

## The Synthesis and Characterization of a Novel Phosphorus-Nitrogen Containing Flame Retardant and its Application in Epoxy Resins

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**ABSTRACT:** A novel, halogen-free, phosphorus–nitrogen containing flame retardant 2[4-(2,4,6-Tris{4-[(5,5-dimethyl-2-oxo-2 $\lambda$ <sup>5</sup>-[1,3,2]dioxaphosphinan-2-yl)hydroxymethyl]phenoxy}-(1,3,5)-triazine (TNTP) was successfully synthesized in a three-step process, and characterized by FTIR, NMR spectroscopy, mass spectra, and elemental analysis. A series of modified DGEBA epoxy resin with different loadings of TNTP were prepared and cured by 4,4-diaminodiphenylsulfone (DDS). Thermal gravimetric analysis and vertical burning test (UL-94) were used to evaluate the flame retardancy of TNTP on DGEBA epoxy resin. The results showed that TNTP had a great impact on flame retardancy. All modified thermosets by using TNTP exhibited higher  $T_g$  than pure DGEBA/DDS. The loading of TNTP at only 5.0 wt % could result in satisfied flame retardancy (UL-94, V-0) together with high char residue (27.3%) at 700°C. The addition of TNTP could dramatically enhance the flame retardancy of DGEBA epoxy resins, which was further confirmed by the analysis of the char residues by scanning electron microscopy and FTIR. Furthermore, no obviously negative effect was found on the Izod impact strength and flexural property of DGEBA epoxy resins when TNTP loading limited in 5.0 wt %. DGEBA/DDS containing 2.5 wt % TNTP could enhance Izod impact strength from 10.47 to 10.94 kJ m<sup>-2</sup>, and showed no appreciable effect on the flexural property (85.20 MPa) comparing with pure DGEBA/DDS (87.03 MPa). Results indicated that TNTP as a phosphorus–nitrogen synergistic intumescent flame retardant could be used for DGEBA epoxy resin. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2014, 131, 41079.

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### INTRODUCTION

Fire risks have been greatly increased as the increasing applications of polymeric materials such as regular epoxy resins in our daily life and industrial production. For example, epoxy resins as thermosetting plastic are widely used in coating, antisepticising, adhesive, electronics, and potting, just to name a few. The use of epoxy resins for electric and electronic application, however, is extremely limited due to its flammability. And once it was on fire, it is hard to extinguish.<sup>1–3</sup> Therefore, flame-retardant epoxy resins should be welcome product especially for the electric and electronic applications.

In general, flame-retardant epoxy resins are prepared by incorporating flame retardants containing halogen, phosphorus, nitrogen, etc., in the matrix. Currently, the halogen-containing flame retardants accounted for more than 70% of the total flame retardant market due to their effectiveness and affordability. However, the conventional halogen-containing flame retardants generate toxic and corrosive fume during combustion, this problem has become a bottleneck for their applications in future.<sup>4–6</sup>

Phosphorus-containing flame retardants have exhibited good market prospects because of they are halogen free, low smoke, low toxicity.<sup>7–16</sup> In the meantime, nitrogen-containing compounds such as triazine have been reported as a great flame retardant.<sup>17–19</sup> Furthermore, phosphorus–nitrogen flame retardants have displayed synergistic effect between phosphorus and nitrogen on flame retardancy.<sup>20,21</sup> Special these phosphorus–nitrogen flame retardant showed advantages in the area of low smoke, low toxicity, and halogen-free, they are considered as environmental friendly flame retardants.<sup>22,23</sup>

Recently, Tang et al.<sup>24</sup> synthesized a novel, phosphorus–nitrogen flame retardant based on triazine and phosphaphenanthrene as tri-(phosphaphenanthrene-(hydroxyl-methyl-ene)-phenoxy)–1,3,5-triazine (Trif-DOPO), which showed good flame retardancy. Its flame retardant mechanism was later reported by Qian et al.<sup>25</sup> Their reports suggested that the excellent flame retardancy was attributed to its flame retardant group-synergic-efficiency. As one of the most common types of organic phosphorus flame retardants, phosphonates were also been widely used as flame retardants due to their high thermal stabilities during processing and molding. A

phosphonates triazine combination may be a good base for eco-friendly flame retardant. However, the study on such phosphonates triazine base was rarely been reported.

Any good flame retardant should be comprehensive of good flame retardancy and no appreciable effect on the mechanical performance. However, many literatures about flame retardants were focused on product's high flame retardancy, but failed to report the impact on mechanical performance. Herein, a novel flame retardant containing phosphonate and triazine unit, [4-(2,4,6-Tris {4-[(5,5-dimethyl-2-oxo-2 $\lambda^5$ -[1,3,2]dioxaphosphinan-2-yl)hydroxymethyl]phenoxy}-(1,3,5)-triazine (TNTP), was synthesized and fully characterized. A series of nTNTP/diglycidyl ether of bisphenol-A (DGEBA)/4,4-diaminodiphenylsulfone (DDS) flame retardant thermosets (n stands for the TNTP content) were also prepared by TNTP, DGEBA, and DDS. We are here to report their thermal properties, flame retardancy, flexural property, and Izod impact strength.

## EXPERIMENTAL

### Materials

Cyanuric chloride, phosphorus trichloride, 2,2-dimethyl-1,3-propanediol, 4-hydroxy benzaldehyde, and DDS as reagent grade were purchased from Sinopharm Chemical Reagent in China. Acetone, 1,2-dichloroethane, toluene, and potassium hydroxide were purchased from Tianjin Fuchen chemical reagents factory in China. The epoxy resin DGEBA with an epoxy equivalent weight (EEW) of 188 g equiv<sup>-1</sup> was obtained from Yuehua organic chemical plant of Yueyang General Petroleum Refining and Petrochemical Works in China.

### Preparation of TNTP Flame Retardant

#### Synthesis of 5,5-Dimethyl-1,3,2-dioxaphosphinane 2-oxide (2).

A solution of phosphorus trichloride 7.56 g (55.00 mmol) in 1,2-dichloroethane (20 mL) was added dropwise to a stirred mixture of 2,2-dimethylpropane-1,3-diol (1) 5.20 g (50.00 mmol) in 1,2-dichloroethane (20 mL) at -5 to 0°C.<sup>26</sup> The resultant mixture was stirred for 2 h at 5–10°C and then heated up to 25°C. A mixing solution of anhydrous ethyl alcohol 2.30 g (50.00 mmol) in 1,2-dichloroethane (15 mL) was further added to the reaction mixture and then refluxed for 1.5 h. The solvent was evaporated at reduced pressure to obtain crude product, which was recrystallized from toluene to yield white solid compound (2).

Yield: 90%; Melting points (M.p.): 56–57°C.

#### Synthesis of 2,4,6-Tris(4-formylphenoxy)-1,3,5-triazine (4).

4-Hydroxybenzaldehyde 1.86 g (15.3 mmol) and sodium hydroxide 0.62 g (15.3 mmol) dissolved in a mixture of acetone and water (30 mL, v/v = 1 : 1), which was added dropwise to a stirred mixture of cyanuric chloride (3) 0.92 g (5.00 mmol) in acetone (15 mL) at 0°C. After refluxed for 1 h, reaction mixture was poured into water (100 mL) and produced white solid product. The solid product was washed with water and acetone, and then was purified by crystallization with ethanol. Desired solid compound (4) could be obtained in 95% yield.

M.p.: 168–170°C. <sup>1</sup>H-NMR [400 MHz, DMSO-*d*<sub>6</sub>, ppm]: 7.48 (d, *J* = 8.3 Hz, 6H, Ar-H); 7.97 (d, *J* = 8.4 Hz, 6H, Ar-H); 9.98

(s, 3H, CHO). <sup>13</sup>C-NMR [100 MHz, DMSO-*d*<sub>6</sub>, ppm]: 191.8, 172.7, 155.6, 134.1, 131.1, 122.3.

#### Synthesis of [4-(2,4,6-Tris{4-[(5,5-dimethyl-2-oxo-2 $\lambda^5$ -[1,3,2]dioxaphosphinan-2-yl)hydroxymethyl]phenoxy}-(1,3,5)-triazine.

A mixture solution of 5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide (2) 7.50 g (50.00 mmol) and 2,4,6-tris(4-formylphenoxy)-1,3,5-triazine (4) 6.30 g (14.30 mmol) in toluene (100 mL) was stirred for 5 h at 110°C. After 5 h, light yellow solid produced from solution. The resultant solid product was filtered and washed with little acetone, and then the crude solid was further purified by crystallization with DMF/H<sub>2</sub>O (4 : 1, v/v) to give the corresponding pure TNTP as white solid in 86% yield.

M.p. 225–227°C; FTIR (KBr cm<sup>-1</sup>): 3438 (-OH), 1610 (C=N), 1258 (P=O), 1061, 1008 (P-O-C); <sup>1</sup>H-NMR [400 MHz, DMSO-*d*<sub>6</sub>, ppm]: 0.85 (s, 9H, CH<sub>3</sub>), 1.15 (s, 9H, CH<sub>3</sub>), 3.96 (d, *J* = 8.8 Hz, 6H, CH<sub>2</sub>), 4.44 (t, *J* = 12.0 Hz, 6H, CH<sub>2</sub>), 5.28 (d, *J* = 11.7 Hz, 3H, CHP), 6.44 (s, 3H, OH), 7.23 (d, *J* = 7.3 Hz, 6H, Ar-H), 7.49 (d, *J* = 6.9 Hz, 6H, Ar-H) <sup>13</sup>C-NMR [101 MHz, DMSO-*d*<sub>6</sub>, ppm]: 173.1, 150.6, 136.2, 128.3, 120.9, 77.8, 77.3 (d, <sup>1</sup>*J*<sub>C-P</sub> = 48.5 Hz), 32.0, 21.4, 19.9. <sup>31</sup>P-NMR [162 MHz, DMSO-*d*<sub>6</sub>, ppm]: 12.80. GC-MS: calcd. for C<sub>39</sub>H<sub>48</sub>N<sub>3</sub>O<sub>15</sub>P<sub>3</sub>: 891.23, found: 891.58. Elem. Anal: calcd. for C<sub>39</sub>H<sub>48</sub>N<sub>3</sub>O<sub>15</sub>P<sub>3</sub>, C (52.53%), H (5.43%), N (4.71%); Found, C (52.53%); H (4.94%), N (4.17%).

### Preparation of the Thermosets

TNTP/DGEBA with five weight ratios 2.5, 5, 10, 15, or 20 % were, respectively, heated to 160°C to form a well-blend mixture, then curing agent DDS at a 2 : 1 equivalent of DGEBA according to the EEW values was added and dissolved completely, and then the mixture was kept in a vacuum oven for 5 min to completely eliminate air bubbles. The mixture was rapidly poured into molds and cured at 120°C for 2 h, then at 150°C for 2 h, finally at 180°C for 1 h to obtain five TNTP/DGEBA/DDS thermosets containing 2.5, 5, 10, 15, and 20 wt % TNTP, respectively. In order to prevent cracking, the epoxy thermosets thereafter were allowed to cool slowly to room temperature.

### Instrumental Analysis and Measurements

**Chemical Structure Identification.** Melting points (M.p.) were measured on an electrothermal melting-point apparatus and uncorrected. Infrared spectra (IR) were recorded as KBr pellets on a Nicolet Avatar 360 Fourier transform infrared (FTIR) spectrophotometer. <sup>1</sup>H-, <sup>13</sup>C-, and <sup>31</sup>P-NMR spectra were recorded in DMSO-*d*<sub>6</sub> solution at 400 MHz (<sup>1</sup>H), 100 MHz (<sup>13</sup>C), and 160 MHz (<sup>31</sup>P), respectively, using tetramethylsilane (<sup>1</sup>H, <sup>13</sup>C) and 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P) as internal standards with a Varian Mercury Plus-400 NMR spectrometer. Mass spectra (MS) was obtained on a Finnigan Trace MS 2000 spectrometry. Elemental analysis was performed with a Vario EL III CHNSO elemental analyzer.

**Thermal Performance.** Differential scanning calorimetry (DSC) experiments were conducted on a Perkin-Elmer DSC-7 thermal analyzer in nitrogen atmosphere. Glass transition temperatures (*T*<sub>g</sub>) were determined by scanning from 30 to 300°C at a scan rate of 10°C min<sup>-1</sup>. Thermal gravimetric analysis (TGA) was

conducted using a thermal gravimetric analyzer (STA 449 C, NETZSCH Instruments, MA). Approximately 10 mg of the sample, cut from the sheet, was equilibrated at ambient conditions and then subjected to heating from 30 to 700°C at a heating rate of 10°C min<sup>-1</sup> under a nitrogen flow (50 mL min<sup>-1</sup>). The weight loss with respect to temperature and the maximum degradation temperature ( $T_{\max}$ ) of samples were recorded.

**Vertical Burning Test.** Vertical burning test (UL-94) was carried out according to the ASTM D 3801 standard with five test sample bars 127.0 × 12.7 × 3.2 mm<sup>3</sup> on a CZF-3 type level vertical flame detector. During the test, the polymer specimen was subjected to two 10-s ignitions. After the first ignition, the flame was removed and the time for the polymer to self-extinguish ( $t_1$ ) was recorded. Cotton ignition would be noted if polymer dripping occurred during the test. After cooling, the second ignition was performed on the same sample and the self-extinguishing time ( $t_2$ ) and dripping characteristics were recorded. If  $t_1$  plus  $t_2$  was less than 10 s without any dripping, the polymer was considered a V-0 material. If  $t_1$  plus  $t_2$  was in the range of 10–30 s without any dripping, the polymer was considered a V-1 material. If  $t_1$  plus  $t_2$  more than 30 s or with polymer dripping to ignite the cotton, the polymer was considered a V-2 material.

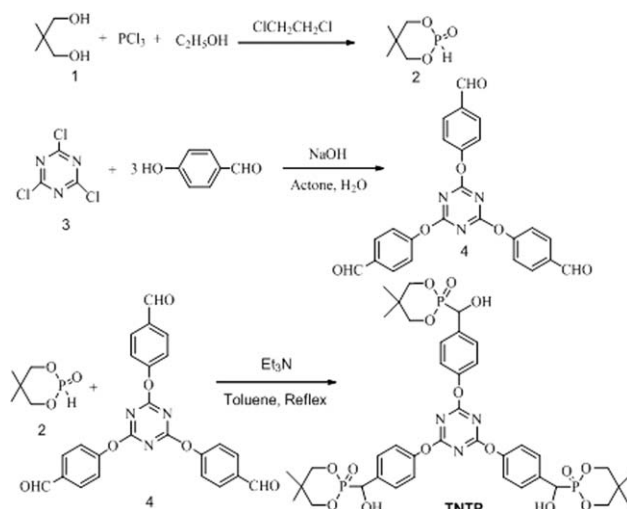
**Scanning Electron Microscopy.** Scanning electron microscopy (SEM) was performed on a JSM-6700F SEM at an accelerating voltage of 10 kV. All samples were coated with a conductive gold layer.

**Mechanical Test.** Mechanical properties of the samples were evaluated through flexural and impact properties. Flexural property was measured using a CMT6503 tensile tester, and performed according to ASTM D790-03 (Procedure A) with five specimens for each sample at rate of crosshead motion of 10.0 mm min<sup>-1</sup>. The sample size was 55.0 × 12.7 × 2.0 mm<sup>3</sup>. Impact property was measured using a ZBC1400-1 impact tester. Izod impact strength was measured as ASTM D256, with five specimens for each sample. The specimen was held in a vertical cantilever beam and broken by a pendulum (4 J). The sample size was 80.0 × 10.0 × 4.0 mm<sup>3</sup>.

## RESULTS AND DISCUSSION

### Synthesis and Characterization

The three-step procedure for the synthesis of 2[4-(2,4,6-Tris {4-[(5,5-dimethyl-2-oxo-2λ<sup>5</sup>-[1,3,2]dioxaphosphinan-2-yl)hydroxymethyl]phenoxy}-(1,3,5)-triazine (TNTP) is outlined in Scheme 1. The title compound TNTP could be easily synthesized by the reaction of 5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide (2) and 2,4,6-tris(4-formylphenoxy)-1,3,5-triazine (4). Intermediate (2) was prepared starting from phosphorus trichloride and 2,2-dimethyl-1,3-propanediol according to literature method.<sup>26</sup> Intermediate (4) was obtained by the nucleophilic substitution of cyanuric chloride (3) and 4-hydroxybenzaldehyde. The chlorine atoms of cyanuric chloride were very easily displaced by nucleophiles. The preparation of mono-, di-, and tri-substituted 1,3,5-triazine could be controlled by temperature to run in a stepwise manner in the presence of acid-binding agent. It was reported mono-substitution of cyanuric chloride could be occurred below



**Scheme 1.** Synthesis of phosphorus–nitrogen containing TNTP.

or at 0°C, di-substitution at room temperature and tri-substitution above 60°C.<sup>27</sup> However, the triazine ring was easily hydrolyzed in alkaline conditions when the synthetic reaction of tri-substituted 1,3,5-triazine (4) was carried out at 60°C. In order to avoid the hydrolysis of triazine ring, the synthetic reaction of (4) was first performed by adding 4-hydroxybenzaldehyde to cyanuric chloride slowly at 0°C. A mixture of mono-, di-, and tri-substituted triazine was observed in this process. Tri-substituted 1,3,5-triazine (4) could be further produced in 95% yield by 1 h reflux reaction.

The structure of title compound TNTP was characterized by <sup>1</sup>H-, <sup>13</sup>C-, and <sup>31</sup>P-NMR spectroscopy. The NMR spectrogram of TNTP was shown in Figure 1. In the <sup>1</sup>H-NMR spectrogram of TNTP, the proton signal corresponding to the methyldyne attached to phosphorus appears at 5.26–5.29 ppm as two doublets caused by the phosphorus nucleus. It was speculated that the proton signal was split into two doublets by low rate of environment exchange due to slow rotation of the P-C bond. The proton signal corresponding to the two methylene groups (CH<sub>2</sub>) appear as two doublets at 3.95–4.46 ppm due to the superposition of two AB systems with different chemical shift between the two mutually coupled protons A and B. In the <sup>13</sup>C-NMR spectrogram of TNTP, two peaks at 77–78 ppm for aliphatic carbons (P-CH) were observed. That is because the <sup>1</sup>J<sub>P-C</sub> coupling further splits the aliphatic carbon into two peaks. The structure of TNTP was further verified by using <sup>31</sup>P-NMR. In the <sup>31</sup>P-NMR spectrogram of TNTP, its chemical shifts appeared as a singlet at δ 12.80 ppm which was consistent with the characterization of phosphonate.

### Thermal Properties

TNTP/DGEBA/DDS thermosets containing 2.5, 5, 10, 15, or 20 wt % TNTP were, respectively, prepared by adding TNTP to DGEBA epoxy resins. The thermal properties of these five epoxy thermosets with different ratio of TNTP and DGEBA/DDS as a control were evaluated. Results are summarized in Table I. The glass transition temperatures ( $T_g$ ) of the epoxy thermosets were tested by DSC.  $T_g$  values of these flame-retarded epoxy thermosets were in the range of 168.3–192.1°C, which were higher

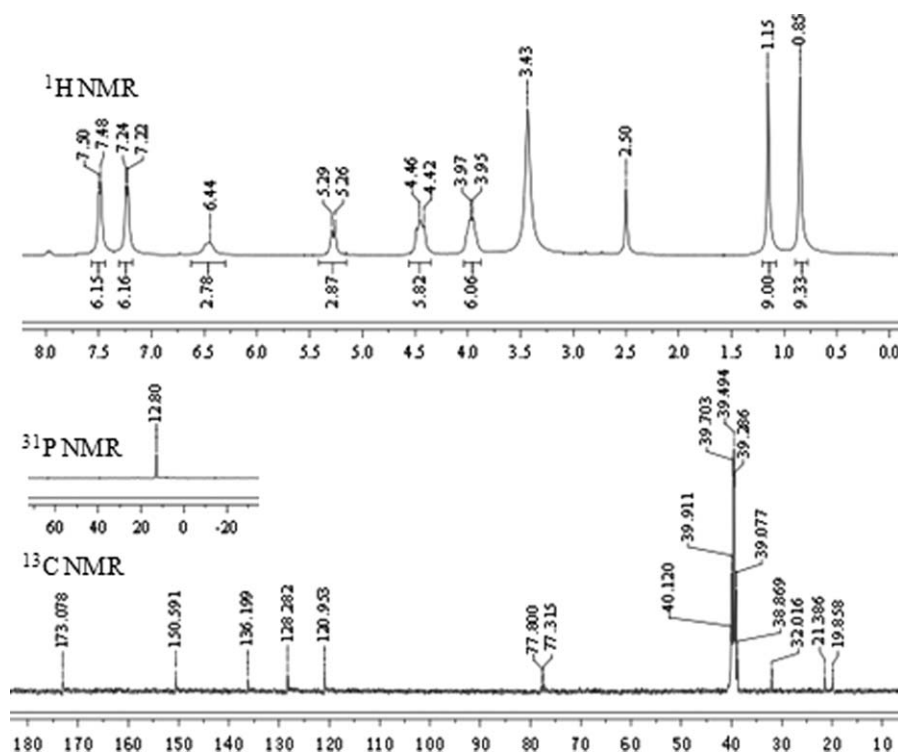


Figure 1.  $^1\text{H}$ -,  $^{13}\text{C}$ -, and  $^{31}\text{P}$ -NMR spectra of TNTP.

than that of pure DGEBA/DDS system ( $162.5^\circ\text{C}$ ). It was found that  $T_g$  values of the cured resins could be increased by adding TNTP into the epoxy resin. In particular, the  $T_g$  value of 20 wt % TNTP/DGEBA/DDS was as high as  $192.1^\circ\text{C}$ . TNTP also acted as crosslinker because the hydroxyl groups of TNTP could participate in the curing reaction and enhanced crosslinking density of these cured resins. The crosslinking density could be further enhanced by increasing the amount of TNTP. Therefore, the cured resins resulted in a much higher crosslinking density by the addition of 20 wt % TNTP. The effect of crosslinking density on  $T_g$  was greater than that of chain flexibility, a higher crosslinking density could lead a higher  $T_g$  value for these DGEBA epoxy thermosets modified by TNTP.

The thermal stability of DGEBA/DDS system and TNTP-containing epoxy thermosets were examined under a nitrogen atmosphere by TGA, which is a standard procedure for evaluating the thermal stability of flame retardant. The data of thermal

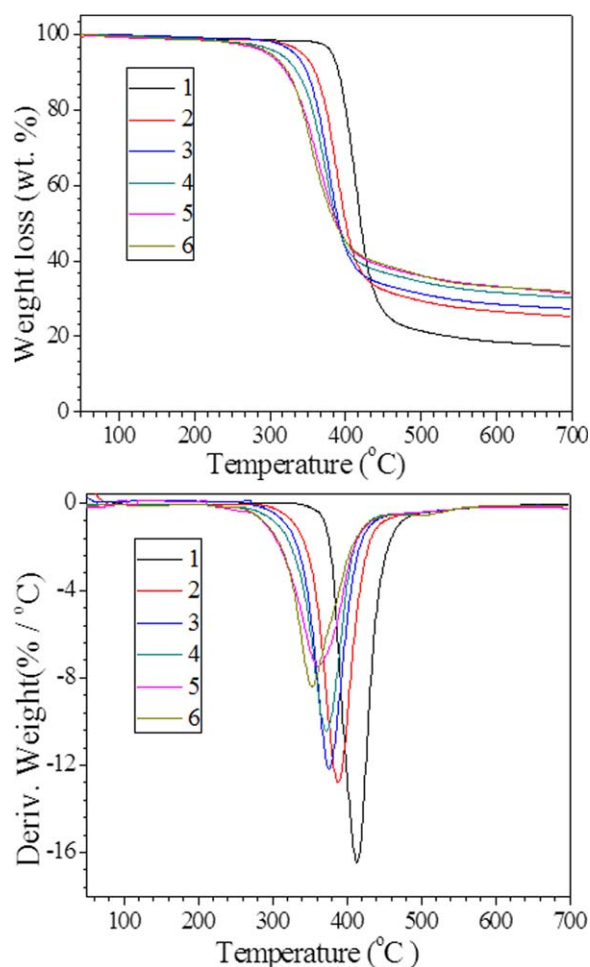
stability for these thermosets are summarized in Table I and their curves figures of TGA and DTG are showed in Figure 2. As seen from Figure 2, all these modified thermosets, TNTP/DGEBA/DDS with different loadings of TNTP had lower decomposed temperature than that of the neat DGEBA/DDS. Table I showed that both  $T_{5\text{ wt \%}}$  (temperatures recorded at specific weight loss of 5 wt %) and  $T_{\text{max}}$  (maximum decomposition temperature) were reversely correlated with the amount of TNTP, especially for the  $T_{5\text{ wt \%}}$ . These results suggested that the lower thermal stability of these modified thermosets came from the decomposition of phosphonate and triazine structure units in TNTP at lower temperature. When the additive amount of TNTP was in the range of 2.5–15.0 wt %, the corresponding  $T_{\text{max}}$  decreased only from 388 to  $361^\circ\text{C}$ .

As seen from Table I, the char yields of five epoxy thermosets TNTP/DGEBA/DDS containing 2.5, 5, 10, 15, and 20 wt % TNTP, respectively, were higher than that of DGEBA/DDS with

Table I. Thermal Property of DGEBA Thermosets

Sample code	Thermosetting system	$T_g$ ( $^\circ\text{C}$ )	$T_{5\text{ wt \%}}$ ( $^\circ\text{C}$ )	$T_{\text{max}}$ ( $^\circ\text{C}$ )	Char yield at $700^\circ\text{C}$
1	DGEBA/DDS	162.5	382.3	413.7	17.5
2	2.5 wt % TNTP/DGEBA/DDS	168.3	342.2	388.3	25.3
3	5.0 wt % TNTP/DGEBA/DDS	177.8	332.2	376.1	27.3
4	10.0 wt % TNTP/DGEBA/DDS	180.8	310.6	372.6	30.2
5	15.0 wt % TNTP/DGEBA/DDS	189.6	295.7	361.5	31.3
6	20.0 wt % TNTP/DGEBA/DDS	192.1	298.6	353.4	31.8

$T_{5\text{ wt \%}}$ , temperature for 5% weight loss;  $T_{\text{max}}$ , maximum decomposition temperature.



**Figure 2.** TGA and DTG curves of DGEBA thermosets: (1) DGEBA/DDS, (2) 2.5 wt % TNTP/DGEBA/DDS, (3) 5.0 wt % TNTP/DGEBA/DDS, (4) 10.0 wt % TNTP/DGEBA/DDS, (5) 15.0 wt % TNTP/DGEBA/DDS, and (6) 20.0 wt % TNTP/DGEBA/DDS. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

no TNTP. It was found that the char yield was strongly depended on the amount of TNTP. With the TNTP content increasing, the char yield of these thermosets could be increased. When 20.0 wt % TNTP was added to epoxy resin, the char yield reached 31.8 wt % at 700°C, while the neat DGEBA/DDS thermoset was only 17.5 wt %. Based upon a

number of literatures, polymers with high char yields often showed good flame retardancy.<sup>28</sup> Therefore, this noteworthy property of TNTP also make it is capable of developing into a new phosphorus–nitrogen containing flame retardant used in DGEBA epoxy resin.

#### Flame-Retardant Performance and Char Analysis

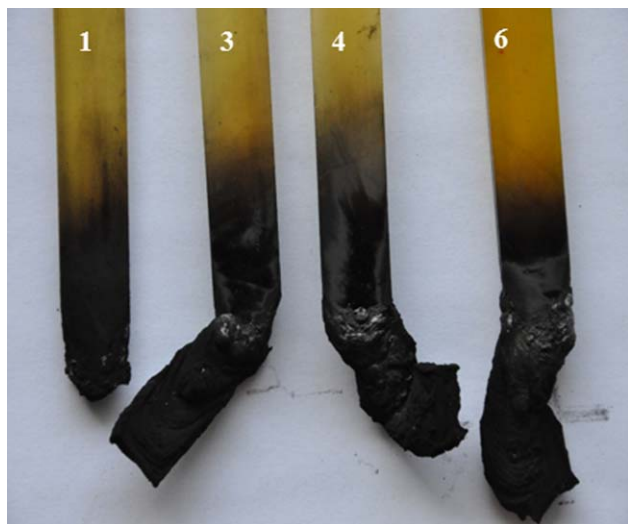
The flame-retardant property of these epoxy thermosets was further evaluated by using the UL-94 vertical flammability test. The neat DGEBA/DDS thermoset was used as a control. Results are listed in Table II, the photos of these three epoxy thermosets with 5, 10, or 20 wt % TNTP, respectively, as representative specimens after tested by UL-94 method are presented in Figure 3. We observed the DGEBA/DDS thermoset as a control could not extinguish spontaneously and accompanied with drippings, which led to failure in the UL-94 test. Even if DGEBA/DDS thermoset was extinguished by artificial factor, only little char was observed on the surface of tested specimen [Figure 3(1)]. When DGEBA was flame retarded by TNTP, clear better flame retardancy such as decreasing burning time and eliminating dripping melt can be observed. When TNTP loading was kept in the range of 5.0–20.0 wt %, the TNTP/DGEBA/DDS thermosets were able to pass the V-0 rating. Meanwhile visible intumescent char was produced on the surface of tested specimen [Figure 3(3), (4), (6)]. Test results indicated that TNTP as flame retardant had exhibited high efficiency in enhancing flame retardancy of DGEBA epoxy resins and eliminating melt drippings.

In order to investigate the effect of TNTP on the flame retardancy, the morphological characteristics of char layer on the surface of these tested specimen including the neat DGEBA/DDS thermoset and three TNTP-modified thermosets were further analyzed by SEM (Figure 4) after the UL-94 vertical test. It was not difficult to discern the differences of the char layer between DGEBA/DDS thermoset and TNTP-modified DGEBA/DDS thermosets. During the vertical burning tests, a smooth surface of char layer on the DGEBA/DDS-tested specimen was formed [Figure 4(1a)], but this char layer was too thin to prevent the combustion of underlying resins, and severely melt drippings were observed. From Figure 4(3a), a morphological character of intumescent, compact and smooth char layer can be observed on the surface of the 5.0 wt % TNTP/DGEBA/DDS thermoset. More intumescent char layer of 10.0 and 20.0 wt % TNTP/DGEBA/DDS thermosets were also observed [Figure 4(4a,6a)].

**Table II.** Flame-Retardant Property of DGEBA Thermosets

Sample code	Thermosetting system	$t_1$ (s)	$t_2$ (s)	UL-94 rating	Observed dripping
1	DGEBA/DDS	>50	–	Fail	Yes
2	2.5 wt % TNTP/DGEBA/DDS	15.01	1.50	V-1	No
3	5.0 wt % TNTP/DGEBA/DDS	8.86	1.14	V-0	No
4	10.0 wt % TNTP/DGEBA/DDS	8.60	1.03	V-0	No
5	15.0 wt % TNTP/DGEBA/DDS	7.53	0	V-0	No
6	20.0 wt % TNTP/DGEBA/DDS	9.76	0	V-0	No

$t_1$ , the burning time after first ignition;  $t_2$ , the burning time after second ignition.

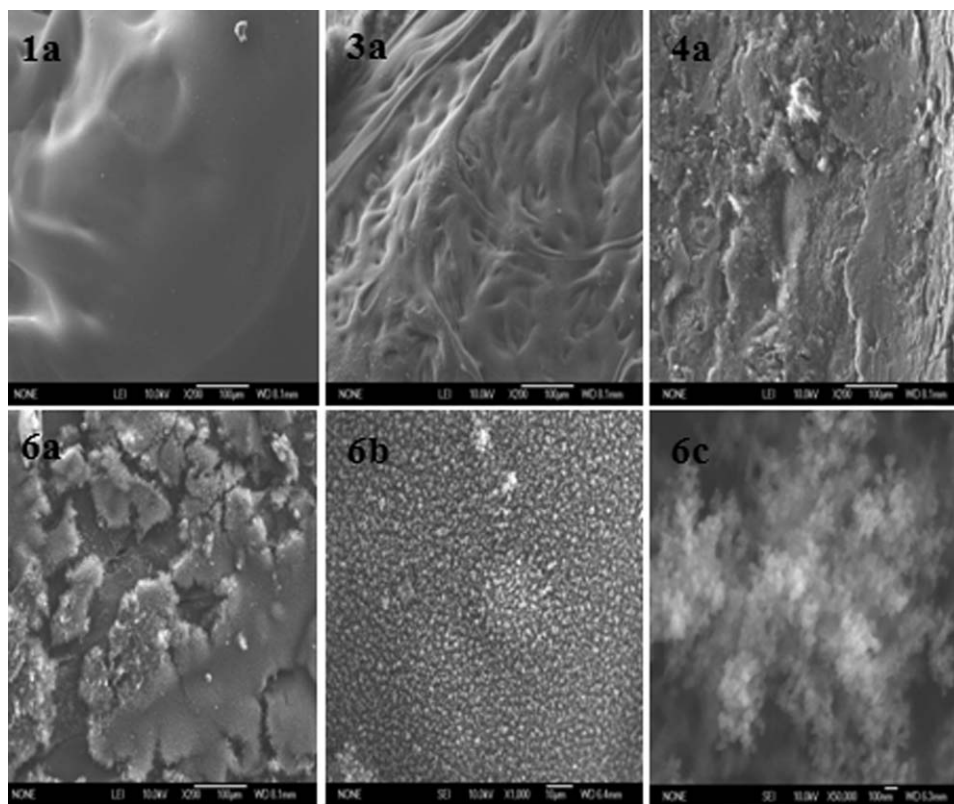


**Figure 3.** Digital photographs of test bars after the vertical burning test: (1) DGEBA/DDS; (3) 5.0 wt % TNTP/DGEBA/DDS; (4) 10.0 wt % TNTP/DGEBA/DDS; and (6) 20.0 wt % TNTP/DGEBA/DDS. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

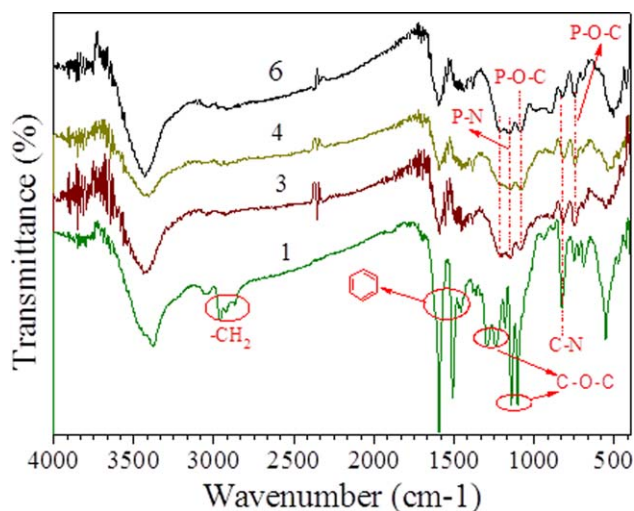
It is noteworthy that a compact char layer with uniform distribution of nano skeleton, which may be nano-ammonium polyphosphate (APP) was formed during the degradation of TNTP at high temperature. This can be also seen from magnified images in Figure 4(6b,6c). It showed that the filling of nanostructures made the char layer more intumescent and stronger

by using 20.0 wt % TNTP. It was thought these intumescent char layer could efficiently prevent both heat transfer and oxygen entering into the combustion zone, retarding the overflow of degradation products during combustion. Therefore, these antifracking epoxy resins containing TNTP should provide better flame retardant properties.

FTIR spectra of the residual chars, which were collected from the UL-94 test of several representative thermosets, are presented in Figure 5. As the control test, the residual char of DGEBA/DDS came from an imperfect combustion. It had to be extinguished by artificial factor because it could not extinguish spontaneously. Its IR spectra indicated the existence of  $-\text{CH}_2$  (vibration adsorption,  $2962\text{ cm}^{-1}$ ), C-O-C (stretching vibration,  $1294$  and  $1144\text{ cm}^{-1}$ ), and aromatic ring (stretching vibration  $1594$ ,  $1509$  and  $1457\text{ cm}^{-1}$ ) in the residual char. In terms of IR spectra, all four tested thermosets [Figure 5(1,3,4,6)] peaked at  $1210\text{ cm}^{-1}$  identified for the stretching vibration of C-N. It suggested that C-N bound exist in the residual chars of all tested thermosets. However, significance difference in IR spectrogram of residual chars between DGEBA/DDS thermoset and three flame-retarded DGEBA/DDS thermosets can be observed in Figure 5. A peak around  $1150\text{ cm}^{-1}$  [Figure 5(3,4,6)] indicates the existence of thermal stable P-N bound in residual chars of three flame-retarded DGEBA/DDS containing 5.0, 10.0, or 20.0 wt % TNTP.<sup>8</sup> It had been reported phosphorus–nitrogen containing flame retardant could perhaps convert to intermediates like phosphamide derivatives through chain scission and molecular rearrangement.<sup>29,30</sup> Then, the self-condensation of intermediates



**Figure 4.** SEM images of the exterior residual chars of some representative thermosets after the vertical burning test: (1) DGEBA/DDS; (3) 5.0 wt % TNTP/DGEBA/DDS; (4) 10.0 wt % TNTP/DGEBA/DDS; and (6) 20.0 wt % TNTP/DGEBA/DDS; (a) 200 $\times$ ; (b) 1000 $\times$  and (c) 50,000 $\times$ .

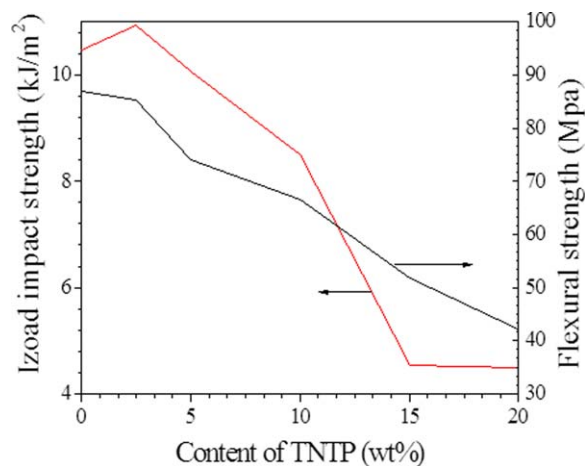


**Figure 5.** FTIR spectra of the residual chars collected from the UL-94 test for some representative thermosets: (1) DGEBA/DDS; (3) 5.0 wt % TNTP/DGEBA/DDS; (4) 10.0 wt % TNTP/DGEBA/DDS; and (6) 20.0 wt % TNTP/DGEBA/DDS. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

might occur to produce P-N bond,<sup>31</sup> which perhaps belong to a crosslinked oxyphosphazene, a crosslinked phosphor-imide or a combination of both structures.<sup>32,33</sup> The nanostructure of char layer in 20.0 wt % TNTP/DGEBA/DDS system can be observed in Figure 4(6c). In their IR spectrogram, the peaks at 1088 and 749  $\text{cm}^{-1}$  in Figure 5(3,4,6) indicate the existence of P-O-C in the char residuals as well. Above observation has further proven the formation of phosphorus-containing char residues coming from the modified thermosets by using TNTP during combustion. Since the char layers of these modified thermosets by using TNTP with the feature of intumescent, and rich in phosphorus and nitrogen element, TNTP could be used as a phosphorus-nitrogen synergistic intumescent flame retardant.

As a phosphorus-nitrogen containing compound, TNTP had a distinct synergistic effect on flame retardancy between phosphorus and nitrogen atoms. It was thought that TNTP played a role of flame retardant mainly via both the condensed phases and gaseous phases.

In the condensed phase, TNTP could be degraded to produce polyphosphoric acid as an acid catalyst, which would accelerate the cleavage of DGEBA/DDS to form an intumescent phosphorus-rich char layer blended with the residue of DGEBA



**Figure 6.** The mechanical property of DGEBA thermosets with different loadings of TNTP. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

in a high yield. It was observed these flame-retarded epoxy resins swelled and a carbonaceous foamed mass was formed on the surface after igniting. The char layer as a barrier could cut the intermaterial off from heat and oxygen. In addition, TNTP containing triazine ring could release nonflammable gases such as  $\text{NH}_3$ ,  $\text{N}_2$ ,  $\text{NO}_2$ , and  $\text{CO}_2$  by thermal degradation during burning to dilute the oxygen concentration at the combustion surface. The heat produced during combustion could be taken away via the process of gas release. This action belonged to gaseous phase fire retardation which played a very important role in self-extinguishing performance of the flame-retarded DGEBA/DDS.

### Mechanical Properties

Mechanical properties including Izod impact strength and flexural property of several TNTP/DGEBA/DDS thermosets and control were evaluated. Results are presented in Table III. The effect of different amount of TNTP on the mechanical performance of epoxy thermosets was also evaluated. Data can be found in Figure 6. In general, the mechanical properties of materials would have some negative effect due to the addition of flame retardants. At 2.5 wt % TNTP, we found no appreciable effect on flexural property (85.20 MPa) comparing with DGEBA/DDS (87.03 MPa). At the same level of TNTP, we notice its Izod impact strength is  $10.94 \text{ kJ m}^{-2}$ , but that of the blank sample is  $10.47 \text{ kJ m}^{-2}$ , which has been slightly enhanced.

**Table III.** The Mechanical Property of DGEBA Thermosets with Different Loadings of TNTP

Sample code	Thermosetting system	Flexural strength (Mpa)	Izod impact strength ( $\text{kJ/m}^2$ )
1	DGEBA/DDS	87.03	10.47
2	2.5 wt % TNTP/DGEBA/DDS	85.20	10.94
3	5.0 wt % TNTP/DGEBA/DDS	74.03	10.07
4	10.0 wt % TNTP/DGEBA/DDS	66.44	8.49
5	15.0 wt % TNTP/DGEBA/DDS	51.86	4.54
6	20.0 wt % TNTP/DGEBA/DDS	42.31	4.50

When TNTP loading was at 5.0 wt %, there were no noticeable effects either on Izod impact strength or flexural property comparing with DGEBA/DDS. However, when TNTP loading >5.0 wt %, their Izod impact strength decreased dramatically and their flexural property also gradually decreased (Figure 6). To some extent, TNTP led less negative effect on flexural property comparing with the effect on Izod impact strength. It showed larger loading of TNTP could make poor compatibility with epoxy thermosets that further caused the mechanical performance loss. The 2.5 wt % TNTP/DGEBA/DDS system showed best mechanical properties, accordingly only UL-94 V-1 rating can be achieved. 5.0 wt % TNTP/DGEBA/DDS system presented satisfied flame retardancy (UL-94, V-0) and acceptable mechanical properties. According to the flame retardancy and mechanical performance, we conclude that the optimum TNTP in the TNTP/DGEBA/DDS system should be between 2.5 and 5.0 wt %.

## CONCLUSIONS

A novel phosphorus-nitrogen flame retardant TNTP has been synthesized and fully characterized. The glass transition temperatures of these TNTP flame-retarded DGEBA epoxy thermosets (168.3–192.1°C) were higher than TNTP-free DGEBA epoxy thermoset (162.5°C). The loading of TNTP as low as 5.0 wt % could result in satisfied flame retardancy (UL-94, V-0) together with higher char residue (27.3%) at 700°C. TNTP showed a desirable effect on the char forming. The phosphorus-containing char residues played a significant role in improving flame retardancy of DGEBA epoxy resin. Data suggested that there was a synergistic effect between phosphorus and nitrogen in the flame retardant system. The 2.5–5.0 wt % TNTP/DGEBA/DDS system showed good performance with thermal stability as well as excellent mechanical properties. Overall, TNTP has demonstrated its potential as a promising flame retardant for the DGEBA epoxy resin. This promising flame retardant should have a wide range of applications including the high-tech field.

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