Synthesis and performance of a novel nitrogen-containing cyclic phosphate for intumescent flame retardant and its application in epoxy resin

Geyun You, Zhiquan Cheng, Hao Peng, Hongwu He

Institute of Organic Synthesis, College of Chemistry, Central China Normal University, Wuhan 430079, China
Correspondence to: H. He (E-mail: he1208@mail.ccnu.edu.cn)

ABSTRACT: A novel nitrogen-containing cyclic phosphate (NDP) was synthesized and well characterized by ^{1}H, ^{13}C, ^{31}P NMR, mass spectra and elemental analysis. NDP was used as an additive intumescent flame retardant (AIFR) to impart flame retardancy and dripping resistance for diglycidyl ether of bisphenol-A epoxy resin (DGEBA) curied by 4,4′-diaminodiphenylsulfone (DDS) with different phosphorus content. The flammability, thermal stability, and mechanical properties of NDP modified DGEBA/DDS thermosets were investigated by UL-94 vertical burning test, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and Izod impact strength and flexural property tests. The results showed that NDP modified DGEBA/DDS thermosets exhibited excellent flame retardancy, moderate changes in glass transition temperature and thermal stability. When the phosphorus content reached only 1.5 wt %, the NDP modified DGEBA/DDS thermoset could result in satisfied flame retardancy (UL-94, V-0). The TGA curves under nitrogen and air atmosphere suggested that NDP had good ability of char formation, and there existed a distinct synergistic effect between phosphorus and nitrogen. The flame retardant mechanism was further realized by studying the structure and morphology of char residues using FT-IR and scanning electron microscopy (SEM). It indicated that NDP as phosphorus-nitrogen containing flame retardant worked by both of the condensed phase action and the vapor phase action. Additionally, the addition of NDP decreased slightly the flexural strength of the flame retarded DGEBA epoxy resins, and increased the Izod impact strength of these thermosets. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41859.

INTRODUCTION

In recent years, epoxy resin has been widely used in coating, adhesive, electronics and building construction because of its excellent characteristics including high strength, low shrinkage, electrical and mechanical resistance. However, high flammability limits its further use in many desirable applications.[1–3] Although many reactive-type flame retardants have been reported as one of the most useful flame retardants to epoxy resin, some reactive-type flame retardants still stay at the laboratory scale because of its high costs and complex synthetic process.[4,5] Additive-type flame retardants are widely used, which are generally incorporated into epoxy resins by physical means. This obviously provides the most economical and expeditious way to promote the flame retardancy of commercial epoxy resins.[6] Some inorganic compounds such as aluminium hydroxide and magnesium hydroxide, *et al.* as traditional additive-type flame retardants have been widely used due to their advantages of effective and low cost. However, these inorganic retardants sometimes have poor compatibility with resins and adversely affect the mechanical, electrical and processing properties of epoxy thermosets because they as flame retardants are usually needed larger dosage.

Organic flame retardants not only present high flame-retardant efficiency, but also show excellent compatibility with epoxy resins. Both of halogen-containing and halogen-free flame retarded epoxy resins have been reported.[7] Due to the environmental issues, studies of halogen-free flame retardants are the favorable trends in either academia or industry.[8] Flame retardants containing phosphorus seem to offer a promising halogen-free and environmental friendly way to render epoxy resins flame retardancy in the future.[6] Flame retardants with phosphate units could produce H_3PO_4 and consequently pyrophosphoric acid during thermal degradation process, and then react with polymer chains to form a glass-like phosphorus-containing solid residues.[9] When phosphorus-containing flame retardants together with nitrogen-containing units or compounds to modified polymers, the phosphorus-containing char residues could be foamed

by the nonflammable degradation products of nitrogen derivatives during the combustion process.[10] This intumescent char layer could effectively prevent the underlying epoxy thermosets from degradation and inhibit the combustion process. Therefore, phosphorus-nitrogen containing intumescent flame retardants could exhibit excellent flame retardancy due to the phosphorus-nitrogen synergistic effect.[11–14]

Three novel polyphosphate esters with –C=N– bonds in the chain were synthesized by Liu et al.,[15] which were exhibited good flame retardancy for EVA (ethylene vinyl acetate) copolymer. We noticed that good char promoting effect, excellent thermal stability and phosphorus-nitrogen synergistic effect could be produced by a combination of phosphate unit and azomethine unit. Sun et al.[16] synthesized three compounds by the addition of 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) to the imine linkage, and used these three phosphorus-nitrogen containing compounds as cocuring agents of diaminodiphenylmethane for epoxy resins. The modified epoxy thermosets exhibited excellent flame retardancy and thermal stability due to the phosphorus-nitrogen synergistic effect. However, phosphorus-nitrogen containing compounds served as comonomers on the flame retardancy for polymers often involve a series of problems such as high cost and complex procedure, which limit their industrial application.[17] It is our goal to explore a novel additive-type phosphorus-nitrogen containing flame retardant that is simple preparation flow, cost-efficient, simplicity in use, environmentally friendly and the like. Given the previous encouraging findings, we are interested to design a novel additive-type intumescent flame retardant (AIFR) based on the structural units of phosphate and azomethine, and explore its usage in epoxy resins.

In this article, a novel nitrogen-containing cyclic phosphate (NDP) N^1,N^4-bis{3,4-bis(5,5-dimethyl-2-oxide-1,3,2-dioxaphosphinan-2-yl)oxy]benzylidene}benzene-1,4-diamine (NDP) was designed and synthesized. It was used as an AIFR in diglycidyl ether of bisphenol-A epoxy resin (DGEBA) with different phosphorus content. The thermal stability, flame retardancy and mechanical performance of these NDP modified DGEBA thermosets were systematic investigated. The flame retardant mechanism of NDP was also discussed.

EXPERIMENTAL
Materials
Triethylamine, 3,4-dihydroxybenzaldehyde (**1**), benzene-1,4-diamine, acetic acid, ethyl alcohol and 4,4′-diaminodiphenylsulfone (DDS) were of reagent grade and purchased from Sinopharm Chemical Reagent. DGEBA epoxy resin (commercial name: YD-128) with an epoxy equivalent weight (EEW) of 188 g/eq was obtained from Yuehua organic chemical plant of Yueyang General Petroleum Refining and Petrochemical Works. Dichloromethane was dried and distilled prior to use. Intermediates 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide (**2**) was synthesized and purified according to the methods described in the literature.[18]

Synthesis of 3,4-Bis[(5,5-dimethyl-2-oxido-1,3,2-dioxaphosphinan-2-yl)oxy]benzaldehyde (PCHO)
A solution of triethylamine 30.3 g (0.3 mol) in dichloromethane (40 mL) was dropwise added into a stirred mixture of 3,4-dihy-droxybenzaldehyde **1** (13.8 g, 0.1 mol) and 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide **2** (36.9 g, 0.2 mol) in dichloromethane (100 mL) at 0°C. The resultant mixture was stirred for 0.5 h at 0°C and then for 2–3 h at 30°C. The dichloromethane layer was washed with 0.1 M hydrochloric acid, statured potassium carbonate, and brine, dried, and concentrated to give the pure intermediate compound PCHO.

White solid; Yield, 93%; Melting point (M.p.) = 159.5–162.4°C; ^{1}H NMR [400 MHz, DMSO-d_6, ppm] 0.87 (d, J = 3.6 Hz, 6H, CH$_3$), 1.23 (s, 6H, CH$_3$), 4.15 (dd, J = 10.4, 3.8 Hz, 4H, CH$_2$), 4.44 (dd, J = 10.2, 5.3 Hz, 4H, CH$_2$), 7.67 (d, J = 8.1 Hz, 1H, Ar-H), 7.89 (d, J = 8.4 Hz, 2H, Ar-H), 9.98 (s, 1H, CHO); ^{13}C NMR [100 MHz, DMSO-d_6, ppm]: 20.0, 20.8, 31.8 (d, J = 6.1 Hz), 78.5, 120.7, 121.6, 128.4, 133.7, 141.1, 145.3, 191.3; ^{31}P NMR [162 MHz, DMSO-d_6, ppm]: −15.51, −14.97. Elem. Anal: calcd. for C$_{17}$H$_{24}$O$_9$P$_2$, C (47.01%), H (5.57%); Found, C (46.39%); H (5.19%). GC-MS: calcd. For C$_{17}$H$_{24}$O$_9$P$_2$: 434.09, found: 434.18.

Synthesis of N^1,N^4-Bis{3,4-bis(5,5-dimethyl-2-oxide-1,3,2-dioxaphosphinan-2-yl)oxy]benzylidene}benzene-1,4-diamine (NDP)
A solution of benzene-1, 4-diamine (0.10 mol), PCHO (0.20 mol) and acetic acid (5 wt % based on weight of PCHO) dissolved in 200 mL ethyl alcohol was stirred at room temperature. The reaction mixture was stirred for 1 h. Then, the yellow precipitate was filtered, washed with little acetone and dried in the atmospheric pressure. After drying, light yellow solid was obtained.

Yield, 96%; M.p.>260°C; ^{1}H NMR [400 MHz, DMSO-d_6, ppm]: 0.87 (s, 12H, CH$_3$), 1.23 (s, 12H, CH$_3$), 4.14 (dd, J = 23.0, 10.3 Hz, 8H, CH$_2$), 4.44 (s, 8H, CH$_2$), 7.39 (d, J = 3.7 Hz, 4H, C$_6$H$_4$), 7.58 (s, 2H, C$_6$H$_3$), 7.82 (s, 2H, C$_6$H$_3$), 8.03 (s, 2H, C$_6$H$_3$), 8.71 (d, J = 3.7 Hz, 2H, CH); ^{13}C NMR [100 MHz, DMSO-d_6, ppm]:19.0, 20.9, 31.8 (d, J = 5.9 Hz), 78.4, 119.7, 121.4, 122.2, 127.1, 134.0, 141.0, 142.8, 149.0, 158.3. ^{31}P NMR [162 MHz, DMSO-d_6, ppm]: −15.20, −14.96. Elem. Anal: calcd. for C$_{40}$H$_{52}$N$_2$O$_{16}$P$_4$, C (51.07%), H (5.57%), N (2.98%); Found, C (51.61%); H (5.04%), N (2.98%). GC-MS: calcd. For C$_{40}$H$_{52}$N$_2$O$_{16}$P$_4$: 940.74, found: 940.51.

Samples Preparation
NDP, a phosphorus-nitrogen containing flame retardant, as an additive was used in DGEBA epoxy resins. Different amount of NDP was applied in 70.0 g DGEBA into a 250-mL flask, depending on the phosphorus content in epoxy thermosets being considered (Table I). First, the mixture was heated at 160°C with frequent agitation to completely dissolve, and thereafter kept in vacuum oven for 5 min to completely eliminated air bubbles. Secondly, 23.0 g DDS severed as curing agent was added to the mixture, stirred at 160°C until DDS dissolved completely. Then, the resin-hardener mixture was kept in a vacuum oven again to eliminate air bubbles, and then rapidly poured into molds with preheating at 120°C. The resin-hardener mixtures were cured at 120°C for 2 h, at 150°C for 2 h, at 180°C for 2 h to make epoxy thermosets, respectively. Thereafter, the epoxy thermosets were allowed to cool slowly to room temperature to prevent cracking. The epoxy thermosets with phosphorus content 0.5, 1.0, and 1.5 wt % were obtained and labelled as NDP-n/DGEBA/DDS (n stands for the phosphorus content).

Table I. The Composition of Thermosets with Different Phosphorus Content

No.	Thermosetting system	P (%)	N (%)	Composites		
				DGEBA (g)	DDS (g)	NDP (g)
1	NDP-0.5/DGEBA/DDS	0.50	2.78	70.0	23.0	3.7
2	NDP-1.0/DGEBA/DDS	1.00	2.79	70.0	23.0	7.6
3	NDP-1.5/DGEBA/DDS	1.50	2.80	70.0	23.0	12.0
0	DGEBA/DDS	0	2.79	70.0	23.0	0

Characterization

Melting points were measured on an electrothermal melting-point apparatus and uncorrected. Infrared spectra were recorded as potassium bromide pellets on a Nicolet Avatar 360 Fourier transform infrared (FTIR) spectrophotometer. The NMR spectra were recorded in DMSO-d_6 solution on a Varian Mercury Plus-400 NMR spectrometer. Mass spectra (MS) was analyzed on a Finnigan Trace MS 2000 spectrometry. Elemental analyses were performed with a Vario EL III CHNSO elemental analyzer.

Differential scanning calorimetry (DSC) experiments were conducted on a Perkin-Elmer DSC-7 thermal analyzer in a nitrogen atmosphere. Glass transition temperature (T_g) were determined by scanning from 30 to 300°C at a scan rate of 10°C/min under nitrogen atmosphere. Thermogravimetric analysis (TGA) were performed on a thermal gravimetric analyzer (STA 449 C, NETZSCH Instruments, MA). The specimens were heated from 30 to 700°C at a heating rate of 10°C/min under nitrogen or air atmosphere.

Vertical Burning Test (UL-94) was carried out according to the ASTM D 3801 standard with five test sample bars 127 × 12.7 × 3.2 mm³ on a CZF-3 type level vertical flame detector.

Flexural property was measured using a CMT6503 tensile tester, and performed according to Plastics-Determination of flexural properties (GB/T9341-2000) with five specimens for each sample at rate of crosshead motion of 1.74 mm/min. The sample size was 80.0 × 10.0 × 4.0 mm³. Izod impact strength was measured using a ZBC1400-1 impact tester according to Plastics-Determination of charpy impact strength of rigid materials (GB/T 1043-93), 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 also 80.0 × 10.0 × 4.0 mm³.

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.

RESULTS AND DISCUSSION

Synthesis and Characterization

The synthetic route of NDP is shown in Scheme 1. The intermediate of phosphate-substituted benzaldehyde PCHO could be successfully prepared by the reaction of 3,4-dihydroxybenzaldehyde (**1**) and 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphinane
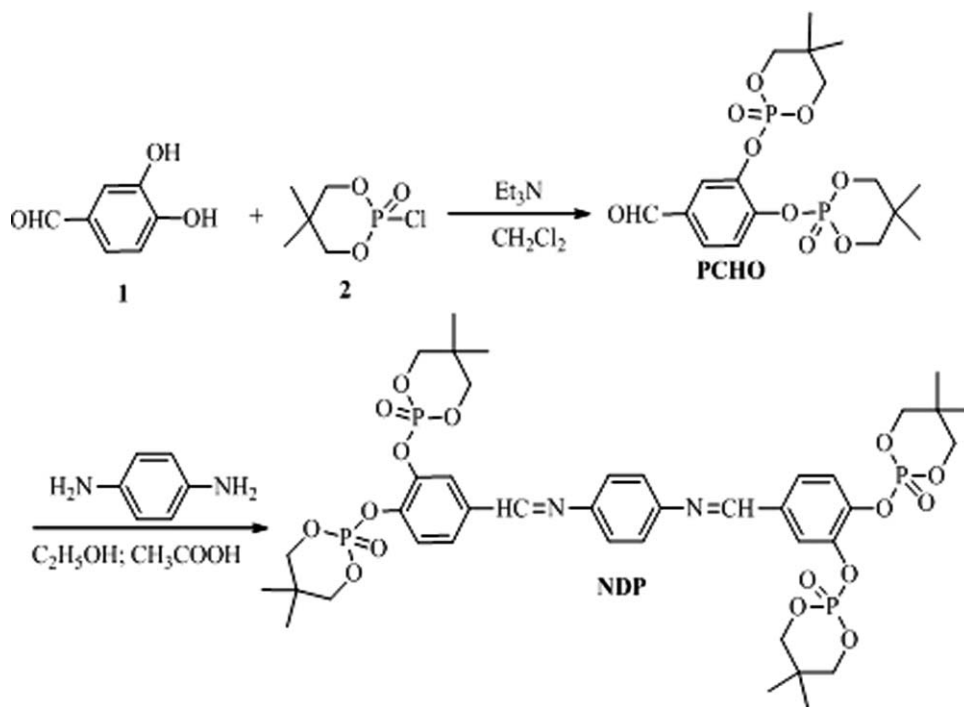
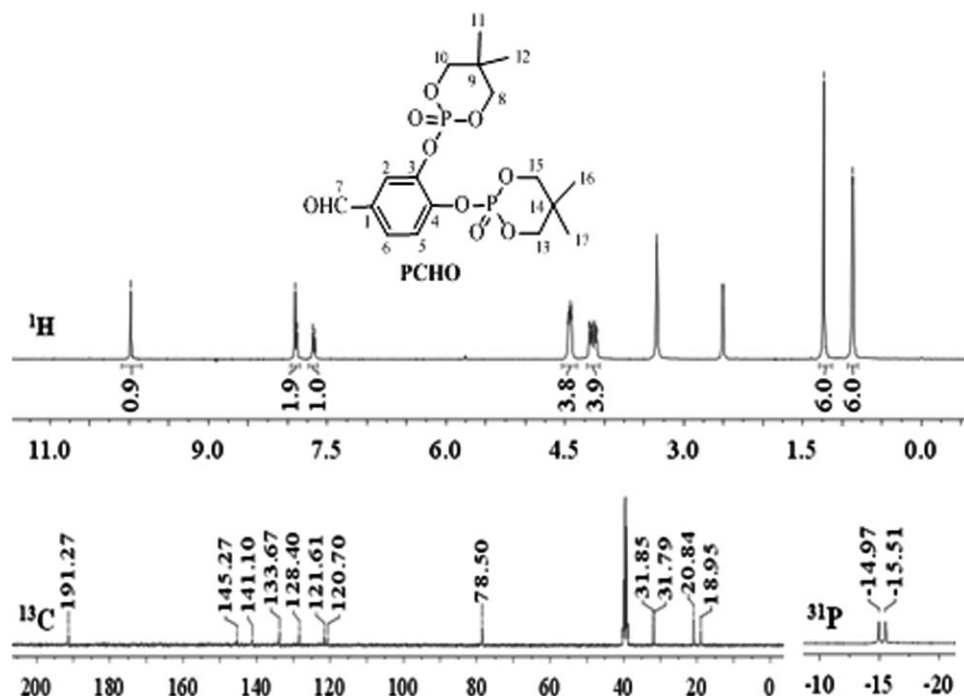**Scheme 1.** Synthesis of nitrogen-containing cyclic phosphate (NDP).

Figure 1. ^{1}H, ^{13}C, and ^{31}P NMR spectrum of PCHO.

2-oxide (**2**) in dichloromethane using triethylamine as acid binding agent. ^{1}H, ^{13}C, and ^{31}P NMR spectrum of PCHO are displayed in Figure 1. The proton peak for the –CHO of PCHO appeared at $\delta = 9.98$ ppm in ^{1}H NMR spectrum, and the corresponding signal of carbon at around 191.3 ppm was observed in the ^{13}C NMR spectrum. Two ^{31}P NMR signals at -14.97 and -15.51 ppm, respectively, were also observed.

The novel phosphorus-nitrogen containing compound NDP was synthesized by the condensation of PCHO with benzene-1,4-diamine. In the presence of acetic acid, the time of synthetic reaction could be shortened obviously and NDP was obtained in 96% yield. ^{1}H, ^{13}C, and ^{31}P NMR spectrums of NDP are shown in Figure 2. The proton signal of imine linkage in NDP appeared at 8.71 ppm. The characteristic peak of imine at
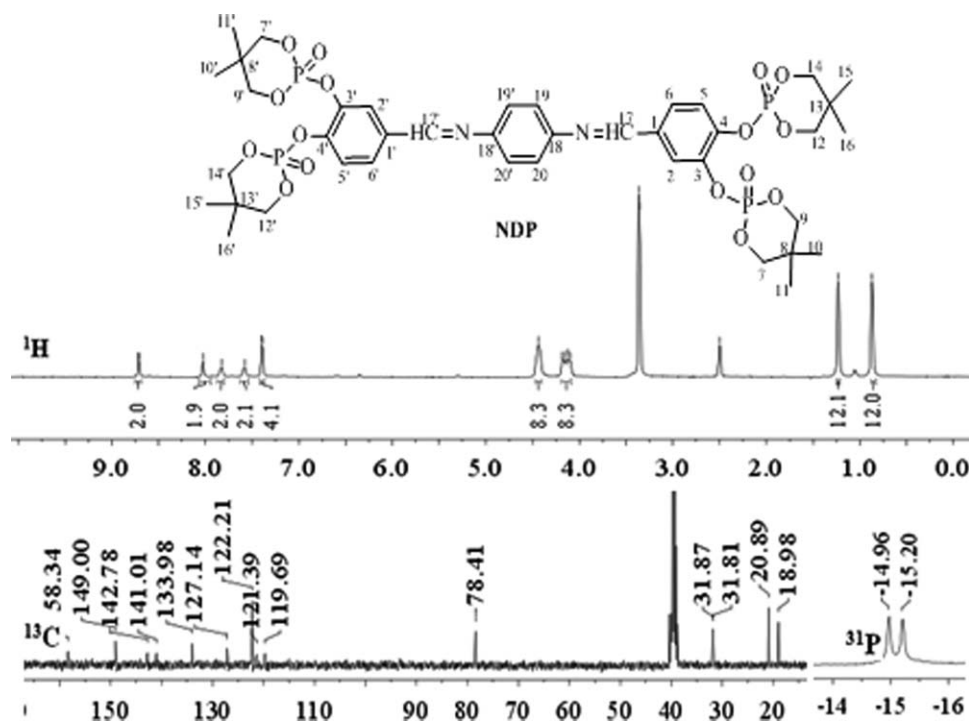

Figure 2. ^{1}H, ^{13}C, and ^{31}P NMR spectrum of NDP.

Table II. Thermal Properties of Epoxy Thermosets Under Nitrogen Atmosphere

No.	Thermosetting system	T_g (°C)	T_{onset} (°C)	T_{max} (°C)	R_c (%)
1	NDP-0.5/DGEBA/DDS	174.3	192.7	377.9	24.2
2	NDP-1.0/DGEBA/DDS	154.5	237.1	365.2	29.0
3	NDP-1.5/DGEBA/DDS	149.0	237.6	357.9	30.8
0	DGEBA/DDS	183.9	241.5	408.0	16.4

T_{g}: glass transition temperature;
T_{onset}: initial decomposition temperature;
T_{max}: maximum decomposition temperature;
R_c: char yield at 700 °C.

around 158.3 ppm was observed in the ^{13}C NMR spectrum which confirmed the condensation of intermediate (**1**) and (**2**). In the ^{31}P NMR spectrum of NDP, its chemical shifts appeared as two signals at −14.96 and −15.20 ppm, respectively, which were consistent with the characterization of phosphate.

Thermal Properties

The glass transition temperature (T_g) of NDP modified epoxy thermosets (NDP-n/DGEBA/DDS), evaluated from DSC curves, in comparison with NDP-free epoxy thermoset (DGEBA/DDS) are listed in Table II. As shown in Table II, the glass transition temperatures for NDP-n/DGEBA/DDS thermosets were recorded at 149.0–174.3°C, and that was lower than DGEBA/DDS (183.9°C). Moreover, with the addition amount of NDP increasing, T_g values of modified epoxy thermosets decreased. This indicated that the four cyclic phosphate groups of NDP increased the polymer free volume and produced a decrease in inter-chain attraction, while the more rigid structure of NDP induced the movement of polymer main chain at higher temperature.

The thermal stability behaviors of NDP-n/DGEBA/DDS and DGEBA/DDS were measured with TGA under nitrogen atmosphere. The initial decomposition temperature (T_{onset}), the maximum decomposition temperature (T_{max}), and the char yield (R_c) for the aforementioned epoxy thermosets are listed in Table II. As shown in Figure 3(A), all the epoxy thermosets showed only one step of decomposition. The neat DGEBA/DDS thermoset began to lose it weight at about 241.5°C, leaving only 16.4 wt % char at 700°C. However, three NDP flame retarded
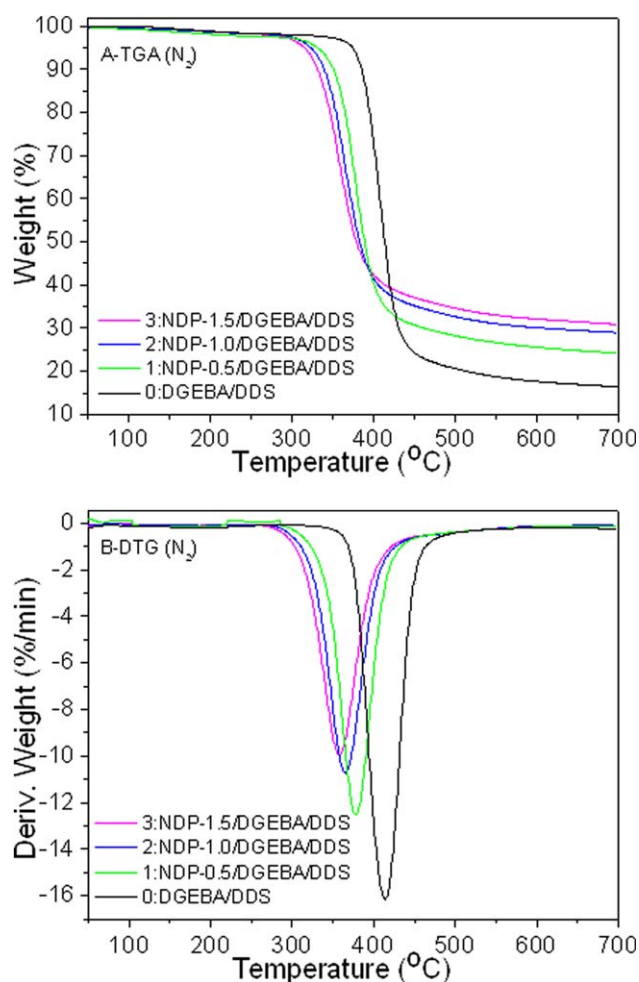

Figure 3. TGA(A) and DTG(B) curves of epoxy thermosets under nitrogen atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
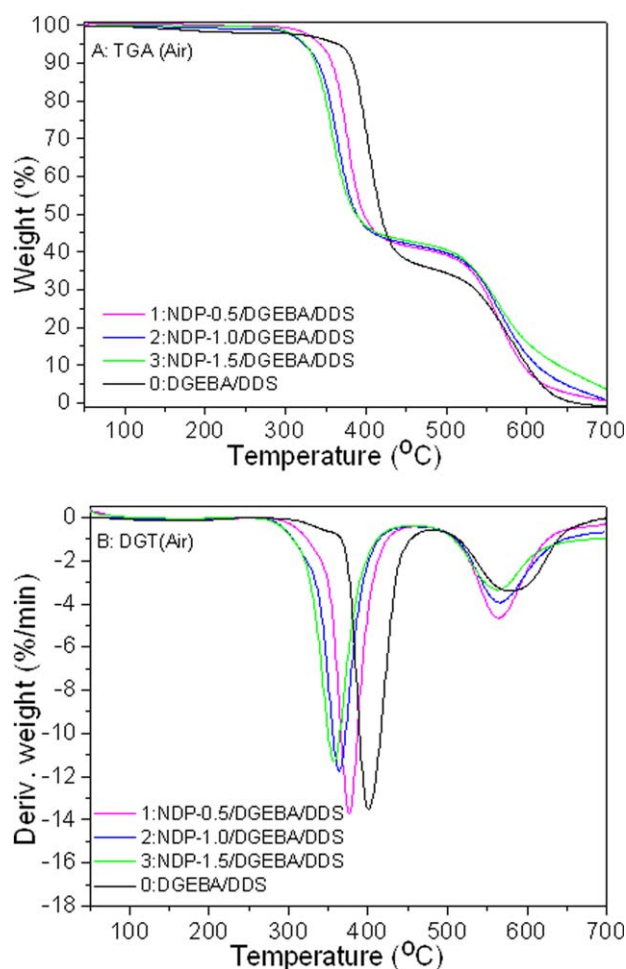

Figure 4. TGA(A) and DTG(B) curves of epoxy thermosets under air atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Thermo-Oxidative Degradation of Epoxy Thermosets Under Air Atomosphere

No.	Thermosetting system	T_{max1} (°C)	Weight loss (wt %) stage 1	T_{max2} (°C)	Weight loss (wt %) stage 2	R_c (%)
1	NDP-0.5/DGEBA/DDS	376.4	59.0	564.0	41.0	0.6
2	NDP-1.0/DGEBA/DDS	363.7	58.1	565.4	41.1	0.9
3	NDP-1.5/DGEBA/DDS	357.0	57.6	563.1	38.7	3.7
0	DGEBA/DDS	400.7	64.1	578.7	36.6	0

$T_{max,}$: maximum decomposition temperature;
$R_{c,}$: char yield at 700 °C.

epoxy thermosets had a lower initial decomposition temperature in the range of 192.7–237.6°C. This was attributed to less stability of P-O-C bond linkage which could decompose below 220°C.[19] The maximum decomposition temperature (T_{max}) was decreased with the increasing loading of NDP, which could be seen obviously from Figure 3(B). When 0.5 wt % phosphorus content was loaded in the DGEBA thermoset, the corresponding T_{max} decreased from 408.0 to 377.9°C. However, the char yield of NDP flame retarded epoxy thermosets at 700°C was higher than neat DGEBA/DDS thermoset. The formulation of NDP-1.5/DGEBA/DDS presented a highest char yield (30.8 wt %) due to the higher phosphorus content in this thermoset. It indicated that NDP had a good effect on char formation.

The thermal oxidation processes of all thermosets were evaluated by TGA under air atmosphere. The TGA and DTG results of DGEBA/DDS and NDP-n/DGEBA/DDS thermosets are presented in Figure 4 and Table III, respectively. Unlike under N_2 atmosphere, the thermal decomposition of DGEBA/DDS under air atmosphere was characterized by two decomposition steps with maximum mass loss rate at 400.7 and 578.7°C, respectively. It yielded almost 0 wt % residues at 700°C. The first stage was in range of 300–450°C. During the first stage, 64.1 wt % weight loss of original sample occurred at this stage, which was due to the thermal oxidative degradation of polymer chain itself, included the scission of the isopropylidene linkage and the branching and crosslinking reactions of molecular chains induced by oxygen.[10] The second stage was in range of 450–700°C, and about 36.6 wt % weight loss occurred at this stage. The second stage corresponded to the thermal oxidative degradation of the char formed in the first step.[20]

The degradation processes of NDP-n/DGEBA/DDS exhibited two maxima of decomposition and considerable amounts of char residues at 700°C. The first maximum decomposition temperature (T_{max1}) was in range of 357.0–376.4°C, and probably

due to the oxidation and destruction of cyclic phosphate, more sensitive to degradation. Except a decrease of T_{max1} at the first decomposition stage, the introduction of NDP in DGEBA/DDS thermoset induced decrease of T_{max2}. The results implied that the introduced NDP could not improve the thermal stability of DGEBA/DDS at high temperature under air atmosphere. Although the thermoset does not have good thermal stability, it can be a good flame retardant if it can produce char or nonflammable gas during a fire.[21,22] According to the weight loss date in Table III and curves A and B in Figure 4, the weight loss of NDP-n/DGEBA/DDS was in range of 57.6–59.0 wt % at the first stage and 38.7–41.1 wt % at the second stage, and that of pure DGEBA/DDS 64.1 wt % at the first stage and 36.6 wt % at the second stage. Although the weight loss at the first stage for NDP-n/DGEBA/DDS was lower than that for pure DGEBA/DDS, the char yield of solid residue was improved. The char yield of NDP-1.5/DGEBA/DDS at 700°C was 3.7 wt % when compared with pure DGEBA/DDS with no char residue. The reason for this phenomenon may be explained as follow. When NDP modified thermosets were heated, the cyclic phosphate units in NDP decomposed firstly and then interacted with the degradation products of thermosets to form the phosphorus-nitrogen containing crosslinking networks, which could prevent further weight loss. At the evaluated temperature, the loss of nitrogen on the networks formed in the first stage was occurred and released a certain number of nitrogen-containing gas such as NH_3, NO, and NO_2. The nonflammable gas could foam char to form an intumescent structure. However, the char residue in the second stage could also be decreased by the release of nonflammable gases and resulted in more weight loss at the second stage. Considering the thermal behaviors of NDP-n/DGEBA/DDS under air atmosphere, it was obvious that introducing NDP into DGEBA epoxy resin obtained excellent flame retardant efficiency, probably resulting from the phosphorus-nitrogen synergistic effect.

Table IV. Flame Retardant Properties of Epoxy Thermosets

No.	Thermosetting system	P (%)	N (%)	t_1 (s)	t_2 (s)	UL-94 rating	Dripping
1	NDP-0.5/DGEBA/DDS	0.5	2.78	15.4	10.3	V-1	No
2	NDP-1.0/DGEBA/DDS	1.0	2.79	10.8	8.1	V-1	No
3	NDP-1.5/DGEBA/DDS	1.5	2.80	7.6	1.9	V-0	No
0	DGEBA/DDS	0	2.79	>50	–	failed	Yes

$t_{1,}$: the burning time after first ignition; $t_{2,}$: the burning time after second ignition.
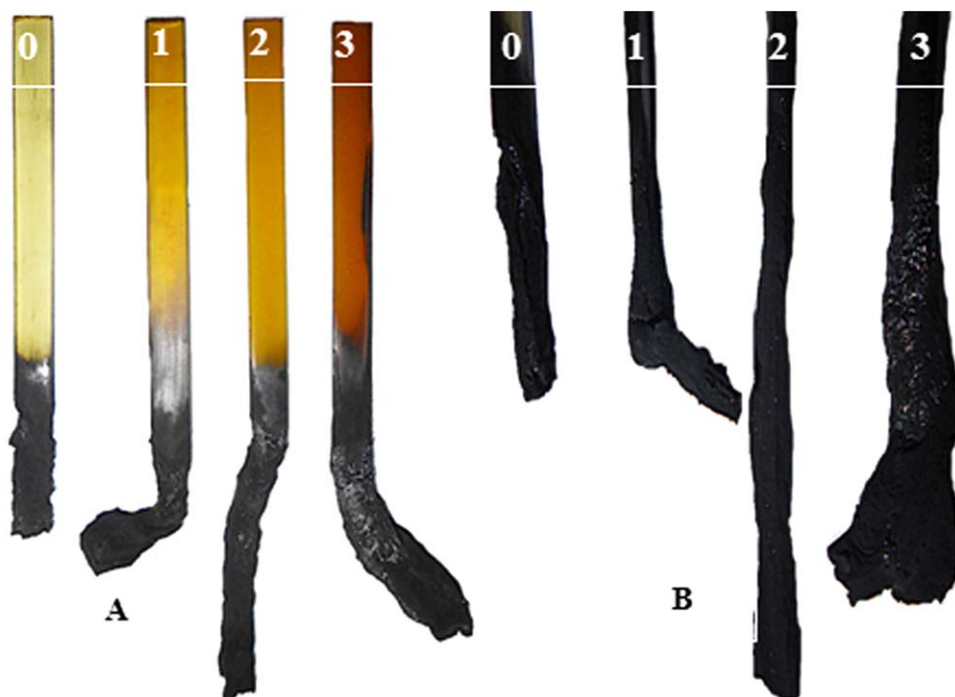
Figure 5. Photographs of the specimens after UL-94 test: front projection (A) and side projection (B). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Flame-Retardant Performance

The epoxy thermosets containing various amounts of NDP were prepared and evaluated by vertical burning tests (UL-94). The testing results are listed in Table IV. The vertical burning test showed that when the neat DGEBA/DDS sample was ignited by the first time, it was difficult to be self-extinguished after 50 s and failed to pass vertical burning test. It indicated that nonflame retarded DGEBA epoxy resin had a high flammability. Nevertheless, the sample of NDP-0.5/DGEBA/DDS with only 0.5 wt % phosphorus content could extinguish spontaneously and accompanied with no droppings. When NDP modified DGEBA thermoset containing 1.5 wt % phosphorus content could reach a UL-94 flammability rating of V-0. These results indicated that the flame retardancy of DGEBA thermosets could be greatly improved by incorporating NDP.
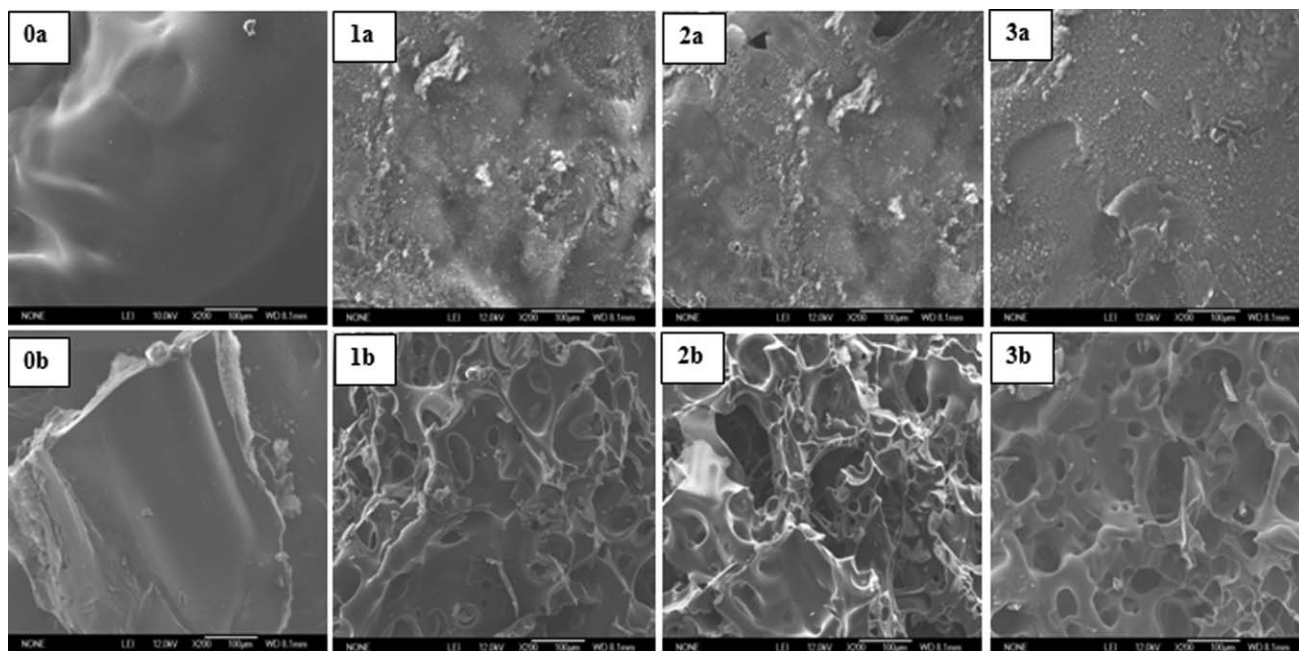

Figure 6. SEM images of char morphology after UL-94 test: the outer surface (a) and the inner surface (b).
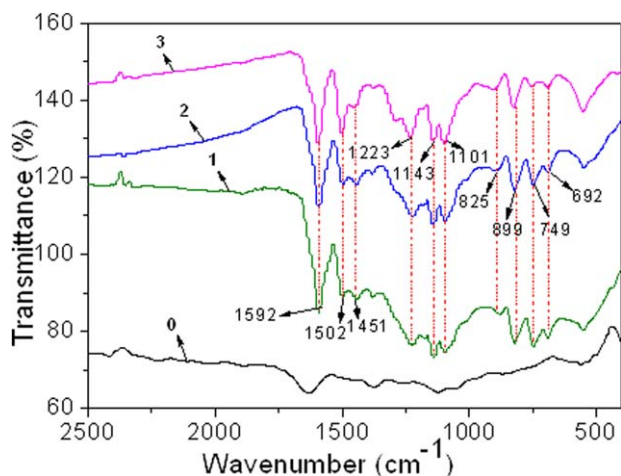
Figure 7. FTIR spectrums of the residual chars collected from the vertical burning test for epoxy thermosets. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The photographs of tested samples after the vertical burning test are shown in Figure 5. The DGEBA/DDS as a control burned continuously with a big smoke after vertical ignition accompanied with flammable dripping. The emission of big smoke during combustion was a major factor in the mass loss of DGEBA/DDS. From our observation, the neat DGEBA/DDS only formed a little char on the surface of its test bar [Figure 5(A0)]. However, it can be seen obviously from Figure 5(B1–B3), the tested bars of flame retarded DGEBA/DDS using NDP as an AIFR were covered with an intumescent char layer. When the loading of NDP increased, the char became heavier and more intumescent. As shown in Figure 5(B3), NDP-1.5/DGEBA/DDS produced a heaviest and most intumescent char layer compared to the other samples. This phenomenon was also validated by the test results of TGA under air atmosphere (Table III), which indicated that NDP could effectively enhance the formation of char layer.

Mechanism of Flame Retardant
The char residues play a significant role in improving flame retardancy of DGEBA epoxy thermosets, the investigation of combustion residues could help to understand the mechanism of NDP. Both the exterior and the interior chars, which were obtained from the muffle furnace, were analyzed by SEM. Their morphologies are shown in Figure 6. It is not difficult to discern the differences of the chars between neat DGEBA/DDS and flame retarded DGEBA thermosets. A compact outer surface and a smooth inner surface can be seen from Figure 6(0). It indicates that the neat DGEBA/DDS thermoset only produced a

thin char layer on the tested samples during combustion. This thin char layer was not sufficient to prevent mass loss and heat transfer. Thus, the neat DGEBA/DDS thermoset with no flame retardancy was hardly self-extinguished. When NDP was applied into DGEBA, a uniform and regulative solid surface could be observed [Figure 6(1a–3a)]. The interior char in NDP-1.5/DGEBA/DDS [Figure 6(3b)] was much more intumescent than that of neat DGEBA/DDS [Figure 6(1b)], For NDP-n/DGEBA/DDS, the interior chars became more intumescent by the addition of NDP, which further indicated that NDP had a good effect to expand the char layers.

In order to further analyze the structure of combustion residues, FTIR spectrums of char residues after UL-94 test are shown in Figure 7. As displayed in Figure 7, significant difference between DGEBA/DDS [Figure 7(0)] and three NDP flame retarded thermosets [Figure 7(1–3)] in the FTIR spectrum of residual chars can be observed from 400 to 2000 cm^{-1}. No obvious absorption bands are found in the FT-IR spectra of DGEBA/DDS sample [Figure 7(0)]. In Figure 7(1–3), the absorption peaks at 1592, 1520, and 1451 cm^{-1} are accounted for the stretching vibration of aromatic ring. The peak at 1223 cm^{-1} is identified for the stretching vibration of P=O.[9] The peaks at 1101 and 899 cm^{-1} show symmetric and asymmetric stretching vibrations indicating the existence of P-O-P bond.[19,23,24] The existence of P-O-P bond in the char residues of NDP-n/DGEBA/DDS indicated that the structural unit of cyclic phosphate could link each other by sharing one oxygen atom which acted as a crosslinker. The peak at 1142 cm^{-1} can be assigned to the stretching vibration of P-O-C.[25] Two peaks at 749 and 692 cm^{-1} are accounted for the vibration of aromatic groups.[26] These indicated that the structural unit of P-O-P could link to different aromatic unit during combustion, which led to the formation of complex phosphorus-carbon structure and producing high char residues.

As a novel AIFR, NDP with cyclic phosphate group degraded at relatively low temperature, which could produce H_3PO_4 and consequently pyrophosphoric acid, and then reacted with thermosets' chains to yield a glass-like phosphorus-containing char residues. Therefore, the condensed phase action would be considered. NDP was also a compound with azomethine moiety which could release nonflammable gases such as NH_3, N_2, NO_2, and CO_2 by thermal degradation during combustion. The nonflammable gases could dilute the oxygen concentration at the surface of thermoset and also take away the heat produced during combustion; meanwhile, it expanded the char layer which could be seen clearly from Figures 5 and 6. This intumescent char layer would prevent the underlying epoxy thermosets from

Table V. Mechanical Properties of Epoxy Thermosets

No.	Thermosetting system	Flexural strength (Mpa)	Izod impact strength (kJ/m²)
1	NDP-0.5/DGEBA/DDS	98.55 ± 2.93	9.53 ± 0.54
2	NDP-1.0/DGEBA/DDS	99.39 ± 2.59	8.22 ± 0.82
3	NDP-1.5/DGEBA/DDS	102.54 ± 3.27	8.20 ± 0.58
0	DGEBA/DDS	103.70 ± 1.90	7.92 ± 0.60

degradation and inhibit the combustion process; the vapor phase action would function to some extent. Therefore, NDP as phosphorus-nitrogen containing intumescent flame retardant worked by both of the condensed phase action and the vapor phase action.

Mechanical Properties

The mechanical properties of NDP-n/DGEBA/DDS thermosets including flexural properties and Izod impact strength were evaluated. The neat DGEBA/DDS were used as a control. The results are presented in Table V. Compared with the control neat thermoset, the addition of NDP only decreased slightly the flexural strength, but increased obviously the Izod impact strength of epoxy thermosets. With the increase of the NDP content in the DGEBA/DDS system, the flexural strength could be gradually increased and reached similar level with control when thermoset containing 1.5 wt % phosphorus. Although impact strength of modified epoxy thermosets were decreased with the increase of NDP content, all these thermosets exhibited higher Izod impact strength than that of the neat DGEBA/DDS. The mechanical properties of the thermoset with NDP-1.5/DGEBA/DDS (UL-94, V-0) decreased by 1.12% for flexural strength and increased by 3.54% for Izod impact strength compared with the neat DGEBA/DDS. No significant negative effect on mechanical properties made NDP to be a potential additive for DGEBA epoxy resin.

CONCLUSIONS

A novel NDP was synthesized and fully characterized. The glass-transition temperatures of NDP modified DGEBA/DDS epoxy thermosets with different phosphorus content (0.5, 1.0, and 1.5 wt %) were in range of 149–174°C. TGA and DTG results under nitrogen or air atmosphere revealed that NDP presented a good synergistic effect between phosphorus and nitrogen element, and promoted to produce an intumescent char layer on the surface of DGEBA/DDS thermosets. The phosphorus-containing intumescent char with multipurpose and compact structure could act as a barrier to inhibit gaseous products and insulate the underlying polymer from heat and air. The NDP modified DGEBA/DDS thermoset with 1.5 wt % phosphorus content (NDP-1.5/DGEBA/DDS) could result in satisfied flame retardancy (UL-94, V-0) and yield 3.7 wt % char residue compared with the neat DGEBA/DDS thermoset with none char residue under air atmosphere. Furthermore, NDP had a positive impact on the Izod impact strength and only a small decline on the flexural property. NDP-1.5/DGEBA/DDS thermoset exhibited best flame retardancy and mechanical performance. Therefore, the halogen-free NDP-1.5/DGEBA/DDS thermoset will have potential applications in electronic fields with consideration of environment, and NDP makes it capable of being utilized as an intumescent flame-retardant additive with DGEBA epoxy.

ACKNOWLEDGMENTS

REFERENCES

1. Lee, H; Neville, K. Handbook of Epoxy Resins; McGraw-Hill: New York, **1972**.

2. Lubin, G. Handbook of Composites; Van Nostrand Reinhold: New York, **1982**.

3. Tao, Z. Q.; Yang, S. Y.; Ge, Z. Y.; Chen, J. S.; Fan, L. *Eur. Polym. J.* **2007**, *43*, 550.

4. Gouri, M. E.; Bachiri, A. E.; Hegazi, S. E.; Rafik, M.; Harfi, A. E. *Polym. Degrad. Stabil.* **2009**, *94*, 2101.

5. Bourbigot, S.; Duquesne, S. *J. Mater. Chem.* **2007**, *17*, 2283.

6. Lu, S.; Hamerton, I. *Prog. Polym. Sci.* **2002**, *27*, 1661.

7. You, G. Y.; Cheng, Z. Q; Peng, H.; He, H. W. *J. Appl. Polym. Sci.* **2014**, *131*, 1.

8. Feng, J.; Hao, J. W.; Du, J. X.; Yang, R. J. *Polym. Degrad. Stabil.* **2010**, *95*, 2041.

9. Hoang, D.; Kim, J.; Jang, B. N. *Polym. Degrad. Stabil.* **2008**, *93*, 2042.

10. Chen, H.; Zhang, K; Xu, J. *Polym. Degrad. Stabil.* **2011**, *96*, 197.

11. Hulicova-Jurcakovab, D.; Seredycha, M.; Lub, G. Q.; Kodiweerac, N. K. A. C.; Stallworthc, P. E.; Greenbaumc, S.; Bandosza, T. J. *Carbon* **2009**, *47*, 1576.

12. Xing, W.; Song, L.; Lv, P.; Jie, G.; Wang, X.; Lv, X.; Hu, Y. *Mater. Chem. Phys.* **2010**, *123*, 481.

13. Cao, Z.; Zhang, Y.; Song, P.; Cai, Y.; Guo, Q.; Fang, Z.; Peng, M. *J. Anal. Appl. Pyrol.* **2011**, *92*, 339.

14. Tai, Q.; Song, L.; Hua, Y.; Yuen, R. K. K.; Feng, H.; Tao, Y. *Mater. Chem. Phys.* **2012**, *134*, 163.

15. Liu, Y.; Zhang, Y.; Cao, Z.; Fang, Z. *Ind. Eng. Chem. Res.* **2012**, *51*, 11059.

16. Sun, D. C.; Yao, Y. W. *Polym. Degrad. Stabil.* **2011**, *96*, 1720.

17. Lin, C. H.; Chang, S. L.; Wei, T. P.; Ding, S. H.; Su, W. C. *Polym. Degrad. Stabil.* **2010**, *95*, 1167.

18. Zhang, S.; Li, B.; Lin, M.; Li, Q.; Gao, S.; Yi, W. *J. Appl. Polym. Sci.* **2011**, *122*, 3430.

19. Zhu, S.; Shi, W. *Polym. Degrad. Stabil.* **2003**, *80*, 217.

20. Qian, X. D.; Song, L.; Hu, Y.; Yuen, R. *Thermochim. Acta* **2013**, *552*, 87.

21. Shin, Y. J.; Ham, Y. R.; Kim, S. H.; Lee, D. H.; Kim, S. B.; Park, C. S.; Yoo, Y. M.; Kim, J. G.; Kwon, S. H.; Shin, J. S. *J. Ind. Eng. Chem.* **2010**, *16*, 364.

22. Liu, Y. L.; Chiu, Y. C.; Wu, C. S. *J. Appl. Polym. Sci.* **2003**, *87*, 404.

23. Bugajny, M.; Bourbigot, S.; Le Bras, M.; Delobel, R. *Polym. Int.* **1999**, *48*, 264.

24. Le Bras, M.; Bourbigot, S.; Revel, B. *J. Mater. Sci.* **1999**, *34*, 5777.

25. Bourbigot, S.; Le Bras, M.; Delobel, R.; Tremillon, J. *J. Chem. Soc. Faraday Trans.* **1996**, *92*, 3435.

26. Setnescu, R.; Jipa, S.; Setnescu, T.; Kappel, W.; Kobayashi, S.; Osawa, Z. *Carbon* **1999**, *37*, 1.