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A novel and feasible approach for one-pack flame-retardant epoxy resin with long pot life and fast curing

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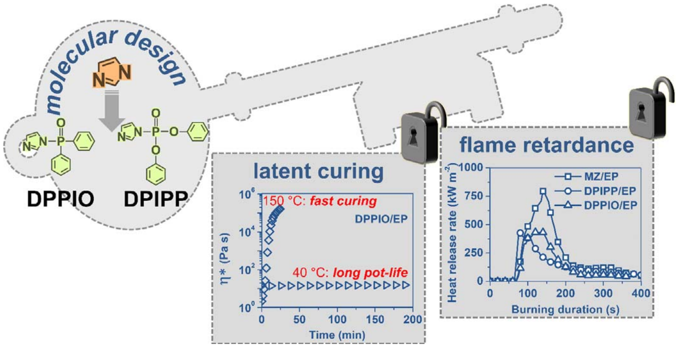
GRAPHICAL ABSTRACT



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ABSTRACT

Liquid epoxy resins (EP), curing agents, as well as other additives such as flame retardants are preferred to be formulated as one-pack materials rather than being mixed just prior to their applications. Therefore, they suffer premature curing with increasing of viscosity during storing and operating. To address the above challenging problem, we designed and synthesized a novel latent flame-retardant curing agent named 1-(diphenylphosphinyl)-1*H*-imidazole oxide (DPPIO) for EP, which was proved exhibiting not only long pot life during storing and fast curing as operating, but also excellent flame retardance after curing. It was observed from dynamic rheometry that, DPPIO/EP kept stable near room temperature for a long time but quickly gelated within only 6.5 min at 150 °C. With only 15 wt% addition of DPPIO, the limiting oxygen index (LOI) of the cured sample increased to 38.0% from 21.0% of the contrast sample, and UL-94 V-0 rating at 1.6 mm thickness was successfully achieved. Peak of heat release rate (PHRR) and total heat release (THR) obtained from cone calorimetry further certified excellent flame retardance of DPPIO/EP. Another typical flame-retardant group with different chemical environment was designed for modifying imidazole to obtain a derivative named diphenyl 1*H*-imidazol-1-ylphosphonate (DPIPP) in the same way. It was verified that DPIPP/EP showed acceptable latent curing efficiency and satisfactory flame retardance as DPPIO/EP did. Therefore, it's a generally effective and facile approach to develop latent flame-retardant curing agents for EP by modifying imidazole with appropriate flame-retardant groups. Taking advantage of the features, these one-pack flame-retardant epoxy materials can bring more chances for widespread applications.

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1. Introduction

Epoxy resins (EP) have long been widely used in electronic devices (as excellent electrical insulators), laminates, encapsulations (covering the integrated circuitry from environment), coatings, adhesives and advanced composite matrices for decades [1–4], owing to their excellent moisture, heat and chemical resistance, low shrinkage on curing, fine toughness, strong adhesion to diverse substrates, as well as satisfactory mechanical and dielectric properties [5–8]. Nonetheless, the flammable nature seriously restricts their widespread applications, especially in the areas requiring high flame retardance such as construction, transportation, aerospace and electrical/electronic fields [9–12].

Under this consideration, several approaches have been proposed to overcome such predicament by introducing different flame retardants [13–16]. In fact, the incorporation of halogen-based flame retardants into epoxy matrices has long been proved to be an efficient way to achieve expected flame retardance. Unfortunately, taking into account the recycling requirement and environmental impact, the use of such halogen-containing substances like tris(dibromopropyl) phosphate (TDBPP) needs to be forbidden [17,18]. For decades, halogen-free flame retardants, particularly phosphorus-containing ones have received more attention for substitute due to the flame-retardant activity both in gaseous and condensed phases [19,20]. Phosphorus-containing flame retardants, or flame-retardant groups, can be expediently introduced into EP by physically mixing or chemically bonding. Comparably, chemically bonding flame-retardant groups, or so-called intrinsically flame retarding endows the resulting materials with long lasting flame-retardant performance and environment tolerance. In our group's previous works [21–23], Wang et al. successfully modified ammonium polyphosphate (APP) as organic-inorganic hybrid flame-retardant curing agents via the cation exchange reaction between APP and different organic amines including diethylenetriamine, piperazine and branched polyethyleneimine. Among them, the piperazine-modified one (PAz-APP) gave excellent flame resistance and smoke suppression efficiency to EP matrices. Furthermore, the incorporation of the hybrid didn't worsen the mechanical properties instead of improving the impact strength of the resulting flame-retardant sample.

In practice, EP, curing agents, as well as other functional and filling additives would like to be formulated as one-pack materials for large batch production rather than being mixed prior to applying. In this case, gradual increasing of viscosity and premature curing of the materials as being stored should be solved, which is of special relevance as amines being used as curing agents [24–26]. Thus, latent curing systems need to be developed to solve the tough problem. The phrase latent curing denotes the curing activity inert at room temperature while promoting a rapid cure at higher temperature. Therefore, at the presence of latent curing agents, EP can be stored under the form of one-pack curing systems over a very long period in the liquid state and fast curing can be triggered at the exact time and place desired by the operator. This approach combines both storing and processing advantages, particularly in the process for electronics such as encapsulation or coatings. Kudo et al. synthetized a kind of imidazole derivative [27] as thermal latent curing agents. Ascribed to the intramolecular hydrogen bond between the phenolic hydroxyl group and the nitrogen atom in the imidazole ring, latent curing reactivity was tailored via the breakage of intramolecular hydrogen bonds at 150 °C; whereas the epoxy composition showed long-term storing stability at room temperature. Except such reversible hydrogen bonds, thermo-labile covalent bonds [28], microencapsulation types [29] and metal-imidazole complexes [30] were also widely reported in order to achieve one-pack epoxy materials containing both epoxy resins and curing agents with long-time storing stability and on-site operating reactivity.

In the present work, two typical phosphorus-containing flame-retardant groups were designed for modifying imidazole to obtain functional derivatives as flame-retardant latent curing agents for EP. As a way to kill two birds with one stone, appropriate latency with long pot life and acceptable curing activity, as well as satisfactory flame retardance were endowed to EP simultaneously. Storage stability and curing behaviour were investigated by differential scanning calorimetry (DSC) and dynamic rheological analysis; and the corresponding curing procedure was explored by X-ray photoelectron spectroscopy (XPS). Thermal properties were studied by thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). At last, flame retardance and burning behaviour were evaluated by the limiting oxygen index (LOI), UL-94 vertical burning test (UL-94 V) and cone calorimetry.

2. Experimental section

2.1. Materials

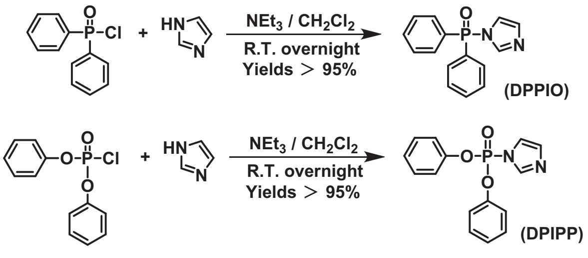
Diphenoxychlorophosphine oxide (98%), diphenylphosphinyl chloride (98%) and 1-methyl imidazole (99%) were purchased from Energy Chemical Co., Ltd. (Shanghai, China); imidazole (99%), anhydrous magnesium sulfate (99%), triethylamine (AR, 99%) and dichloromethane (99.5%) was provided by Kelong Chemical Reagent Co., Ltd. (Sichuan, China); diglycidyl ether of bisphenol A type EP (E-44, EEW = 210–240 g·eq^{-1}, viscosity = 15–23 Pa·s (25 °C)) was obtained from Xingchen Synthetic Materials Co., Ltd. (Nantong, China). Triethylamine and dichloromethane were utilized after being dried, and other materials were used as received.

2.2. Preparation of DPIPP and DPPIO

In N_2 atmosphere, imidazole and the equivalent triethylamine were dissolved in 250 ml dichloromethane at ambient temperature. And then the equivalent diphenylphosphinyl chloride was dropwise added into the solution. After stirring overnight, triethylamine hydrochloride was filtered off, and then the filtrate was washed with excessive water and dried over anhydrous magnesium sulfate. After evaporation of the solvent in vacuum, the product 1-(diphenylphosphinyl)-1*H*-imidazole (DPPIO) was obtained as a white solid product. The diphenyl 1*H*-imidazol-1-ylphosphonate (DPIPP) was prepared in a similar way. The corresponding synthesis routes of DPPIO and DPIPP were shown as Scheme 1. (Yield > 95%) ^{1}H NMR (400 MHz, DMSO-d_6), DPIPP: δ 8.97 (s, 1H, CH), 7.61 (d, 2H, CH), 7.23 (t, 4H, CH), 7.14 (d, 4H, CH), 6.97 (t, 2H, CH); DPPIO: δ 8.14 (s, 1H, CH), 7.71 (t, 4H, CH), 7.40 (d, 6H, CH), 7.21 (s, 2H, CH). ^{31}P NMR (400 MHz, DMSO-d_6), DPIPP: δ 11.55; DPPIO: δ 18.75. The melting point, DPIPP: 82–83 °C; DPPIO: 101–102 °C.

2.3. Curing

Different amount of DPIPP or DPPIO (as mass fraction) was dispersed with EP under stirring prior to curing. The composition was removed bubbles in a vacuum oven and poured into a Teflon mold; then cured at 120 °C for 2 h and 180 °C for another 2 h. For comparison, a reference sample cured by 1-methyl imidazole (MZ/EP) was cured following the similar procedure but heated at different temperatures: 70 °C and 140 °C for every 2 h, respectively. Apparently, no sedimentation of the curing agent occurred in all cured samples.



Scheme 1. Synthesis routes of DPPIO and DPIPP.

2.4. Characterizations

^{1}H NMR and ^{31}P NMR spectra were obtained on a Bruker AV II-spectrometer (Bruker, Germany).

DSC was carried on a TA Q200 DSC (TA, USA) equipped with a thermal analysis data station at a heating rate of 10 °C·min^{-1} under N_2 atmosphere.

The storage stability and curing behaviour were investigated by a dynamic rotational rheometer (ARES Rheometer, TA, USA) with disposable aluminum parallel plates (20 mm in diameter with a gap of 0.1 mm). The experiments were performed at a frequency of 1 Hz and amplitude of 10%.

XPS spectra were recorded by a XSAM80 apparatus (Kratos Co., UK) by utilizing Al Kα excitation radiation ($h\upsilon$ = 1486.6 eV).

Dynamic mechanical analysis was performed in a three-point bending model by using a DMA Q 800 apparatus (TA, USA) (constant frequency = 1.0 Hz, oscillation amplitude = 10.0 μm and heating rate = 5 °C·min^{-1}). The specimen dimension for dynamic mechanical analysis was 20 mm × 1 mm × 4 mm.

Thermal stability of the cured samples was evaluated on thermogravimetry (TG) 209 F1 (NETZSCH, Germany). The samples (about 5 mg) were heated from 40 to 700 °C at a rate of 10 °C·min^{-1} in N_2 or air flow of 50 ml·min^{-1}.

Flame retardance of the cured samples was evaluated by limiting oxygen index (LOI) and an Underwriter Laboratory 94 vertical burning test (UL-94 V). LOI values were measured on a HC-2C oxygen index meter (Jiangning, China) with a bar of 130 mm × 6.5 mm × 3.2 mm according to ASTM D2863-97. UL-94 V rating was evaluated on a CZF-2 instrument (Jiangning, China) according to ATSM D 3801. Sample with different testing thickness were clipped into size of 130 mm × 1 mm × 3.2 and 130 mm × 1 mm × 1.6 mm, respectively.

Combustion behaviour was recorded with a cone calorimeter (Fire Testing Technology, UK). A sample (100 mm × 100 mm × 3 mm) was exposed to a radiant cone in a heat flux of 35 kW·m^{-2}.

The surficial morphologies of the char residues after burning were observed by using a JEOL JSM 5900 LV scanning electronic microscope (SEM, Japan) at the accelerating voltage of 20 kV. Energy dispersive X-ray spectrometer (EDX) was equipped for the elemental analysis under the surface scanning model.

3. Results and discussion

3.1. Storage stability and curing behaviour

Non-isothermal curing scans of EP with different imidazole derivatives were shown in Fig. 1. For MZ/EP, its DSC trace exhibited a single exothermal peak at around 120 °C, due to the addition reaction of the tertiary amine and epoxy groups, as well as further reactions leading to polymerization of epoxy groups [31,32]. The well-founded curing route for MZ/EP components was illustrated in Scheme 2. At the first step, a pyridine-type of nitrogen in an imidazole derivative reacted with the epoxy group to form a 1:1 adduct (zwitterion), then further reactions resulted in epoxy chain propagation. Moreover, there were two possible options of the following reactions in the cross-linked epoxy system, both leading to regeneration of 1-alkylimidazoles. Either a cyclic epoxy polymer structure was formed because of the *N*-dealkylation reaction, or an unsaturated structure coming from *β*-elimination was finally transformed into a carbonyl group. By contrast, the DSC curves for DPIPP/EP and DPPIO/EP showed totally different compared with MZ/EP. Thus, the networks formation of DPIPP/EP and DPPIO/EP should be different to that of MZ/EP. The distinct peak with a side shoulder around 130 °C showed a detail of further etherification between epoxides and alcoholic hydroxyl groups (OH-etherification). It's worth noting that the OH-etherification occurred only in the 1-unsubstituted imidazole epoxy composition [33,34]. Accordingly, it was presumed that DPIPP and DPPIO removed the strong electron-deficient imidazole ring during the curing process. Then the generated imidazole derivatives served as a catalytic intermediate accelerating the curing process. As a consequence, the exothermic regions initiated at 150 °C were owed to the further curing reactions including etherification.

Generally, the storage stability of epoxy mixtures was measured by rotational viscometer on a scheduled interval for a long time [35,36]. It was labor-intensive and time consuming, as well as a bit rough that the changes of viscoelastic behaviors were unavailable. Therefore, in this work, storage stability of the one-pack epoxy materials was monitored by a dynamic rheometer, so as to get further information of the curing process. Firstly, epoxy compositions were monitored by the rheometer at 40 °C as a simulative storage procedure. As shown in Fig. 2(a), (b) and (c), the storage modulus (G′), loss modulus (G″) and complex viscosity (η*) of MZ/EP increased by orders of magnitude within several hours; those of DPIPP/EP and DPPIO/EP, by contrast, hardly changed under the same conditions. Accordingly, MZ/EP showed low stability (curing occurred at near room temperature), unsuitable for one-pack materials. As for DPIPP/EP and DPPIO/EP, three rheological parameters all kept stable in a long time, suggesting they're practical and operable for large batch production within long pot life. Both steric hindrance and electron withdrawing effect of the substituent groups (phosphoryl groups) resulted the inert curing activity. Afterward, the curing process at 150 °C was utilized on DPIPP/EP and DPPIO/EP. In a general way, the crossover between G′ and G″ curves was regarded as the "gel point" [36,37]. Notably, a sudden increase in viscosity was therefore observed with the occurrence of gelation, which led to an infinite molecular weight. As shown in Fig. 2(d) and (e), DPIPP/EP and DPPIO/EP showed great changes in

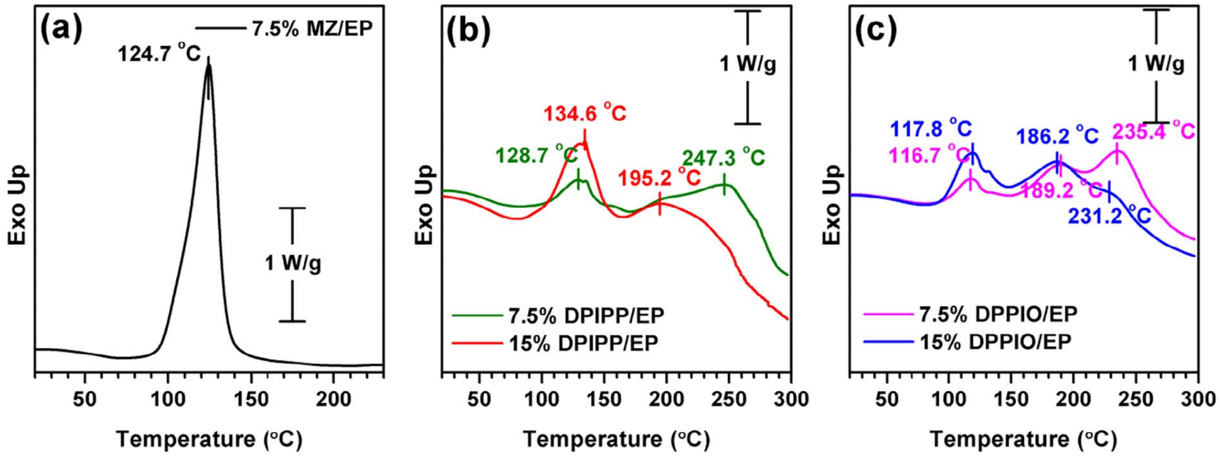
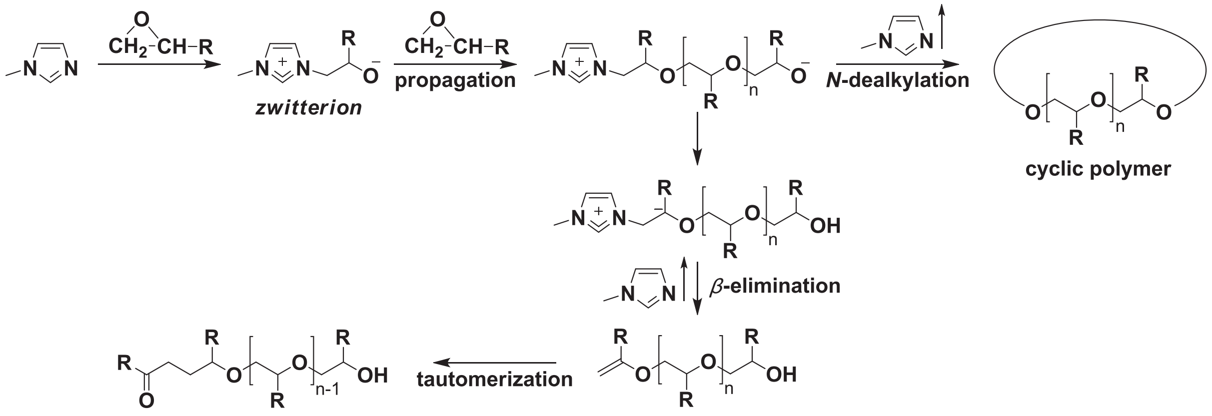


Fig. 1. DSC heating scans for MZ/EP (a), DPIPP/EP (b) and DPPIO/EP (c).



Scheme 2. The curing procedure of MZ/EP.

viscoelastic behaviors, indicating the curing happened. As for DPIPP/EP, it gelated within 144 min at 150 °C, that the complex viscosity increased to over 10^3 Pa·s thereafter. Unexpectedly, DPPIO/EP gelated within only 6.5 min, and the complex viscosity increased to 10^5 Pa·s within 25 min at the same conditions. Therefore, both DPIPP/EP and DPPIO/EP could cure efficiently under heating, and the latter one even satisfied the requirement for fast curing. In this case, DPPIO/EP are suitable for molding or coating formulations where a long shelf life and a fast curing are required. Finally, according to the results, it's confirmed both DPIPP/EP and DPPIO/EP are qualified to be latent curing materials.

But for DPPIO and DPIPP, with the similar chemical structure (1-substituted imidazole by phosphoryl groups), why did they show such different curing actions on EP? To study the detailed curing procedures of EP using DPPIO and DPIPP as the curing agents, XPS measurements were carried out, and the corresponding *N1s* and *P2p* high resolution spectra of DPIPP and DPPIO as well as the relevant cured resins were exhibited in Fig. 3. The shift in binding energies when comparing the curing agent and the corresponding resins provided further details of the curing procedures. With regarded to DPPIO/EP, the *N1s* signal exhibited a peak at 401.8 eV, which was assigned to the imidazolium [38,39], inducing homogeneous polymerization. Besides, *P2p* spectrum of the cured resins shifted to 133.5 eV for DPPIO/EP, which was related to the *P—O* bond such as phosphonate groups [40,41]. Thus, it indicated that firstly, DPPIO added to epoxy groups, then released a kind of 1-alkyl substituted imidazole during the curing process, which acted as the active catalytic intermediate to cure the resins efficiently. This is the reason why DPPIO/EP can cure quickly in short time under heating. Like what DPPIO did, DPIPP also removed its imidazole ring by replacement of a hydroxyl group during the curing process, which was confirmed that the *N1s* signal of DPIPP/EP also had a binding energy peak at 401.8 eV. Furthermore, the signal presented an extra peak at 399.1 eV, which was unusually low for the nitrogen in imidazole groups. For explaining such phenomenon, an assumption was proposed that the diphenyl phosphate was attacked by a kind of imidazole derivative, and then resulted in a sort of "ionic bonds" between the imidazolium cation and phosphate anion. In this case, the heterocyclic ring attached with benzene formed a delocalized conjugated system, where the phenyl group served as a strong electron donor. As a consequence, the nitrogen linked to benzene shifted to a much lower binding energy (399.1 eV). In addition, the *P2p* spectrum of DPIPP/EP was expected to have a single peak at 132.7 eV, which was attributed to the pentavalent phosphate-like structure [41,42]. It indicated that phosphates were the dominating structures in the cured resins. As a result, the active catalytic intermediate would be spent in the process, thus DPIPP/EP showed a much lower curing efficiency than DPPIO/EP did. Notably, phosphorus-containing groups were incorporated onto the epoxy chains resulting intrinsic flame retardance, therefore endowing the resulting materials with long-lasting flame retardance and environment tolerance. Accordingly, the curing procedures of the above epoxy systems were proposed as shown in Fig. 4.

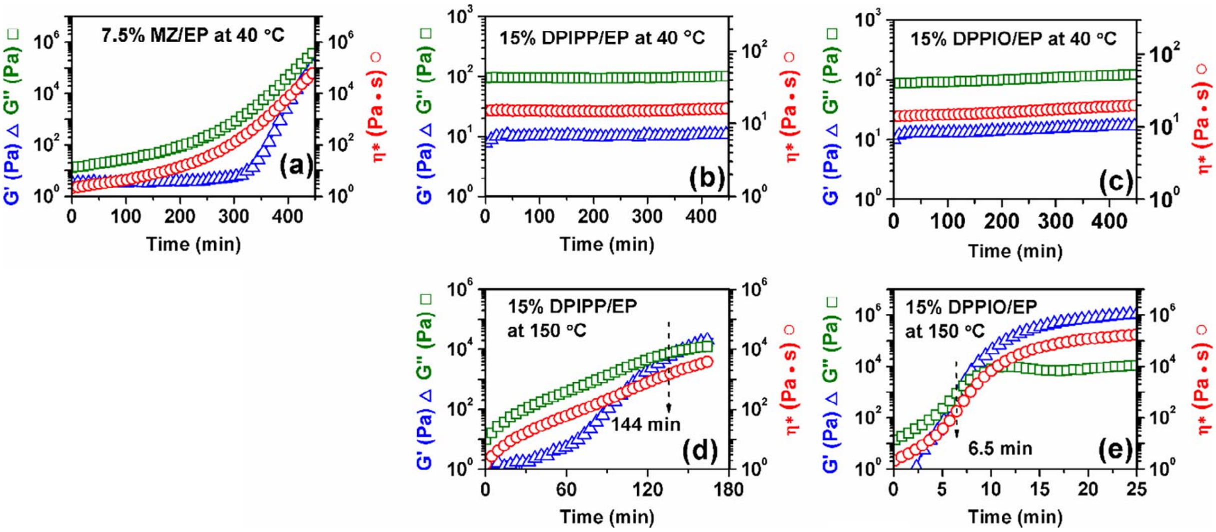


Fig. 2. Changes of G′, G″ and η^* of epoxy mixtures during the simulative storage procedure (a, b and c) and curing process (d and e).

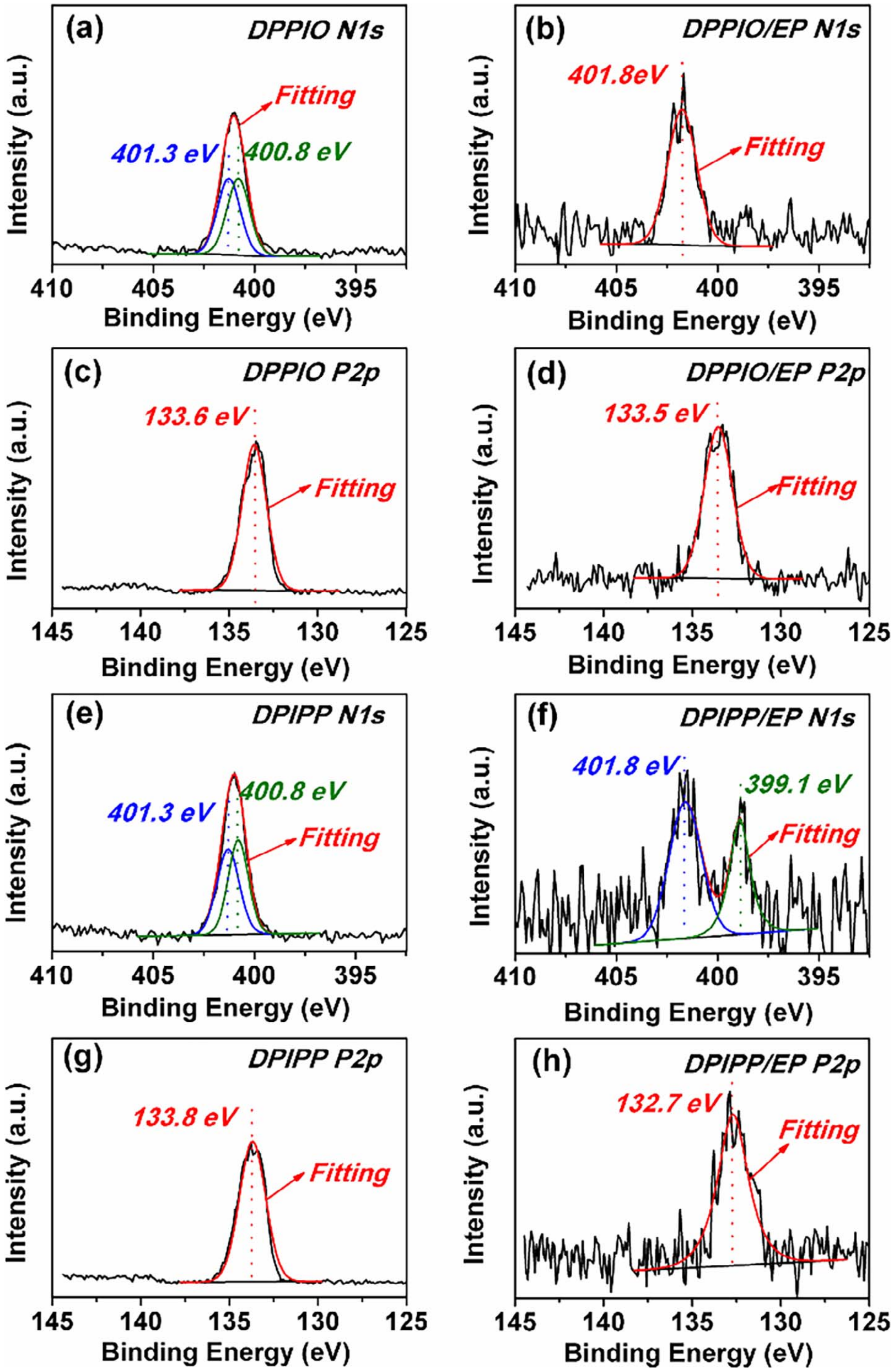


Fig. 3. *N1s* and *P2p* high resolution spectra of DPIPP, DPPIO, DPIPP/EP and DPPIO/EP.

3.2. Thermal properties

The thermo-mechanical behaviour of EP networks was explored by DMA. Fig. 5 presented G′, G″ and loss factor (tan δ) versus temperature for MZ/EP, DPIPP/EP and DPPIO/EP. Generally, the peak of tan δ is preferred as the characteristic temperature of the glass transition (T_g). Besides, as a typical performance for thermosets, all the EP samples displayed a "rubbery plateau" in storage modulus curves in the temperature region above Tg. The rubbery state modulus of the MZ/EP was as high as 17.8 MPa, indicating a highly cross-linked network. Nonetheless, its Tg was as low as 140.9 °C, owing to the plasticizing effect resulted from small molecules such as remaining curing agents. As for DPIPP/EP, they presented a quite high modulus at the temperature below Tg, which was even over 2800 MPa at 50 °C. The result demonstrated that DPIPP served as a fortifier giving strength improvement to the resins, where the "ionic bond" provided the extra stiffness by strong electrostatic interaction [43,44]. Furthermore, the peak value of tan δ of DPIPP/EP was particularly high, due to the "ionic bond" as physical crosslinking point to restrict the mobility of molecular chains. Moreover, DPIPP/EP displayed a quite low rubbery state modulus, indicating a very low crosslink density for such epoxy polymers cured by DPIPP. This phenomenon was explained as follows: the course of forming "ionic bond" consumed essential active curing catalysts (imidazole-type intermediates), and then resulted in weak networks dominated by non-covalent bonds. In contrast, DPPIO/EP had better cured networks than DPIPP/EP. With only 7.5 wt% additions of DPPIO, the final resin

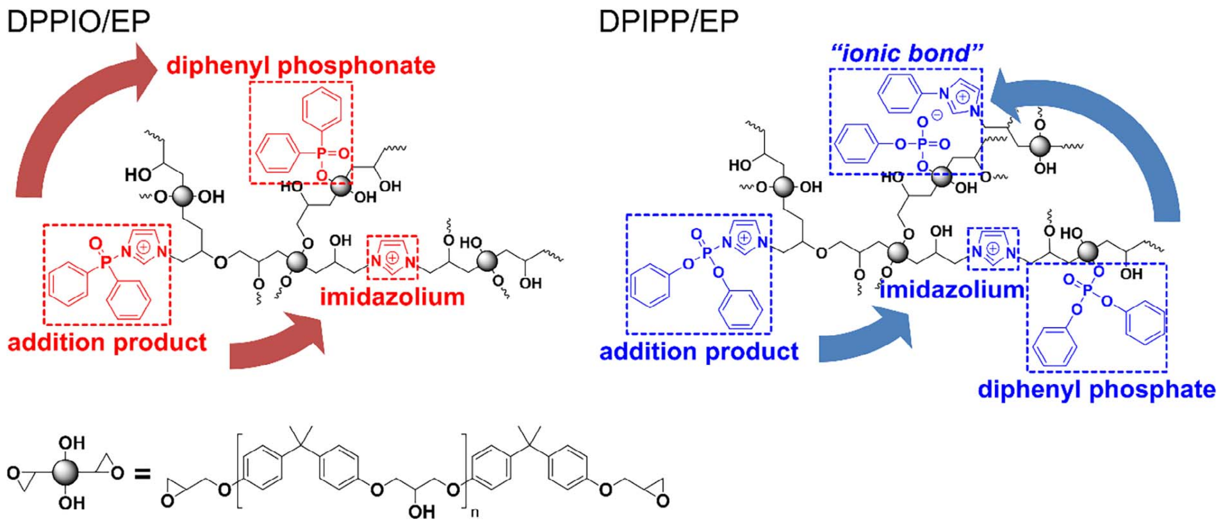


Fig. 4. The curing procedures of DPPIO/EP and DPIPP/EP.

presented a Tg beyond 155 °C as well as a rubbery state modulus about 13.6 MPa. It was owed to the comparatively high curing efficiency with a fine covalent crosslinking network. As far as thermo-mechanical behaviors are concerned, DPPIO seems to be the better one as a latent curing agent for EP.

The TG and derivative thermogravimetric (DTG) curves were presented in Fig. 6, and the corresponding data were listed in Table 1. In N_2 atmosphere, MZ/EP exhibited a one-stage degradation process where the temperature of maximum weight loss rate (T_{max}) appeared at 440.8 °C, suggesting an expected thermal stability. However, MZ/EP started slightly but continually losing weight near 200 °C, resulting the $T_{5\%}$ (defined as the initial decomposition temperature) was even as low as 300 °C. This phenomenon was explained as follows. On the one hand, the strong electron-deficient imidazolium adducts likely tended to eliminate under heating; on the other hand, excessive curing agents in the matrix resulted in early weight loss. DPIPP/EP and DPPIO/EP, as a contrast, presented a similar one-stage degradation process like MZ/EP did. However, T_{max} of both DPIPP/EP and DPPIO/EP decreased considerably, particularly when a high content of the curing agents was added. Furthermore, as shown in Fig. 6(c) and (d), both the maximum weight loss rate in N_2 and air atmosphere considerably decreased. Generally, for flame-retardant samples, the weight loss under heating (producing fuel for flames) was suppressed. Meanwhile, the residual weight at 700 °C (W_{700}) of the flame-retardant samples greatly increased, and that of 15 wt% DPIPP/EP was even as high as 25.3 wt%, over 2.5 times to MZ/EP reference. The high char yield, beyond doubt, was beneficial to flame-retardant effects, particularly in the condensed phase. In air atmosphere, all the samples no surprisingly displayed two-step weight loss. The first decomposition was induced by the decomposition of macromolecular networks; and the second weight losing

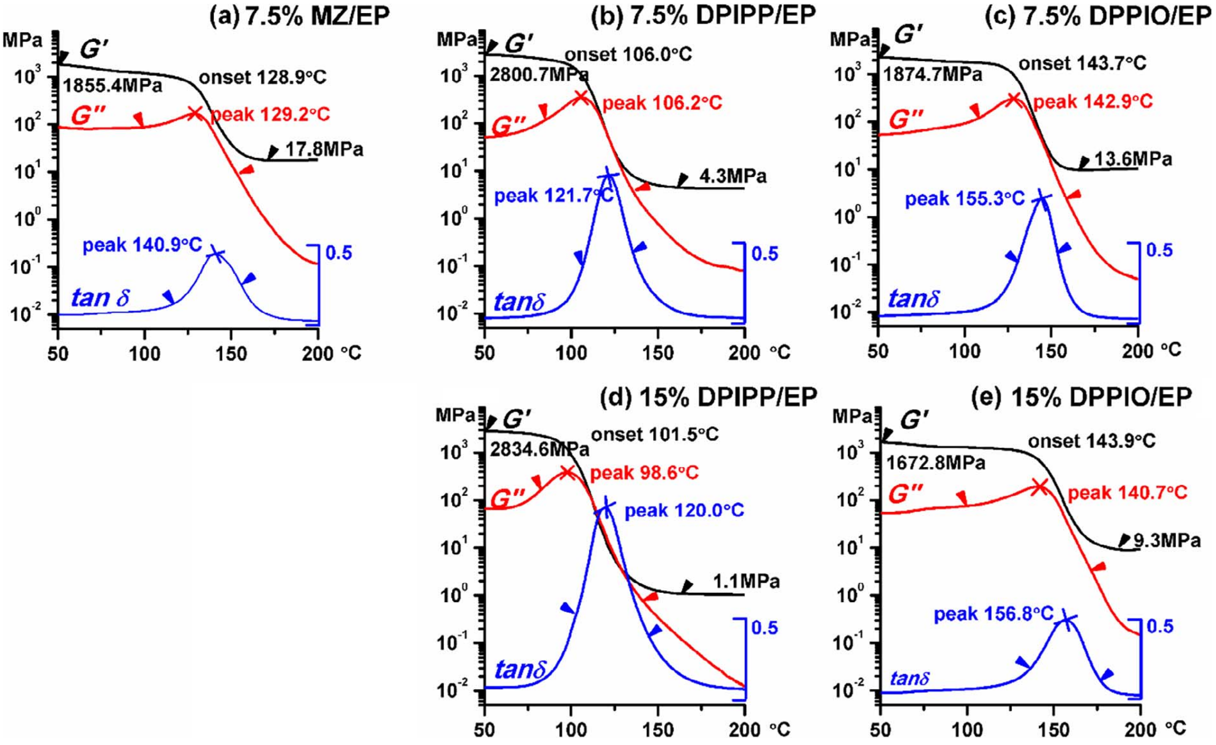


Fig. 5. G′, G″ and tan δ curves of the cured MZ/EP, DPIPP/EP and DPPIO/EP.

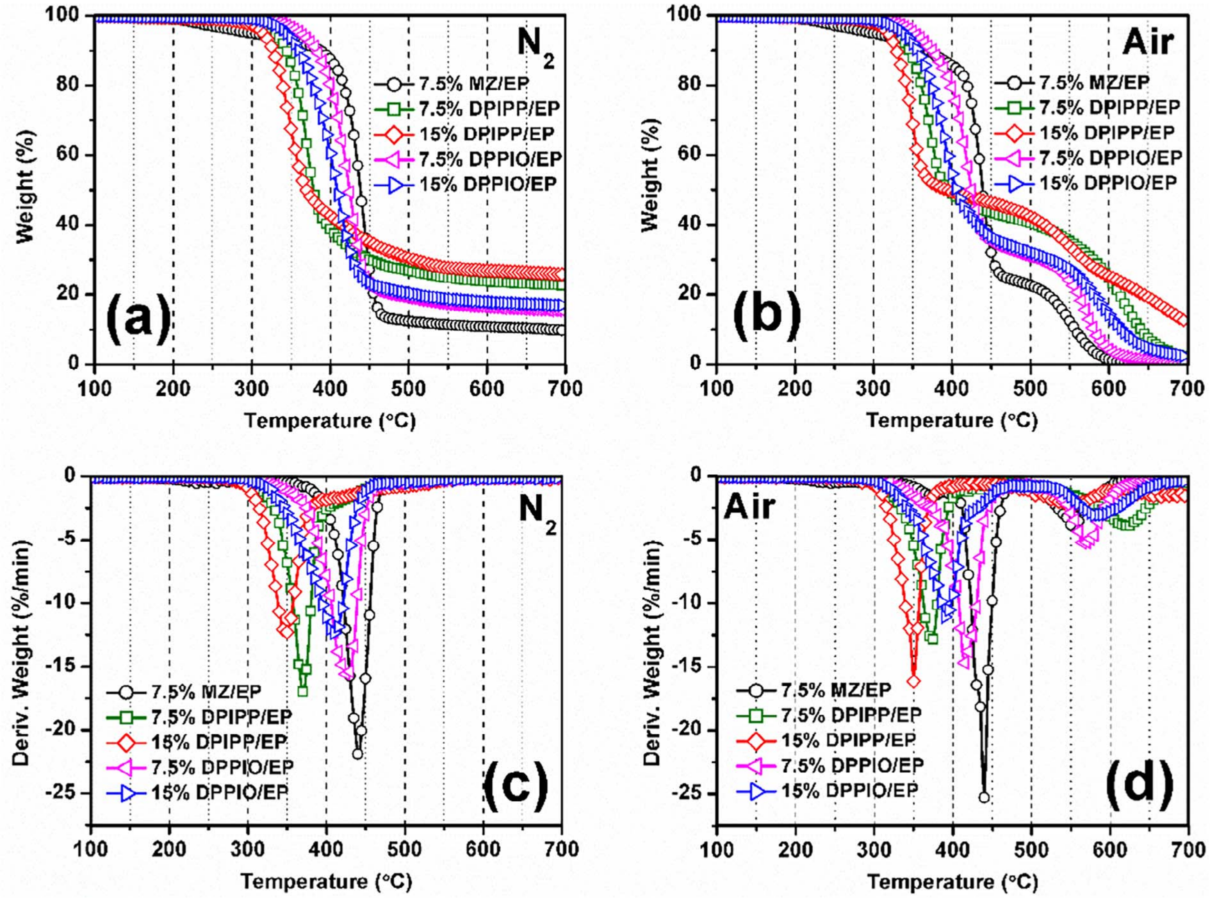


Fig. 6. TG (a, b) and DTG curves (c, d) of the cured MZ/EP, DPIPP/EP and DPPIO/EP in N_2 and air atmospheres.

step was attributed to the further oxidation of the char layer. Notably, in air atmosphere, 15% DPIPP/EP displayed the highest residue weight (12.0 wt%) after TGA. Because the P-O and P-O-C groups in DPIPP/EP preferred to generate a few acids such as phosphoric and poly-/pyro-/ultra-phosphoric acids, acting as dehydrating agents for carbonization. As a result, the residue weight of DPIPP/EP in both N_2 and air atmosphere was much higher than those of MZ/EP and DPPIO/EP. Finally, all the above results indicated that DPIPP/EP and DPPIO/EP exhibited potential to achieve better flame retardance by the higher char yield and the lower degradation rate.

3.3. Flame retardance

LOI and UL-94 V test results of all samples were shown in Table 2. The LOI value of 7.5% MZ/EP was 21.0% and they failed to pass UL-94 V ratings, suggesting that imidazole-cured EP was very flammable in a

Table 2
Flammability test results of EP samples cured by different curing agents.

Samples	P%[a]	LOI (%)	UL-94 V			
			3.2 mm		1.6 mm	
			t_1/t_2[b]	Ratings	t_1/t_2	Ratings
7.5% MZ/EP	–	21.0	> 1 min/–	NR[c]	–	–
7.5% DPIPP/EP	0.77	27.5	> 1 min/–	NR	–	–
15% DPIPP/EP	1.55	31.5	2 s/1 s	V-0	13 s/9 s	V-1
7.5% DPPIO/EP	0.86	33.0	> 1min/–	NR	–	–
15% DPPIO/EP	1.72	38.0	2 s/1 s	V-0	4 s/3 s	V-0

[a] Calculated content of phosphorous (%).

[b] Average burning time after the 10 s ignition.

[c] No rating.

Table 1
Thermogravimetric data of the cured MZ/EP, DPIPP/EP and DPPIO/EP.

Samples	N_2			Air			
	$T_{5\%}$[a] (°C)	T_{max}[b] (°C)	W_{700}[c] (%)	$T_{5\%}$ (°C)	T_{max1} (°C)	T_{max2} (°C)	W_{700} (%)
7.5% MZ/EP	300.0	440.8	9.8	297.4	439.7	558.8	0
7.5% DPIPP/EP	329.1	370.7	22.7	328.6	373.0	623.0	2.2
15% DPIPP/EP	318.6	353.6	25.3	318.4	350.2	554.4	12.0
7.5% DPPIO/EP	362.4	426.8	15.5	352.0	414.8	564.9	0.3
15% DPPIO/EP	344.6	410.5	16.0	338.5	390.8	581.8	2.3

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

[b] The temperature where the maximum weight loss occurred.

[c] The residual weight at 700 °C.

Table 3
Cone calorimetric results of the cured MZ/EP, DPIPP/EP and DPPIO/EP.

Samples	TTI (s)	THR ($MJ{\cdot}m^{-2}$)	TTPHRR (s)	PHRR ($kW{\cdot}m^{-2}$)	FIGRA ($kW{\cdot}m^{-2}s^{-1}$)	MAHRE ($kW{\cdot}m^{-2}$)	TSP ($m^2{\cdot}m^{-2}$)	Residue (%)
7.5% MZ/EP	66	86.3	145	793.5	5.5	287.2	25.0	9.7
7.5% DPIPP/EP	56	61.3	90	535.2	5.9	258.1	21.8	21.5
15% DPIPP/EP	59	53.7	80	427.5	5.3	174.0	13.3	37.3
7.5% DPPIO/EP	62	60.0	130	583.1	4.5	214.4	29.5	19.9
15% DPPIO/EP	63	48.4	120	432.9	3.6	194.4	28.7	23.1

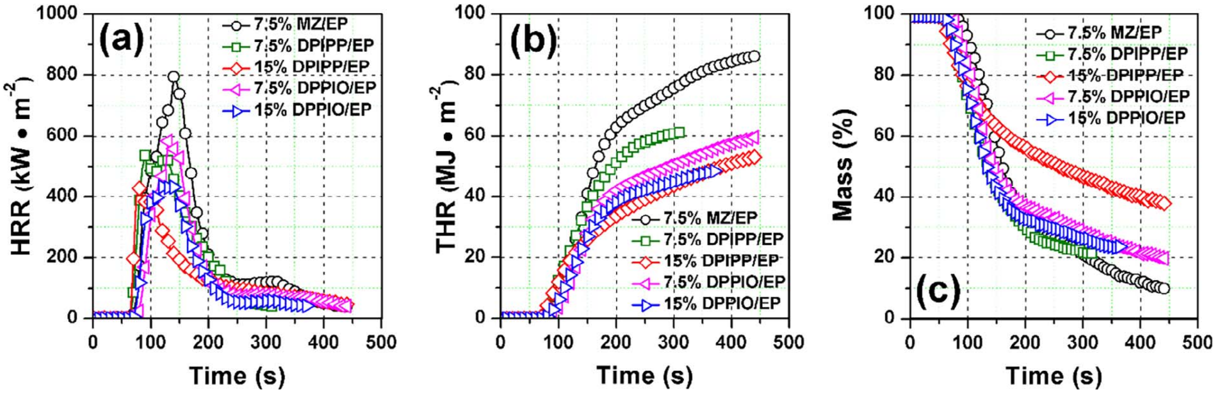


Fig. 7. HRR (a), THR (b) and residue mass (c) plots of the cured MZ/EP, DPIPP/EP and DPPIO/EP obtained from cone calorimetry.

general way. However, when the curing agent was changed to DPIPP and DPPIO, higher LOI values were obtained. As 7.5 wt% DPIPP was used to cure EP, the LOI value was as high as 27.5%. Then a 1.55% phosphorous loading (cured by 15 wt% DPIPP) was sufficient to improve LOI value to 31.5%, and achieve UL-94 V-0 rating at 3.2 mm thickness and V-1 rating at 1.6 mm thickness. Comparatively, only 7.5 wt% DPPIO increased the LOI value of the final resin to 33.0%. If the content of DPPIO was further improved to 15 wt% (1.72% phosphorous loadings), the corresponding resin had a higher LOI value about 38.0%. At this point, it achieved V-0 rating at the thickness of both 3.2 mm and 1.6 mm. According to the results of TGA, DPIPP/EP obtained flame retardance by a dominating effect in condensed phase. By contrast, DPPIO/EP acted more in gas phase, which made flames quenching faster. All the results showed that DPIPP and DPPIO as curing agents endowed the final resin with satisfactory flame-retardant effects, and the later one shows a better efficiency.

The cone calorimeter was used to research the burning behaviour of the cured EP. Various parameters, including time to ignition (TTI), total heat release (THR), time to peak of heat release rate (TTPHRR), peak of heat release rate (PHRR), fire growth rate (FIGRA = PHRR/TTPHRR), maximum average heat rate emission (MAHRE), total smoke production (TSP) and residual weight were summarized in Table 3. Besides, the curves of heat release rate (HRR), THR and mass residue versus time respectively were illustrated in Fig. 7. Obviously, compared with MZ/EP, DPIPP/EP were ignited much earlier, then reached PHRR quickly after being sparked, due to their weak thermal stability according to the result of TGA. However, HRR, THR and MARHE of DPIPP/EP obviously decreased, presenting definite flame retardance. Particularly, with 15 wt% addition of DPIPP, the TSP of DPIPP/EP dropped to 13.3 $m^2{\cdot}m^{-2}$ and the final burning residue was as high as 37.3%, showing a typical flame-retardant effect in condensed phase. Furthermore, DPPIO/EP also showed quite good flame retardance, especially reflecting in the obvious reduction of FIGRA. For instance, FIGRA of 15% DPPIO/EP reduced to 3.6 from 5.5 $kW{\cdot}m^{-2}s^{-1}$ with comparison to that of 7.5% MZ/EP. Notably, a lower FIGRA indicated that the fire spreading was suppressed, meaning more time to evacuate people in distress and/or reach for the fire extinguishers. However, TSP value of DPPIO/EP increased slightly compared with that of the reference sample. Accordingly, it suggested DPPIO/EP show dominating flame-retardant effect in vapor phase.

Additionally, further research was carried out on the morphology observation and chemical composition analysis of the burning residue. As shown in Fig. 8, the residue of 15% DPIPP/EP and 15% DPPIO/EP exhibited numerous bubbles without obvious cracks and fissures on the surface. It indicated the burning char of flame-retarded resins were much dense rather than cracked. Moreover, the merged EDX elemental mapping images of the char provided the direct evidence that the phosphorus enriched in residues by acting as the crosslinking joints of

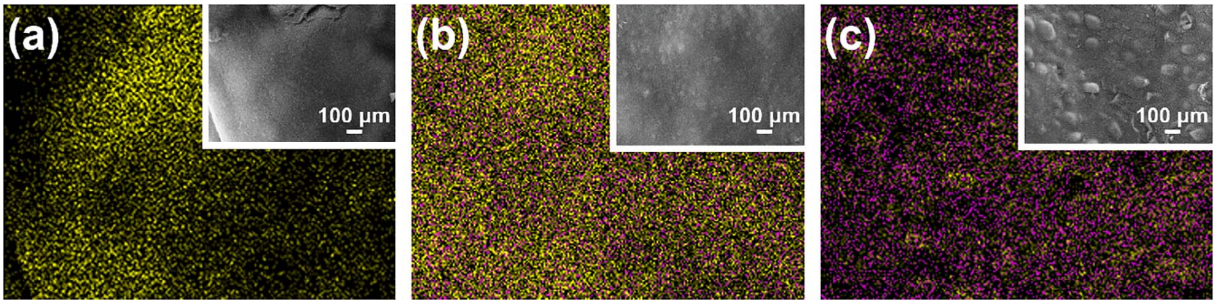


Fig. 8. SEM micrographs and merged EDX elemental mapping images (C and P in yellow and violet signal, respectively) of burning residues of 7.5% MZ/EP (a), 15% DPIPP/EP (b) and 15% DPPIO/EP (c).

aromatic segments. During fire, such kind of the hetero-charring layer behaved as the heat- and oxygen-resistant barrier and then to shield the underlying materials from flames. In other words, DPPIO/EP and DPIPP/EP assuredly both showed flame retardation in condensed phase, and the effect was particularly apparent for the latter.

4. Conclusions

Construction of one-pack flame-retardant epoxy materials containing both EP, curing agents and other additives with long pot life, acceptable curing activity as well as satisfactory fire safety performance is of particular interests in academia and industrial circles for years but lack of comprehensive study. In this work, for the first time, two kinds of phosphorus-containing imidazole derivatives (DPPIO and DPIPP) were designed, synthesized and utilized as latent flame-retardant curing agents for EP. Both DPIPP/EP and DPPIO/EP mixture kept stable at room temperature, but cured efficiently under heating. In particular, at 150 °C, DPPIO/EP gelated within 6.5 min and quickly achieved its complete curing, suggesting the potential application for electrical and electronic devices such as encapsulation and coating. XPS results revealed that DPPIO and DPIPP removed the imidazole ring by replacement of a hydroxyl group at the beginning of curing. In particular, DPIPP/EP emerged a sort of “ionic bond” and phosphate as the dominating structure. As a consequence, DPIPP served as the fortifier strengthening the resins, where the “ionic bond” provided the extra stiffness by electrostatic interaction, as reflected in DMA results. TGA showed that DPPIO/EP and DPIPP/EP both exhibited higher char yields and lower degradation rates than MZ/EP. The flame retardance and burning behaviour were also comprehensively investigated. Thanks to the phosphorus-containing cationic segments, with only 15 wt% additions, the LOI values of DPIPP/EP and DPPIO/EP were increased to 31.5% and 38.0%, respectively; and the latter one further achieved UL-94 V-0 rating at the thickness of both 3.2 mm and 1.6 mm. Cone calorimetric results indicated that DPIPP/EP and DPPIO/EP had excellent flame-retardant properties; and the former one obviously ameliorated smoke suppression due to the dominant flame-retardant activity in condensed phase. Therefore, it is a significant and fruitful attempt to design and develop latent flame-retardant curing agents for EP by modifying imidazole with appropriate flame-retardant groups. Benefiting from the advances, the flame-retardant latent curing EP can be used as one-pack materials for large batch production where high-standard fire safety demands are emphasized.

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Appendix A. Supplementary data

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References

[1] R. Auvergne, S. Caillol, G. David, B. Boutevin, J.P. Pascault, Biobased thermosetting epoxy: present and future, Chem. Rev. 114 (2014) 1082–1115.

[2] H. Gu, C. Ma, J. Gu, J. Guo, X. Yan, J. Huang, Q. Zhang, Z. Guo, An overview of multifunctional epoxy nanocomposites, J. Mater. Chem. C 4 (2016) 5890–5906.

[3] X.Y. Jian, Y. He, Y.D. Li, M. Wang, J.B. Zeng, Curing of epoxidized soybean oil with crystalline oligomeric poly(butylene succinate) towards high performance and sustainable epoxy resins, Chem. Eng. J. 326 (2017) 875–885.

[4] J. Wan, Z.Y. Bu, C.J. Xu, B.G. Li, H. Fan, Preparation, curing kinetics, and properties of a novel low-volatile starlike aliphatic-polyamine curing agent for epoxy resins, Chem. Eng. J. 171 (2011) 357–367.

[5] R. Wang, D. Zhuo, Z. Weng, L. Wu, X. Cheng, Y. Zhou, J. Wang, B. Xuan, A novel nanosilica/graphene oxide hybrid and its flame retarding epoxy resin with simultaneously improved mechanical, thermal conductivity, and dielectric properties, J. Mater. Chem. A 3 (2015) 9826–9836.

[6] J.M. Raquez, M. Deléglise, M.F. Lacrampe, P. Krawczak, Thermosetting (bio)materials derived from renewable resources: a critical review, Prog. Polym. Sci. 35 (2010) 487–509.

[7] J. Wan, C. Li, Z.Y. Bu, C.J. Xu, B.G. Li, H. Fan, A comparative study of epoxy resin cured with a linear diamine and a branched polyamine, Chem. Eng. J. 188 (2012) 160–172.

[8] Y.T. Pan, J. Wan, X. Zhao, C. Li, D.Y. Wang, Interfacial growth of MOF-derived layered double hydroxide nanosheets on graphene slab towards fabrication of multifunctional epoxy nanocomposites, Chem. Eng. J. 330 (2017) 1222–1231.

[9] R.K. Jian, P. Wang, L. Xia, X.Q. Yu, X.L. Zheng, Z.B. Shao, Low-flammability epoxy resins with improved mechanical properties using a Lewis base based on phosphaphenanthrene and 2-aminothiazole, J. Mater. Sci. 52 (2017) 9907–9921.

[10] J. Wan, B. Gan, C. Li, J. Molina-Aldareguia, Z. Li, X. Wang, D.Y. Wang, A novel biobased epoxy resin with high mechanical stiffness and low flammability: synthesis, characterization and properties, J. Mater. Chem. A 3 (2015) 21907–21921.

[11] C. Liu, T. Chen, C.H. Yuan, C.F. Song, Y. Chang, G.R. Chen, Y.T. Xu, L.Z. Dai, Modification of epoxy resin through the self-assembly of a surfactant-like multi-element flame retardant, J. Mater. Chem. A 4 (2016) 3462–3470.

[12] J. Wan, B. Gan, C. Li, J. Molina-Aldareguia, E.N. Kalali, X. Wang, D.Y. Wang, A sustainable, eugenol-derived epoxy resin with high biobased content, modulus, hardness and low flammability: synthesis, curing kinetics and structure-property relationship, Chem. Eng. J. 284 (2016) 1080–1093.

[13] X.L. Wang, L. Chen, J.N. Wu, T. Fu, Y.Z. Wang, Flame-retardant pressure-sensitive adhesives derived from epoxidized soybean oil and phosphorus-containing dicarboxylic acids, ACS Sustain. Chem. Eng. 5 (2017) 3353–3361.

[14] P. Chao, Y. Li, X. Gu, D. Han, X. Jia, M. Wang, T. Zhou, T. Wang, Novel phosphorus-nitrogen-silicon flame retardants and their application in cycloaliphatic epoxy systems, Polym. Chem. 6 (2015) 2977–2985.

[15] S. Qiu, W. Xing, X. Feng, B. Yu, X. Mu, R.K.K. Yuen, Y. Hu, Self-standing cuprous oxide nanoparticles on silica@polyphosphazene nanospheres: 3D nanostructure for enhancing the flame retardancy and toxic effluents elimination of epoxy resins via synergistic catalytic effect, Chem. Eng. J. 309 (2017) 802–814.

[16] X. Wang, W. Xing, X. Feng, B. Yu, H. Lu, L. Song, Y. Hu, The effect of metal oxide decorated graphene hybrids on the improved thermal stability and the reduced smoke toxicity in epoxy resins, Chem. Eng. J. 250 (2014) 214–221.

[17] B. Schartel, U. Braun, A.I. Balabanovich, J. Artner, M. Ciesielski, M. Döring, R.M. Perez, J.K.W. Sandler, V. Altstädt, Pyrolysis and fire behaviour of epoxy systems containing a novel 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide-(DOPO)-based diamino hardener, Eur. Polym. J. 44 (2008) 704–715.

[18] S.B. Wath, M.N. Katariya, S.K. Singh, G.S. Kanade, A.N. Vaidya, Separation of WPCBs by dissolution of brominated epoxy resins using DMSO and NMP: a comparative study, Chem. Eng. J. 280 (2015) 391–398.

[19] Z.B. Shao, C. Deng, Y. Tan, M.J. Chen, L. Chen, Y.Z. Wang, An efficient mono-component polymeric intumescent flame retardant for polypropylene: preparation and application, ACS Appl. Mater. Interface 6 (2014) 7363–7370.

[20] C. Ma, S. Qiu, B. Yu, J. Wang, C. Wang, W. Zeng, Y. Hu, Economical and environment-friendly synthesis of a novel hyperbranched poly(aminomethylphosphine oxide-amine) as co-curing agent for simultaneous improvement of fire safety, glass transition temperature and toughness of epoxy resins, Chem. Eng. J. 322 (2017) 618–631.

[21] Y. Tan, Z.B. Shao, X.F. Chen, J.W. Long, L. Chen, Y.Z. Wang, Novel multifunctional organic-inorganic hybrid curing agent with high flame-retardant efficiency for epoxy resin, ACS Appl. Mater. Interface 7 (2015) 17919–17928.

[22] Y. Tan, Z.B. Shao, L.X. Yu, J.W. Long, M. Qi, L. Chen, Y.Z. Wang, Piperazine-modified ammonium polyphosphate as monocomponent flame-retardant hardener for epoxy resin: flame retardance, curing behavior and mechanical property, Polym. Chem. 7 (2016) 3003–3012.

[23] Y. Tan, Z.B. Shao, L.X. Yu, Y.J. Xu, W.H. Rao, L. Chen, Y.Z. Wang, Polyethyleneimine modified ammonium polyphosphate toward polyamine-hardener for epoxy resin: thermal stability, flame retardance and smoke suppression, Polym. Degrad. Stab. 131 (2016) 62–70.

[24] M.A.M. Rahmathullah, A. Jeyarajasingam, B. Merritt, M. VanLandingham, S.H. McKnight, G.R. Palmese, Room temperature ionic liquids as thermally latent initiators for polymerization of epoxy resins, Macromolecules 42 (2009) 3219–3221.

[25] S. Naumann, M. Speiser, R. Schowner, E. Giebel, M.R. Buchmeiser, Air stable and latent single-component curing of epoxy/anhydride resins catalyzed by thermally liberated N-heterocyclic carbenes, Macromolecules 47 (2014) 4548–4556.

[26] S.J. Park, F.L. Jin, J.R. Lee, J.S. Shin, Cationic polymerization and physicochemical properties of a biobased epoxy resin initiated by thermally latent catalysts, Eur. Polym. J. 41 (2005) 231–237.

[27] K. Kudo, M. Furutani, K. Arimitsu, Imidazole derivatives with an intramolecular hydrogen bond as thermal latent curing agents for thermosetting resins, ACS Macro Lett. 4 (2015) 1085–1088.

[28] K. Arimitsu, S. Fuse, K. Kudo, M. Furutani, Imidazole derivatives as latent curing

agents for epoxy thermosetting resins, Mater. Lett. 161 (2015) 408–410.

[29] Y.R. Ham, D.H. Lee, S.H. Kim, Y.J. Shin, M. Yang, J.S. Shin, Microencapsulation of imidazole curing agent for epoxy resin, J. Ind. Eng. Chem. 16 (2010) 728–733.

[30] J.M. Barton, G.J. Buist, I. Hamerton, B.J. Howlin, J.R. Jones, S. Liu, Preparation and characterization of imidazole-metal complexes and evaluation of cured epoxy networks, J. Mater. Chem. 4 (1994) 379–384.

[31] H. Maka, T. Spychaj, R. Pilawka, Epoxy resin/ionic liquid systems: the influence of imidazolium cation size and anion type on reactivity and thermomechanical properties, Ind. Eng. Chem. Res. 51 (2012) 5197–5206.

[32] X. Fernández-Francos, A.O. Konuray, A. Belmonte, S. De La Flor, À. Serra, X. Ramis, Sequential curing of off-stoichiometric thiol-epoxy thermosets with a custom-tailored structure, Polym. Chem. 7 (2016) 2280–2290.

[33] M.S. Heise, G.C. Martin, Curing mechanism and thermal properties of epoxy-imidazole systems, Macromolecules 22 (1989) 99–104.

[34] Y.R. Ham, S.H. Kim, Y.J. Shin, D.H. Lee, M. Yang, J.H. Min, J.S. Shin, A comparison of some imidazoles in the curing of epoxy resin, J. Ind. Eng. Chem. 16 (2010) 556–559.

[35] F.F. Wong, K.L. Chen, C.M. Lin, M.Y. Yeh, New investigation of 1-substituted imidazole derivatives as thermal latent catalysts for epoxy-phenolic resins, J. Appl. Polym. Sci. 104 (2007) 3292–3300.

[36] A.A. Silva, S. Livi, D.B. Netto, B.G. Soares, J. Duchet, J.F. Gérard, New epoxy systems based on ionic liquid, Polymer 54 (2013) 2123–2129.

[37] C. Tung, P. Dynes, Relationship between viscoelastic properties and gelation in thermosetting systems, J. Appl. Polym. Sci. 27 (1982) 569–574.

[38] M.J. Park, J.K. Lee, B.S. Lee, Y.W. Lee, I.S. Choi, S.G. Lee, Covalent modification of multiwalled carbon nanotubes with imidazolium-based ionic liquids: effect of anions on solubility, Chem. Mater. 18 (2006) 1546–1551.

[39] I.J. Villar-Garcia, E.F. Smith, A.W. Taylor, F. Qiu, K.R. Lovelock, R.G. Jones, P. Licence, Charging of ionic liquid surfaces under X-ray irradiation: the measurement of absolute binding energies by XPS, Phys. Chem. Chem. Phys. 13 (2011) 2797–2808.

[40] J. Gorham, J. Torres, G. Wolfe, A. d'Agostino, D.H. Fairbrother, Surface reactions of molecular and atomic oxygen with carbon phosphide films, J. Phys. Chem. B 109 (2005) 20379–20386.

[41] C. Viornery, Y. Chevolot, D. Léonard, B.O. Aronsson, P. Péchy, H.J. Mathieu, P. Descouts, M. Grätzel, Surface modification of titanium with phosphonic acid to improve bone bonding: characterization by XPS and ToF-SIMS, Langmuir 18 (2002) 2582–2589.

[42] A.M. Puziy, O.I. Poddubnaya, R.P. Socha, J. Gurgul, M. Wisniewski, XPS and NMR studies of phosphoric acid activated carbons, Carbon 46 (2008) 2113–2123.

[43] C.F. Kins, D. Dudenko, D. Sebastiani, G. Brunklaus, Molecular mechanisms of additive fortification in model epoxy resins: a solid state NMR study, Macromolecules 43 (2010) 7200–7211.

[44] C.F. Kins, G. Brunklaus, H.W. Spiess, New phosphonate-based additives for fortification in model epoxies, Macromolecules 46 (2013) 2067–2077.