TSP curve of EP/TDA-5 thermoset was under that of the neat EP thermoset. It can be observed that the value of TSP reduced from 29.49 m^2/kg of pure EP to 21.32 m^2/kg of EP/TDA-5, and the TSP of EP/TDA-5 thermoset decreased by 27.7% compared with that of the neat EP thermoset at the end of the experiment. Therefore, it can be deduced that the introduction of phosphorus, nitrogen, and silicon into the system can stimulate the formation of a protective char layer on the surface, and the dense char layer of EP/TDA-5 thermoset that formed initially is conducive to restrict the intensity of combustion and reduce the quantity of smoke release at the same time.

The EHC, which is defined as the ratio of heat release to per mass loss measured at a certain point during combustion, can exactly reflect the burning degree of volatile species in a gas phase, and it is helpful to analyze the flame-retardant mechanism in the meantime.[42,49] As presented in Table 4, after the addition of TDA, the average value of EHC (av-EHC) dramatically decreased from 20.60 MJ/kg for pure EP to 14.34 MJ/kg for the EP/TDA-5 sample. The lower EHC value of the EP/TDA-5 sample proves the existence of nonflammable gases in the gas phase. It is inferred that the result may be due to two reasons: on the one hand, the cured EP thermosets containing

TDA can decompose to release noncombustible gases with dilution effect such as N_2, NO_2, NH_3, and volatile phosphide during the combustion, which can effectively dilute the concentration of combustible gases to avoid the rapid combustion of materials, and thus the combustion intensity of gas phase was inhibited, and then the combustion heat of gas phase was also reduced; on the other hand, this result further supports the quenching effect of TDA, and the decomposition of TDA can release phosphorus-containing free radicals, which can capture free radicals containing oxygen and hydrogen in the gas phase and hamper the free radical chain reaction, finally resulting in the incomplete combustion of volatiles in the gas phase.[50,51] It is also reflected in the production of more incomplete combustion products (av-COP) and less complete combustion products (av-CO_2P), as shown in Table 4. Therefore, based on the above analysis of results, it is proved that TDA with synergistic effect of various elements can effectively improve the flame retardancy of the materials.

Flame-Retardant Mechanism. For the purpose of further illustrating the relationship between the flame-retardant mechanism and the morphology of the char residues, the micromorphologies of the burning residues of EP/TDA-5 and pure EP after cone calorimetry tests were observed by SEM, and the relevant micrographs together with the digital pictures of the char residues are exhibited in Figure 6. From the digital
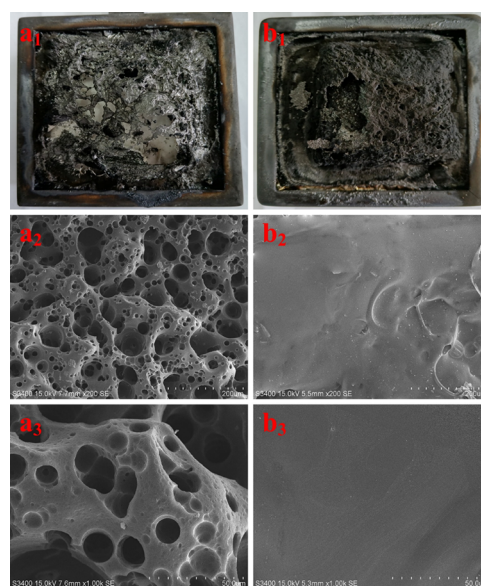

Figure 6. Digital images of the char residues after CC test: (a_1) EP and (b_1) EP/TDA-5; SEM micrographs of the char residues after the CC test: (a_2,a_3) EP and (b_2,b_3) EP/TDA-5.

photo of pure EP (Figure 6a_1), it is obvious that pure EP was almost burnt out and only left a small amount of char residue after the cone calorimetry test. However, the EP/TDA-5 sample yielded more char residues with an integral structure shown in Figure 6b_1. As can be clearly observed from the SEM images, the surface of the pure EP residue was not only very rough but also full of large numbers of tiny holes with different sizes. This phenomenon could be explained by the fact that a good deal of gases was produced during combustion, and as a result, the release process of generated gases created numerous holes.[52] By contrast, after the incorporation of TDA with the

synergistic effect of phosphorus, nitrogen, and silicon, the EP/TDA-5 sample presented a more compact and smooth char layer, such a continuous and thermally stable structure of a char layer can act as a protective barrier, which can effectively restrain the transfer of mass as well as heat between the gas phase and condensed phase, thus preventing the inner EP matrix from further combustion. In addition to this, such a dense structure of a char layer is able to suppress the release of flammable volatiles into the gas phase as well. In conclusion, the introduction of TDA with the synergistic effect of phosphorus, nitrogen, and silicon is of great help to improve the flame retardancy and thermal stability of the EP matrix.

To further explore the flame-retardant mechanism of TDA in the condensed phase, the FTIR spectra and EDS of the char residues were conducted in order to reveal the synergistic effects of phosphorus, nitrogen, and silicon. The FTIR spectrum of the char residues of EP and EP/TDA-5 after the cone calorimeter test is presented in Figure 7. As shown in
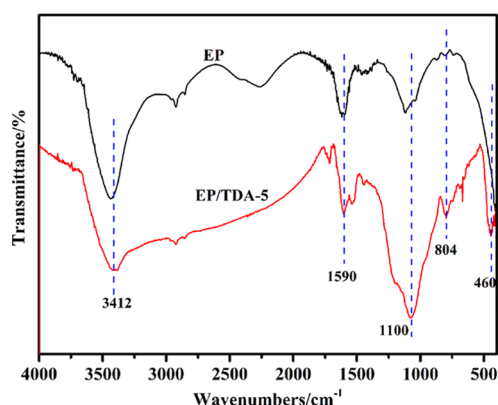

Figure 7. FTIR spectra of the char residues for EP and EP/TDA-5.

Figure 7, the characteristic absorption peaks at 1590 cm^{-1} belong to the C=C stretching vibration of polyaromatic carbons, and it is obvious that there are many differences between the spectra of the two samples, and the absorption peaks at 3412 cm^{-1} of EP/TDA-5 becomes broader, which is attributed to the stretching vibrations of −OH from the P−OH group, suggesting that there might be alcohol groups in the char.[39] The broad peak at around 1110 cm^{-1} appeared, which indicates the formation of the Si−O−Si structure and

P−O−P structure.[20,29] In addition, the characteristic absorption peaks at 804 and 460 cm^{-1} of EP/TDA-5 belong to the deformation vibration of the Si−O−C structure and the stretching vibrations of the Si−C structure, respectively. These results suggested that the synergistic effect between P and Si leads to the formation of Si−O and P−O-containing compounds in the char, which can promote the matrix to form a more stable and compact char layer, thus enhancing the flame retardancy of the char during the decomposition.

In order to analyze the difference between the exterior char and the interior char after combustion, the elemental contents of the char residues after the cone calorimeter test were determined by EDS. As presented in Figure 8, the existence of phosphorus and silicon indicates the formation of the chemical structures containing phosphorus and silicon. It can be found that the oxygen and nitrogen contents of the exterior char were higher than that of the interior char, while the carbon content of the exterior char was lower than that of the interior char, and the reason for this phenomenon may be that the exterior char was directly exposed to air during combustion. It is worth noting that the phosphorus and silicon contents of the exterior char were also higher than that of the interior char, which may be due to the fact that phosphoric groups could generate a phosphate structure, and silicic groups could form silica during the combustion process.[8,53] In addition, the silicon content was higher than phosphorus both in the exterior char and the interior char, this indicates that parts of the phosphorus may be released into the gas phase during combustion, and thus phosphorus also plays an important role in gas phase flame retardation. On the basis of the above FTIR results of the char residue (Figure 7), it can be concluded that phosphorus, nitrogen, and silicon all play an important role in the condensed phase during combustion. The phosphate and silica generated on the surface of the char can effectively enhance the thermal stability of the char, and thus resulting in high char yields.

GC−MS Analysis. TDA was investigated by Py-GC/MS to further explore its pyrolysis behavior and flame-retardant mechanism in the gas phase. The typical fragment flows with plenty of characteristic ionic peaks that were selected, and the results are shown in Figure 9.

As presented in Figure 9, the m/z of fragments at 47 and 63 are determined as ·PO and ·PO$_2$ free radicals, respectively. The m/z of fragments at 168 and 169 are assigned to dibenzofuran
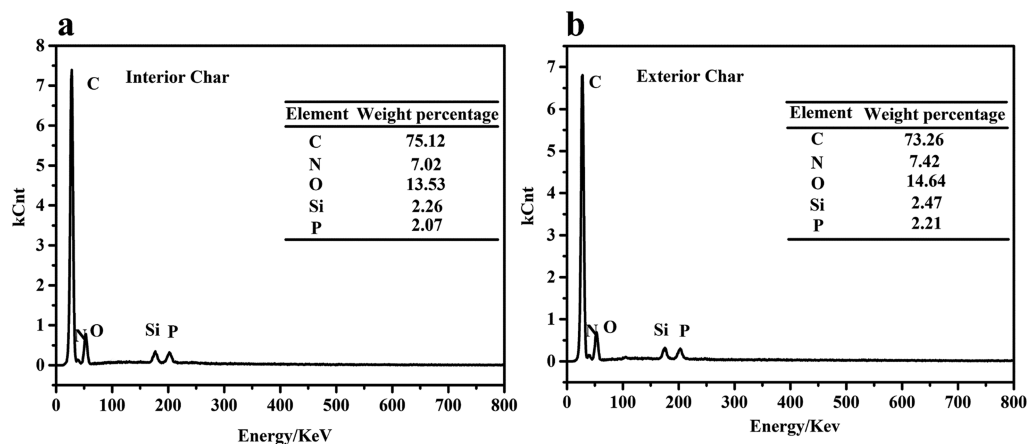

Figure 8. EDS analysis of (a) interior and (b) exterior char residues of EP/TDA-5.
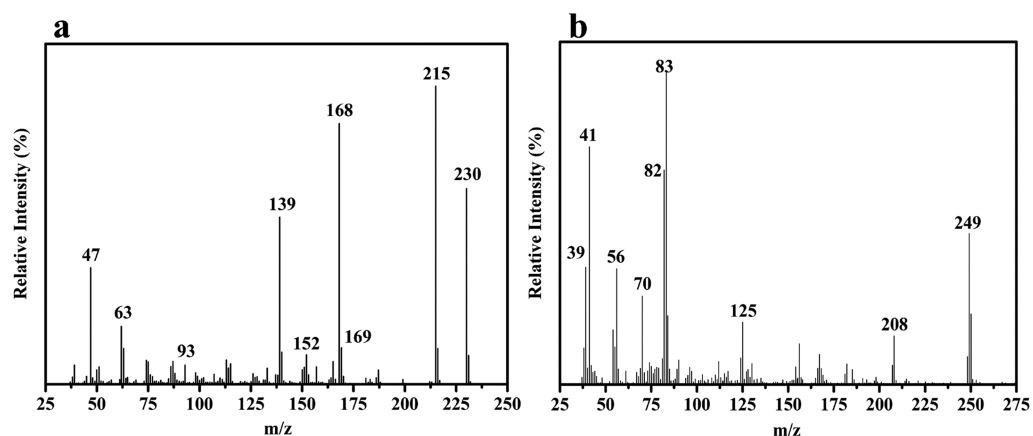
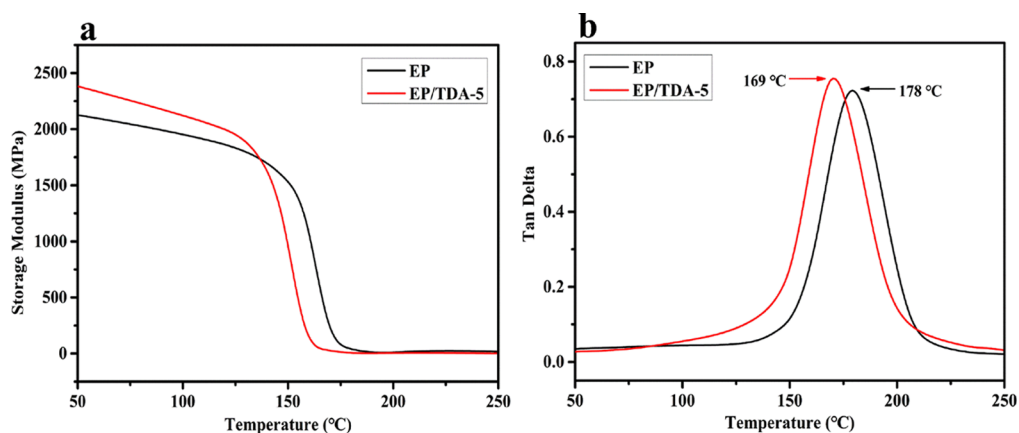**Figure 9.** MS spectra of main fragments of the pyrolyzed TDA at 500 °C (a,b).

Figure 10. Storage modulus (a) and tan δ (b) of EP and EP/TDA-5.

and o-phenylphenoxyl free radical, respectively. The m/z of fragment at 139 is assigned to the O=P−O−Ph free radical. In addition, the m/z of fragments at 249, 208, 83, and 41 (active allyl radical) infer that different nitrogen-containing fragments were generated during the pyrolysis of TDA. On the one hand, such phosphorus-containing inert free radicals can capture and quench radicals containing oxygen and hydrogen such as O, OH, or H free radicals, thus interrupting the free radical chain reaction and inhibiting the combustion intensity during the combustion process.[54] On the other hand, nitrogen-containing noncombustible compounds produced by TDA can contribute to dilute the oxygen concentration around the flame and flammable gases released by the matrix, thereby suppressing the burning intensity and reducing the burning heat. According to the above research results, it can be inferred that both phosphorus and nitrogen play a crucial role in gas phase flame retardation, and the results further demonstrate that the free radicals with quenching effect and nonflammable gases with dilution effect were generated during the pyrolysis of TDA, which is consistent with the discussion on av-EHC.

Mechanical and Dynamic Mechanical Properties. Dynamic mechanical analysis (DMA) was applied to investigate the dynamic mechanical properties of the cured epoxy thermosets. The storage modulus and tan δ curves of EP and EP/TDA-5 are illustrated in Figure 10. As shown in Figure 10, with the incorporation of TDA, the storage modulus at 50 °C increased from 2115 MPa of pure EP to 2387 MPa of EP/TDA-5, indicating that EP/TDA-5 thermoset possesses higher

rigidity at the initial temperature. The glass transition temperature (T_g) is defined as the peak temperature of the tan δ curve, and it can be seen from Figure 10 that EP/TDA-5 had a slight decrease in T_g compared with pure EP, the reason is that TDA with bulky and rigid DOPO units may inhibit the mobility of macromolecular chain on the one hand, and on the other hand, it will hinder the curing process of epoxy resin, thus resulting in the decrease of cross-linking density.[22,43] Therefore, it can be deduced that the decrease in cross-linking density was the main reason for the reduction of T_g. In addition, it can be observed that the tan δ curves of the EP thermosets showed a single T_g, which demonstrated that the flame retardant has good compatibility with the matrix.

To further determine the influence of TDA on the mechanical properties of the EP matrix, the tensile strength and elongation at break of all samples were tested. As presented in Figure 11, EP exerted a tensile strength of 59.06 MPa and elongation at break of 6.50%. It can be noted that the incorporation of TDA increased the tensile strength of EP thermoset. The tensile strength increased from 59.06 MPa for pure EP to 70.41 MPa for EP/TDA-5, corresponding to an obvious increase of 19.2%. The enhancements in tensile strength may be attributed to the introduction of rigid DOPO and triazine−trione groups.[46] As far as the elongation at break, it had a slight decrease as the content of TDA increased from 6.50% of pure EP to 5.80% of EP/TDA-2 and to 5.37% of EP/TDA-5. It is speculated that this may be due to the incorporation of bulky and rigid DOPO units into the epoxy
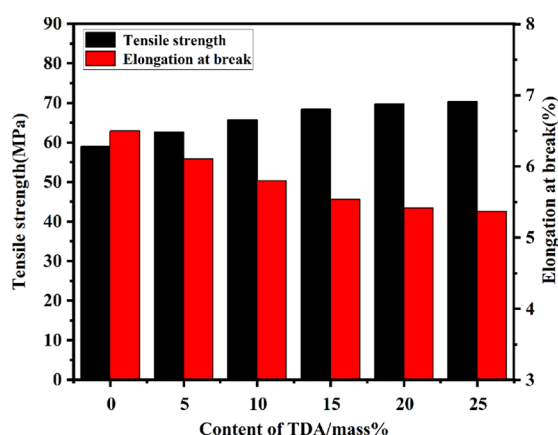
Figure 11. Tensile strength and elongation at break of epoxy thermosets.

resin matrix, resulting in a polymer network that imposes greater restrictions on molecular motion.[55] Consequently, after the introduction of TDA, the mechanical properties of EP thermoset are well improved on the whole rather than destroyed.

CONCLUSIONS

In this work, a novel flame retardant (TDA) simultaneously containing phosphorus, nitrogen, and silicon was successfully synthesized and characterized, and then TDA was blended with DGEBA to prepare flame-retardant epoxy resins. The thermal stability, flame retardancy, combustion behavior, and mechanical properties were all investigated. The results of TGA demonstrate that FREPs maintained good thermal stability with only a little decrease in $T_{5\%}$ and achieved higher carbon residue yields with a significant increase of 76.18%. The results indicate that with the addition of 25 wt % TDA, the flame-retarded EP thermoset achieved an LOI value of 33.4% and got UL-94 V-0 rating easily. At the same time, the THR and TSP of the EP/TDA-5 sample decreased by 28.9 and 27.7% in the CC test, respectively. Additionally, the digital pictures and SEM images of residue chars after CC tests obviously show that after the introduction of TDA, the residual char of the EP/TDA-5 sample was more compact and smoother than that of the pure EP sample. The synergistic effect of phosphorus, nitrogen, and silicon contributes to the formation of a dense and uniform carbon layer during combustion, which can effectively act as a physical barrier to prevent the inner EP matrix from further combustion. Furthermore, the tensile strength was significantly improved although the elongation at break of FREPs decreased slightly. Therefore, FREP thermosets also possess good mechanical properties. In conclusion, all the results demonstrate that TDA exerts efficient flame-retardant properties while maintaining a good comprehensive performance and has promising application prospect in various industrial fields.

EXPERIMENTAL SECTION

Materials. Diglycidyl ether of bisphenol-A (DGEBA) and the epoxy resin used (DGEBA, commercial name: E-51, epoxy value: 0.51) was provided by Shanghai Yuanbang Chemical Manufacturing Co., Ltd. (Shanghai, China). 4,4′-Diaminodiphenyl sulfone (DDS) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). 3-Aminopropyltriethoxysilane (APTES), *N,N*-dimethylacetamide

(DMAc), and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) were supplied by Shanghai Aladdin Chemical Reagent Co., Ltd. (Shanghai, China). 1,3,5-Triglycidyl isocyanurate (TGIC) and ethanol were both purchased from Shanghai Titan Scientific Co., Ltd. (Shanghai, China).

Synthesis of TDA. TDA was synthesized through the addition reaction between TGIC, DOPO, and APTES. DOPO (17.28 g, 0.08 mol) was introduced into a 500 mL, four-necked round-bottom glass flask equipped with a mechanical stirrer, reflux condenser, and thermometer. The temperature was elevated to 135 °C until DOPO was completely melted. After that, TGIC (23.76 g, 0.08 mol) was added into the reaction system at a rate of 2.38 g per 20 min. The above mixture was dissolved into DMAc, and its solid content was 20 wt %. The reaction temperature was further elevated to 170 °C, and the mixture was stirred for 3 h. After reducing the reaction temperature to 100 °C, 3-aminopropyltriethoxysilane (APTES) was slowly poured into the above solution and mixed at 50 °C for 12 h in a nitrogen atmosphere. Thereafter, the solvent was removed by a rotary evaporator. Moreover, the obtained product named TDA was washed by ethanol for several times and then dried in vacuo at 80 °C overnight. Finally, the novel flame retardant was obtained, and the corresponding synthetic route of TDA is shown in Scheme 1.

Preparation of Flame-Retardant Epoxy Resin Specimens. The cured samples were obtained by using a thermal curing process. Epoxy resin and TDA were blended at 100 °C until a homogeneous solution was obtained. Then, DDS as a curing agent was added into the above mixture and stirred constantly to blend thoroughly. After the mixture was deaerated under a vacuum, it was immediately poured into the mold with fixed sizes and thermally cured in an air convection oven at 150 °C for 3 h and 180 °C for 5 h. After curing, the samples were cooled to room temperature slowly, and the flame-retardant epoxy resins (FREPs) were obtained. The samples were labeled as EP/TDA-1, EP/TDA-2, EP/TDA-3, EP/TDA-4, and EP/TDA-5 based on the mass fraction of TDA in the EP thermoset. The formulations of all samples are listed in Table 1.

Characterization. Fourier transform infrared (FTIR) spectra were carried out using a Nicolet 6700 infrared spectrometer (Thermo Fisher Scientific, US) to characterize the chemical structure of TDA. The powdered samples were thoroughly mixed with KBr and then pressed into small flakes. The wavenumber range was set from 4000 to 500 cm^{-1}.

^{31}P NMR spectra were obtained by a Bruker Avance III-400 MHz spectrometer (Bruker, US) using DMSO-d_6 as a solvent.

X-ray photoelectron spectroscopy (XPS) spectra of TDA were examined using a Thermo Scientific K-Alpha$^+$ spectrometer (Thermo Fisher Scientific, US) with Al Kα excitation radiation in ultrahigh vacuum conditions ($h\gamma$ = 1486.6 eV).

The limiting oxygen index (LOI) values were measured using a JF-3 oxygen index meter (Jiangning Analysis Instrument Company, China) according to ISO 4589-2:2006 standard (sample dimension: 130 × 6.5 × 3.0 mm). Three specimens of each material modification were tested, and the average values were calculated. The vertical burning (UL-94) tests were carried out using an NK8017A instrument (Nklsky Instrument Company, Ltd., China) according to ASTM D3801-19 standard (sample dimension: 130 × 13 × 3 mm). Three specimens of each material modification were tested. The results of burning grade are sorted as NR (no rating), V-2,

V-1, and V-0 of which V-0 is defined as the best flame retardation of a refractory material.

Cone calorimeter (CC) tests were performed to analyze the combustion behavior of the samples with an FTT cone calorimeter (West Sussex, UK) according to the ISO 5660 standard under an external heat flux of 50 kW/m^2 (sample dimension: 100 × 100 × 3 mm). The measurement for each specimen was repeated three times, and the error values were within ±5%.

Thermogravimetric analysis (TGA) was measured using a TA Instrument Q500 at a heating rate of 10 °C/min within a temperature range from ambient temperature to 800 °C under a nitrogen flow of 20 mL/ min.

Pyrolysis gas chromatography/mass spectrometry (Py-GC/MS) was performed to recognize the pyrolysis fragments of TDA with an Agilent 7890/5975 GC/MS (Agilent, USA). The injector temperature was 250 °C, 1 min at 50 °C, and then the temperature was elevated to 280 °C at a rate of 8 °C/min. The temperature of the GC/MS interface was 280 °C, and the cracker temperature was 500 °C.

Morphological analysis on the residual chars after cone calorimeter tests was conducted by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800) at an acceleration voltage of 15 kV. The FE-SEM instrument was integrated with an energy-dispersive spectrometry (EDS) microanalyzer to make an elemental analysis.

Dynamic mechanical analysis (DMA) of the cured samples was measured with a DMA Q800 (TA, USA) dynamic mechanical analyzer in a three-point bending pattern. The specimens with dimensions of 50 × 10 × 5 mm^3 were tested at a constant frequency of 1 Hz and heated from 25 to 250 °C at a heating rate of 3 °C/min.

The tensile properties were tested in the room temperature by using a Gotech AI-700M testing machine (Gotech Testing Machines Inc., China) with a crosshead speed of 1 mm/min according to ASTM D638-99. Each sample was measured for more than five times, and the results were from the average values.

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