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Latent Curing Epoxy System with Excellent Thermal Stability, Flame Retardance and Dielectric Property

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Abstract

To obtain a latent curing epoxy system with satisfactory thermal stability, flame retardance and dielectric properties, imidazolium dibenzo[c,e][1,2]oxaphosphate (IDOP) was synthesized by a facile way and utilized as a latent flame-retardant curing agent for epoxy resins (EP). It was confirmed that IDOP/EP one-pack system kept reactive inert near room temperature and cured efficiently under heating with a moderate heat release. The curing procedure was explored by X-ray photoelectron spectroscopy (XPS), confirming that the flame-retardant group was incorporated into epoxy chains by covalent and/or ionic bonds, hence the intrinsic flame retardance and excellent thermal stability were given to the cured resins finally. With only 15 wt% IDOP additions, the limiting oxygen index (LOI) increased to 37.0% from 20.5% of the reference sample, and UL-94 V-0 rating was achieved. The results of cone calorimetry test further certified that IDOP/EP showed satisfactory flame retardance dominating in gaseous phase, which was confirmed by the results of thermogravimetric analysis/infrared spectrometry (TG-IR). The thermal mechanical behavior of IDOP/EP was also evaluated by dynamic mechanical analysis (DMA). Especially, the incorporation of the flame-retardant group didn't deteriorate the dielectric properties of the cured resin.

Benefiting from the advances, the latent curing epoxy system with excellent comprehensive performance exhibited potential for versatile applications.

Key words: Epoxy resin, Latent curing agent, Flame retardance, Thermal stability, Dielectric property

1. Introduction

Globally, epoxy resins (EP) account for approximately 70% of the market of thermosetting polymers (polyurethanes not being included), being widely applied in electrical/electronic fields such as printed circuit boards (PCB), conductive adhesives, flip chip encapsulation, bonding of leads, surface mounting adhesives and conformal coatings, etc. [1-4]. This is owing to their excellent mechanical and electrical properties, high adhesion strength, low shrinkage on curing, as well as fine resistant to heat, chemical and corrosion [5-8]. Actually, all satisfactory properties of EP come from the curing process, where a low molecular weight linear prepolymer transforms into a thermoset with three-dimensional cross-linking networks. Various kinds of curing agents have been used for epoxy polymers including phenols, thiols, acid anhydrides, carboxylic acids, amines and imidazoles, etc. Each of curing agents gives diverse properties to the final resins, which can be further modulated by curing conditions and the ratio of resins to curing agents [9-12].

Particularly, imidazole and its derivatives have been applied as either the accelerator or the main curing agent owing to their efficient catalytic action, as well as the expected mechanical performance and insulating property producing in the cured resins. So far, an epoxy/imidazole resin system has been used to form anisotropic conducting films (ACFs) for applications in electronic equipment such as liquid crystal displays (LCDs) [13, 14]. Herein, imidazoles are added to epoxy systems to induce the anionic homopolymerization of epoxy groups, thus reduce the in-mold time and vastly improve the production efficiency. However, unmodified imidazoles exhibit low stability once being mixed with EP (curing even occurs at room temperature), making them unsuitable for preparing one-pack materials containing epoxy

oligomers, curing agents and other additives such as conductive particles for large-scale production [15]. Therefore, for the past few years, many researchers have designed various imidazole derivatives, especially imidazole ionic liquids (IILs) as latent curing initiators [16, 17]. The quaternized imidazoles with a thermolabile group can block the active site effectively to extend the pot-life, whereas release 1-alkylimidazole to initiate polymerization as being heated. Thus, the so-called “latent curing” has been successfully constructed. In the case, the system can be stored as the one-pack material for a long time in the liquid state, besides polymerization will be induced under heating when on-site operation is conducted. Nevertheless, IILs are usually not easy to synthesize and purify; in addition, the initiating curing temperature of IILs/EP is usually quite high, due to the stability of *N-C* bond that should break as curing occurs [18, 19].

Moreover, as the one of main drawbacks of EP, the inflammability always restricts their applications in areas requiring high-standard fire safety such as electrical/electronic fields since high integration of the present electronic devices leads to overheat, which results in more fire hazards. Herein, epoxy materials are required to meet defined flame-retardant standards (e.g. UL-94 V-0 rating). In view of the above, many approaches especially using phosphorus-containing flame retardants have been proposed to solve this tough problem [22-25]. As a high-performance and eco-friendly flame retardant or flame-retardant precursor, 6*H*-dibenz[*c,e*][1,2]oxaphosphorin-6-oxide (DOPO) has been frequently researched and widely applied in the flame-retardant polymers [26-28]. By incorporating DOPO or its derivatives into the cured EP, whether physically blended or chemically reacted, great improvement on flame retardance will be achieved while thermal stability of the matrix won't deteriorate excessively [29-32]. Liu *et al* modified the polyhedral oligomeric silsesquioxane (POSS) with DOPO through an efficient one-pot Kabachnik-Fields reaction to obtain a surfactant-like flame retardant named POSS-bisDOPO [33]. With 20 wt% loading of POSS-bisDOPO, the limiting oxygen index (LOI) value increased from 25.4% of the reference sample to 34.5% without a considerable decrease on mechanical properties. Wang *et al* synthesized dicarboxylic acids containing DOPO pendant groups as the reactive flame-retardant monomers for bio-based epoxy

pressure-sensitive adhesives (PSAs) [34]. The PSAs with expected flame retardance, thermal stability and adhesive properties showed the potential to replace petroleum-based ones in a broad range of applications, including the application in flexible electronic devices, cars and aircraft.

In our previous work [35], a feasible approach by chemically modifying imidazole with typical flame-retardant groups to develop two kinds of 1-substituted phosphorus-containing imidazole derivatives (DPPIO and DPIPP) as flame-retardant curing agents for EP with long pot life and fast curing was reported. Nevertheless, a latent curing epoxy material used for versatile applications, especially electrical/electronic fields, needs to meet the demands for thermal, dielectric and flame-retardant properties simultaneously. Herein, a DOPO-based imidazole derivative was designed and synthesized successfully by a facile way in high yield to prepare a latent curing epoxy system with excellent comprehensive performance. Notably, modifying imidazole with a DOPO-based acid on the one hand, could suppress their high reactivity with epoxy groups; on the other hand, efficient flame-retardant groups also were incorporated into epoxy systems by the way, thus excellent intrinsic flame retardance was finally achieved. The storage stability and curing behavior of the one-pack epoxy materials were evaluated by differential scanning calorimetry (DSC) and dynamic rheological analysis. The curing procedure was proposed and verified by X-ray photoelectron spectroscopy (XPS). The thermal decomposition behavior was studied by thermogravimetric analysis (TGA) and thermogravimetry/infrared spectrometry (TG-IR). Thermal mechanical properties were explored by dynamic mechanical analysis (DMA). The dielectric properties were investigated by broadband dielectric spectrometer. Finally, the flame retardance and burning behavior were evaluated by LOI, UL-94 V and cone calorimetry.

2. Experimental Section

2.1. Materials

DOPO (AR, 97%) was purchased from Aladdin Industrial Co., Ltd. (Shanghai, China); hydrogen peroxide (AR, 30%) was supplied by Jinshan Chemical Reagent Co., Ltd. (Sichuan, China); imidazole (AR, 99%)

and ethanol (AR, 99%) was provided by Kelong Chemical Reagent Co., Ltd. (Sichuan, China); diglycidyl ether of bisphenol A type EP (E-44, room temperature viscosity = 15-23 Pa·s, EEW = 210-240 g/eq) was obtained from Xingchen Synthetic Materials Co., Ltd. (Nantong, China). All materials were used as received.

2.2. Synthesis of IDOP

A DOPO-based acid, dibenzo[c,e][1,2]oxaphosphinic acid (abbreviated as DOPA) was prepared from the oxidation of DOPO by hydrogen peroxide through a method similar to our previous literatures [36, 37]. Next, DOPA and the equivalent imidazole were mixed in ethanol at room temperature, then the mixture solution was stirred continuously for 30 min. After evaporation of the solvent, imidazolium dibenzo[c,e][1,2]oxaphosphate (abbreviated as IDOP) as a vitreous solid was obtained with a yield of about 99%. The recrystallization from ethyl acetate/ethanol was carried out if needed. ^1H NMR (400 MHz, DMSO- d_6), δ 8.72 (s, 1H, CH), 7.96 (d, 1H, CH), 7.94 (d, 1H, CH), 7.71 (q, H, CH), 7.54 (t, H, CH), 7.44 (s, 2H, CH), 7.40 (t, H, CH), 7.29 (t, H, CH), 7.13 (t, H, CH), 7.08 (d, H, CH). ^{31}P NMR (400 MHz, DMSO- d_6), δ 1.5. Melting point, 91-92 °C.

2.3. Curing

The flame-retardant EP samples cured by IDOP were prepared in a similar procedure to the reference sample cured by imidazole. Different mass proportions, for example 5 wt%, of imidazole were dispersed in EP by stirring. Next, the mixture was put into a vacuum oven to remove bubbles at 60 °C, and then poured into a preheating Teflon mold. The EP samples were cured under different conditions: the reference sample cured by the imidazole (MZ/EP) was heated at 70 °C and 140 °C for each 2 h, respectively; a flame-retardant sample cured by IDOP (IDOP/EP) was cured at 120 °C and 180 °C for each 2 h, respectively. Apparently, no sedimentation or coacervation of IDOP occurred during curing.

2.4. Characterization

^1H and ^{31}P NMR spectra were obtained on a Bruker AV II-400 MHz spectrometer (Bruker, Germany), and DMSO- d_6 was used as the solvent.

X-Ray single-crystal diffraction (XRSD) data were collected on an Oxford Xcalibur E single crystal diffractometer.

DSC was carried out on a TA Q200 DSC (TA, USA) with a thermal analysis data station, operating at a heating rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ from 40 to $300\text{ }^\circ\text{C}$ under N_2 atmosphere.

Dynamic rheological analysis was investigated by ARES Rheometer (TA, USA) with a frequency of 1 Hz and an amplitude of 10%, operating on disposable aluminum parallel plates (20 mm in diameter with a gap of 0.1 mm).

XPS spectra of powder-like samples were recorded by a XSAM80 apparatus (Kratos Co., UK), using Al K α excitation radiation ($h\nu = 1486.6\text{ eV}$).

Thermal stability of the cured resins was evaluated by using TG 209 F1 (NETZSCH, Germany). The sample (about 5 mg) was heated from 40 to $700\text{ }^\circ\text{C}$ at a rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ in nitrogen or air flow of $50\text{ ml}\cdot\text{min}^{-1}$. For identifying the evaporated components of the cured samples during decomposition, TG-IR was taken from 40 to $700\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ under nitrogen atmosphere through a heated transfer line set at $280\text{ }^\circ\text{C}$.

Dynamic mechanical analysis was performed on specimens with a size of $20\text{ mm} \times 10\text{ mm} \times 4\text{ mm}$, in a three-point bending model by using a DMA Q 800 apparatus (TA, USA) (constant frequency = 1.0 Hz, oscillation amplitude = $10.0\text{ }\mu\text{m}$ and heating rate = $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$).

Flame retardance of the cured samples was tested by LOI and UL-94 V tests. LOI values were carried out on a HC-2C oxygen index meter (Jiangning, China) with a sheet dimension of $130\text{ mm} \times 6.5\text{ mm} \times 3.2\text{ mm}$ according to ASTM D2863-97. The UL-94 rating was evaluated on a CZF-2 instrument (Jiangning, China) according to ATSM D 3801. The samples were made with a size of $130\text{ mm} \times 13\text{ mm} \times 3.2\text{ mm}$.

Combustion data of the sample were recorded by a cone calorimeter (Fire Testing Technology, U.K.). The

sample with size of 100 mm × 100 mm × 3 mm was tested under a heat radiation of 35 kW·m⁻².

The dielectric properties were measured by a broadband dielectric spectrometer (Novocontrol Concept 80, Germany) in the frequency range of 1 to 10⁶ Hz at room temperature. The samples are molded as disc-like flakes with a diameter of 20 mm and a thickness of 2 mm.

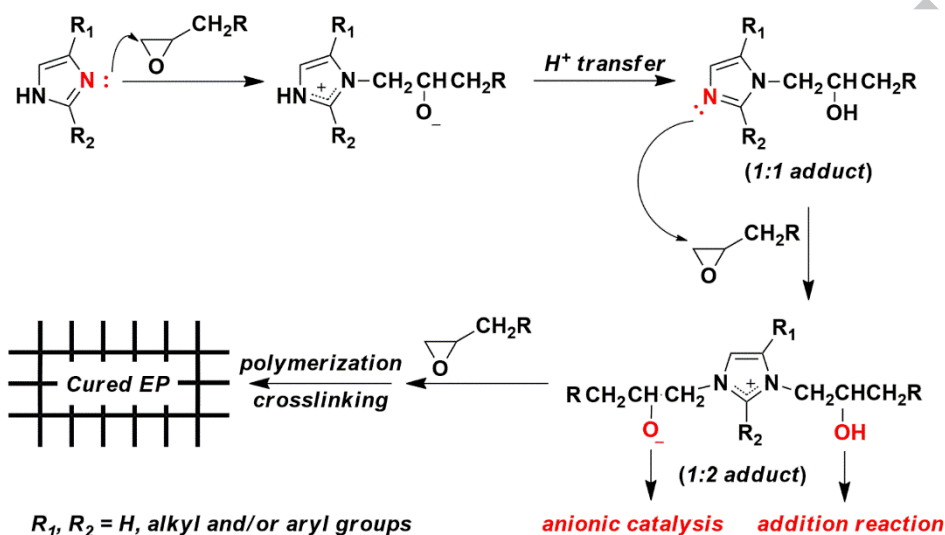
Morphology observation and the corresponding elemental mapping of the burning residues after cone calorimetry were conducted on a JEOL JSM 5900 LV scanning electronic microscope (SEM, Japan) together with the energy dispersive X-ray spectrometer (EDX) in the surface scanning model. All the samples were coated with gold before test.

3. Results and discussion

3.1. Storage stability and curing behavior

The curing reaction of EP with 1-unsubstituted imidazole has been well explored before [38, 39], as shown in **Scheme 1**. Firstly, the pyridine-type nitrogen reacted with the epoxy group to form the 1:1 adduct. Secondly, the intramolecular H^+ transfer changed the pyrrole-type nitrogen into the pyridine-type one. Thirdly, the newly generated pyridine-type nitrogen reacted with the epoxy group to form the 1:2 adduct with a reactive alkoxide anion ($-O^-$) and hydroxyl ($-OH$). Lastly, the polymerization and further crosslinking were induced by alkoxides and hydroxy groups via a series of etherification reactions. In this work, DSC was used to trace the non-isothermal curing process of MZ/EP and IDOP/EP, as shown in **Fig. 1**. For MZ/EP system, a secondary peak at 97.5 °C was owed to the formation of the 1:1 adduct between the imidazole and epoxy group; and the following primary exothermic region (the peaks at 118.1 and 156.5 °C) was assigned to the generation of the 1:2 adduct as well as the further polymerization and crosslinking. As a contrast, the flame-retardant EP samples with different proportions of IDOP displayed two evident exothermic regions: the first one ranging from 80 to 150 °C was attributed to the reactions between the epoxy group and the imidazole freed from the salt bonds; and the next one beginning at 150 °C was owed to the further reactions forming polymer networks. Comparatively, the released curing

heat of IDOP/EP was much lower than that of MZ/EP. Notably, a drastic heat release generally leads to shrinkage and cleavage on curing, which is undesirable in fast-curing process, such as potting, coating or encapsulating applications. Herein, IDOP/EP system can be the appropriate one that cures efficiently with a moderate curing heat release.



Scheme 1. Curing process of 1-unsubstituted imidazole/EP.

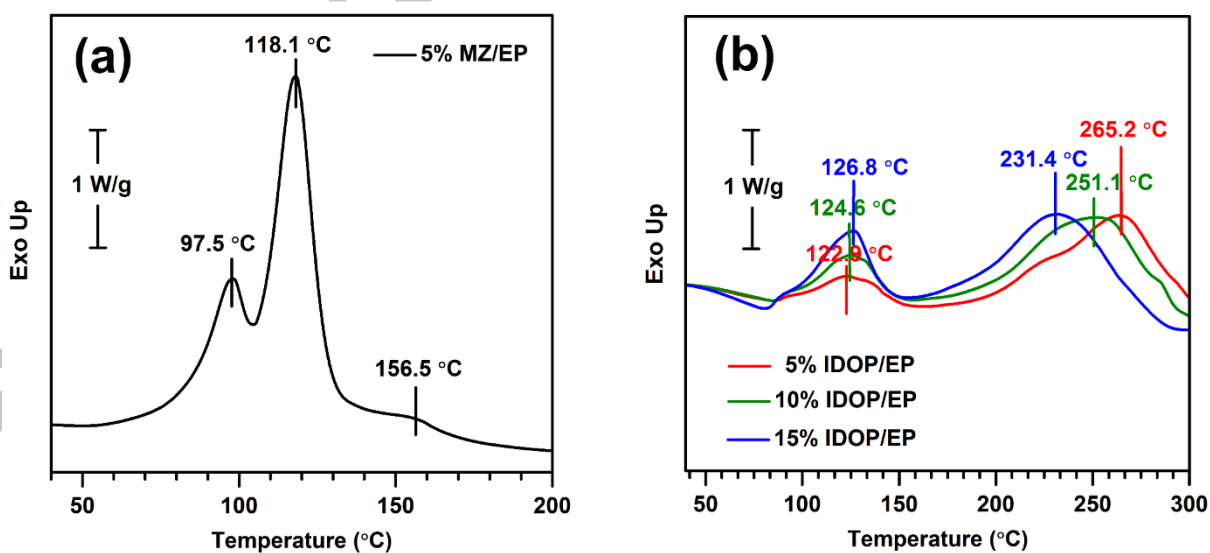


Figure 1. Non-isothermal curing scans of MZ/EP (a) and IDOP/EP (b) by DSC.

To explore the storing and curing behavior of the one-pack EP samples at the presence of IDOP, a dynamic rheometer was applied to real-timely monitor the relevant process. In this case, an isothermal and a dynamic condition were employed to closely simulate the storing and curing process, respectively. The results, as shown in **Fig. 2 (a)**, exhibited that the storage modulus (G'), loss modulus (G'') and complex viscosity (η^*) of MZ/EP continuously increased by orders of magnitude as being heated at 40 °C for a short while, indicating that MZ/EP started curing near room temperature. Those parameters of IDOP/EP shown **Fig. 2 (b)**, as a contrast, hardly changed under the same condition, and the system stayed in liquid state (viscous flow) all along, implying that IDOP/EP systems with good flowability for moldings were practicable and operable for large-scale production as one-pack materials. Architecturally, both the steric hindrance of the bulky pendent group in DOPA and protonated of imidazole resulted the chemically inert activity of IDOP with epoxy groups. Subsequently, the simulative curing process of IDOP/EP was conducted under dynamic condition at a heat rating of 5 °C·min⁻¹ from 40 to 200 °C. As shown in **Fig. 2 (c)**, the complex viscosity of the composition constantly decreased in the temperature region below 100 °C (only about 1 Pa·s at 100 °C), and then increased drastically from 120 °C. It coincided with the results of DSC and demonstrated satisfactory curing activity of IDOP/EP under heating. Furthermore, obvious curing behavior was observed in a short period when the material was heated at 150 °C. In general, the gel time can be determined from the intersection between G' and G'' curves at constant temperature. At the moment, gelation occurs when a growing molecule reaches a mass large enough to interconnect every boundary of the system [38, 40]. As shown in **Fig. 2 (d)**, IDOP/EP gelled within 140 minutes at 150 °C with the complex viscosity upward to 10³ Pa·s, showing an acceptable curing rate under heating. Hence, IDOP/EP systems are suitable as latent curing systems, especially for encapsulating or coating where the befitting flowability and curing rate are needed.

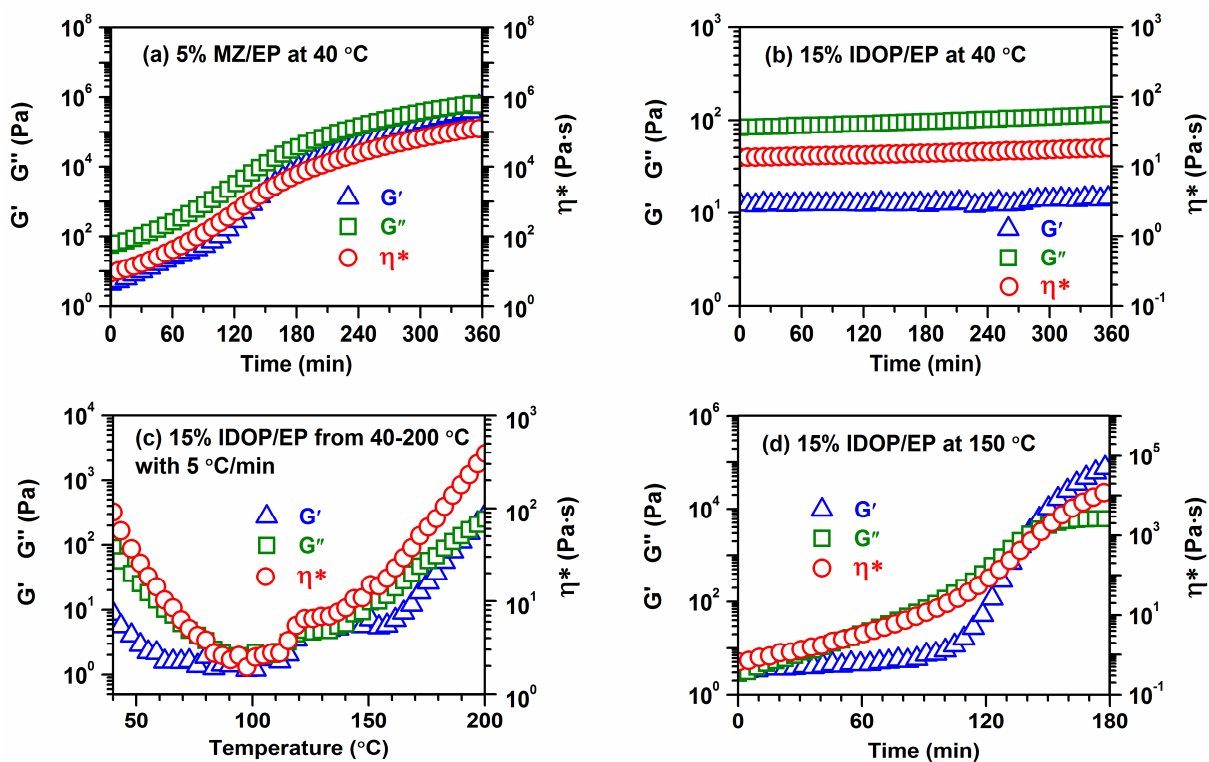


Figure 2. Changes of G' , G'' and η^* of one-pack epoxy materials during the simulative storing and curing process.

To further research the detailed curing routes of IDOP/EP system, XPS measurement was carried out, and the corresponding $N1s$ and $P2p$ high resolution spectra of IDOP as well as the final cured resins were exhibited in **Fig. 3 (a) and (b)**. As is shown, $N1s$ spectrum of the curing agent displayed a peak at 401.3 eV, which was attributed to the protonated imidazole where both nitrogen atoms stood at parity for delocalized π bonds in the N -heterocyclic ring. Regarding the cured resins, by contrast, the $N1s$ signal exhibited a peak at 401.8 eV, which was assigned to the imidazolium adducts from the addition reaction between the epoxy group and the imidazole freed from ionic bonds [41, 42]. For sure, the imidazolium adducts efficiently induced homopolymerization of epoxy groups by a series of etherification reactions as mentioned above. Besides, $P2p$ spectrum of the cured resin was expected to be divided into two peaks at 133.6 eV and 132.6 eV (a newly generated peak compared with that of IDOP). In general, a variation in the $P2p$ binding energies within this scope are related to the change of the relevant O environment [43, 44].

Therefore, the result indicates that further changes of the chemical structures occurred in the phosphaphenanthrene ring, perhaps resulting in the phosphonate ester and/or other ring-opening products. In that case, the flame-retardant group (DOPO derivatives) permanently attached to the epoxy chain through the ionic and/or covalent bonds, thus endowing the resulting materials with intrinsic flame retardance. Accordingly, the corresponding curing process of the IDOP/EP system was proposed as shown in Fig. 3 (c).

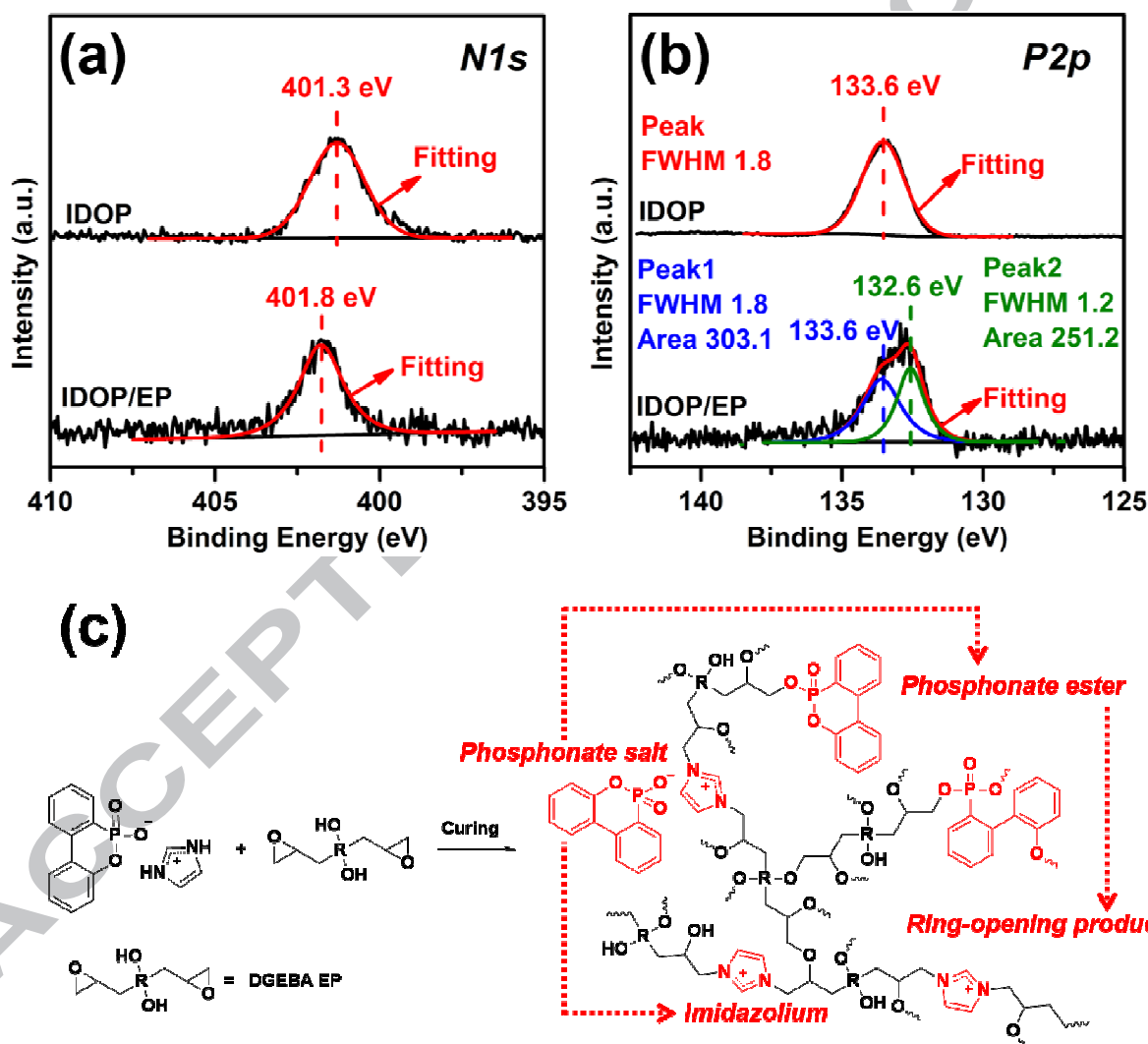


Figure 3. $N1s$ and $P2p$ high resolution spectra of IDOP and IDOP/EP (a, b) and the corresponding curing process of IDOP/EP (c).

3.2. Thermal stability

TG and derivative thermogravimetric (DTG) curves of MZ/EP and IDOP/EP in N₂ and air atmospheres were presented in **Fig. 4**, and the corresponding data were listed in **Table 1**. In N₂ atmosphere, the IDOP/EP sample exhibited a one-stage degradation process similar to MZ/EP, which was attributed to the decomposition of the cured networks. Besides, T_{5%} (the temperature where 5 wt % of the weight loss) of IDOP/EP, defined as the initial decomposition temperatures, was slightly decreased compared with that of MZ/EP (358.8 °C) as expected. Extraordinarily, as the content of IDOP increased, T_{5%} of IDOP/EP elevated gradually, and the cured sample with 15% of IDOP exhibited a T_{5%} as high as 355.4 °C. On the one hand, the flame-retardant groups were chemically incorporated into the epoxy chains; on the other hand, integrated curing networks were finally formed at the presence of sufficient imidazoles as the curing groups generated from higher content of IDOP. As a consequence, the final cured resins obtained the expected thermal stability close to MZ/EP.

Moreover, in air atmosphere, the addition of IDOP promoted the decomposition of EP as the situation in N₂ atmosphere, further stabilized the char at higher temperatures against oxidization: e.g. T_{max1} of 15% IDOP/EP decreased to 382.1 from 426.0 °C of MZ/EP while T_{max2} increased to 567.1 from 556.5 °C of the reference sample. In addition, it's worth noting that IDOP/EP samples even showed much better thermal stability than EP cured by traditional curing agents such as polyamide, aliphatic and cycloaliphatic amines (polyamide 650, diethylenetriamine, polyethyleneimine and piperazine for instance), according to our previous works [45-48]. By contrast, ordinary phosphorus-containing flame retardants always cause the polymer decomposing prematurely, therefore the material displays a poor resistance to heat. Beyond doubt, the high heat resistance of IDOP/EP can bring more chances for widespread applications.

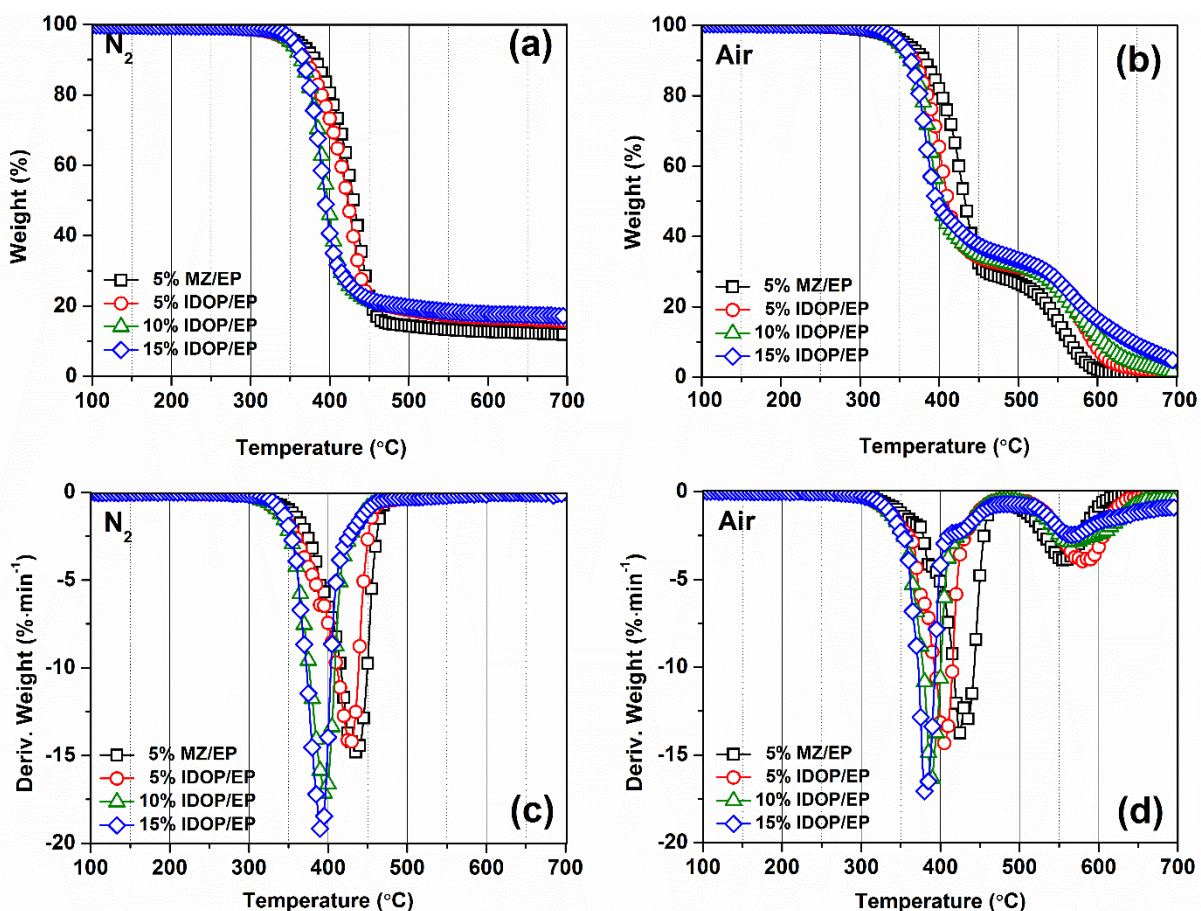


Figure 4. TG and DTG curves of the cured resins in N₂ and air atmospheres.

Table 1 TGA data and flame-retardant test results of the cured resins.

Sample	P % ^a	N ₂			Air				LOI (%)	UL-94 V
		T _{5%} ^b (°C)	T _{max} ^c (°C)	W ₇₀₀ ^d (%)	T _{5%} (°C)	T _{max1} (°C)	T _{max2} (°C)	W ₇₀₀ (%)		
5% MZ/EP	-	358.8	435.7	11.8	356.3	426.0	556.5	0.5	20.5	NR ^e
5% IDOP/EP	0.51	349.7	427.7	15.8	348.3	404.8	581.3	1.3	27.0	NR
10% IDOP/EP	1.03	350.9	396.9	16.4	349.1	388.8	564.3	1.3	34.5	V-1
15% IDOP/EP	1.55	355.4	391.6	17.1	350.8	382.1	567.1	4.5	37.0	V-0

^a calculated content of phosphorus (wt%).

^b the temperature where 5 wt % of weight was lost.

^c the temperature where the maximum weight loss occurred.

^d the residual weight at 700 °C.

^e No rating.

3.3. Flame retardance and combustion behavior

LOI and UL-94 V tests were conducted to investigate the flame retardance of the cured resins, and the related results were listed in **Table 1**. 5% MZ/EP had a LOI value as low as 20.5% and failed to pass UL-94 V rating, indicating a very flammable nature despite the presence of the aromatic groups along the epoxy networks. Nevertheless, when the curing agent was changed into the flame-retardant one, excellent flame retardance was given to the final resins. Only 5 wt% IDOP additions increased the LOI value to 27.0%. When the content of the flame-retardant curing agent was improved to 10 wt%, the LOI value of the flame-retardant sample was as high as 35.0%, and it passed UL-94 V-1 rating. As being cured by 15 wt% IDOP (phosphorus content as 1.55 wt%), LOI value of EP further improved to 37.0%, and V-0 rating was easily achieved.

Cone calorimeter has been a widely used apparatus for evaluating the combustion behavior of various polymer materials under a simulate fire condition [49, 50]. Herein, the curves of heat release rate (HRR), total heat release (THR) and mass versus to time respectively were illustrated in **Fig. 5**. Various parameters, including time to ignition (TTI), THR, peak of heat release rate (p-HRR), maximum average heat rate emission (MAHRE), peak of CO production rate (p-COPR), total smoke production (TSP), peak of specific extinction area (p-SEA) and residual weight obtained from cone calorimetry were summarized in **Table 2**. Surprisingly, the incorporation of IDOP into the epoxy networks led to a longer TTI (> 1 min) rather than being ignited prematurely like the other traditional flame-retardant polymers. Generally, the preceding decomposition of the phosphorus-containing flame retardants produced active fragments serving as free radical captures or gaseous dilutions, thus delayed the ignition [37, 51]. Furthermore, the addition of IDOP led to the decrease in p-HRR, THR and MAHRE; however, due to incorporation of the flame-retardant groups, p-COPR, p-SEA and TSP increased without exception, potentially indicating incomplete combustion and a dominating vapor-phase flame-retardant effect [22, 35]. In addition, IDOP/EP had a slightly higher residual yield than the reference sample. Especially, the char residue of 15%

IDOP/EP increased to 19.6% from 10.3%, suggesting the condensed-phase flame-retardant activity. As shown in **Fig. 6**, the burning residue of IDOP/EP was much denser than that of the reference sample. The EDX elemental mapping images of the residue provided the evidence that the phosphorus enriched in the char of IDOP/EP, which further enhanced the heat- and oxygen-resistant barrier during fire.

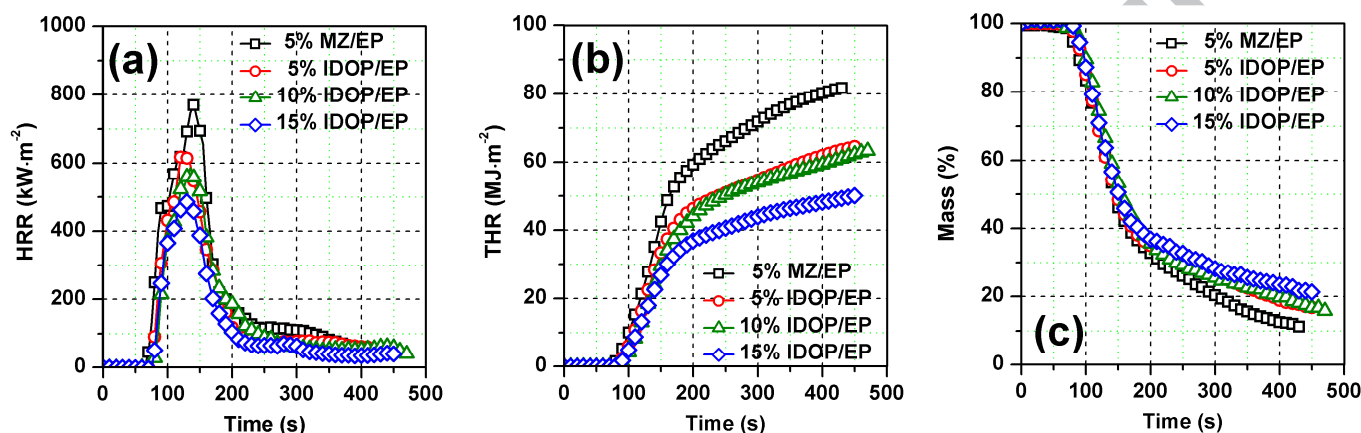


Figure 5. HRR (a), THR (b) and mass (c) curves of the cured resins obtained from cone calorimetry.

Table 2 Cone calorimetric results of the cured resins.

Samples	TTI (s)	THR (MJ·m ⁻²)	p-HRR (kW·m ⁻²)	MAHRE (kW·m ⁻²)	Residue (%)	p-COPR (g·s ⁻¹)	p-SEA (m ² ·kg ⁻¹)	TSP (m ²)
5% MZ/EP	57	82.6	770.1	310.2	10.3	0.57	1280.0	23.8
5% IDOP/EP	65	65.8	617.5	239.4	15.1	1.26	1953.8	24.7
10% IDOP/EP	67	64.2	586.5	222.6	15.3	0.92	2819.1	28.7
15% IDOP/EP	68	51.2	485.6	191.2	19.6	0.95	3681.0	25.5

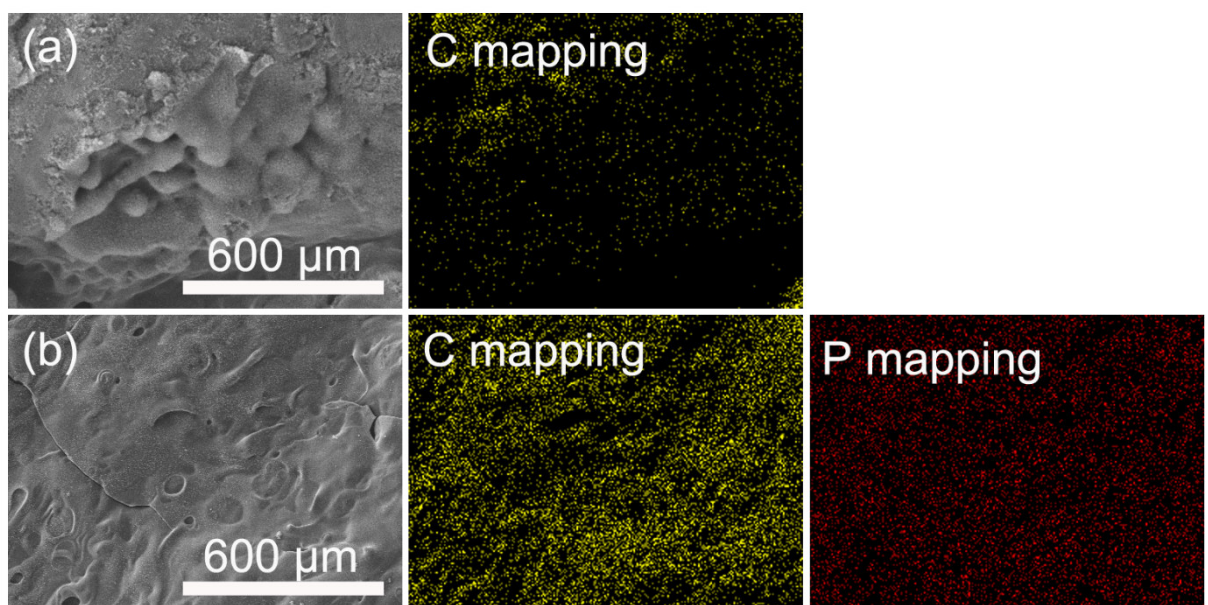


Figure 6. SEM and EDX elemental mapping images of the burning residues of 5% MZ/EP (a) and 15% IDOP/EP (b) after cone calorimetry.

To further explore the flame-retardant effect in vapor phase of the DOPO-based flame retardants, the gas products decomposed from 5% MZ/EP and 15% IDOP/EP were detected by using a TG-IR technique. IR spectra of the decomposed products from MZ/EP and IDOP/EP at different temperatures from 300 to 500 °C were shown in **Fig. 7**. It was observed that the release of the decomposed volatiles of both the reference sample and flame-retardant one began at about 350 °C, but IDOP/EP displayed that the maximum release started at a much lower temperature (375 °C versus 425 °C). For both two samples, the characteristic signals of the decomposed products appeared in the same regions of 3500-3750 cm^{-1} , 2750-3200 cm^{-1} , 1400-1900 cm^{-1} , 1000-1375 cm^{-1} and 600-900 cm^{-1} , which were owed to normal thermal decomposition products of bisphenol A type EP, such as phenols/ H_2O , hydrocarbons, aldehydes/ketones, ethers and aromatic compounds [52, 53]. Particularly, the spectra of the flame-retardant sample exhibited an absorption band at 924 cm^{-1} , which was assigned to the structure containing P-O-Ph groups. Moreover, other typical absorption bands, such as stretching vibration of P=O at around 1250 cm^{-1} was actually overlapped with the characteristic peaks of Ph-O-C or C-N bonds [54, 55]. Finally, it was convinced that

the phosphorus-containing gas or fragments from DOPO-based groups really appeared in the decomposed volatiles and suggested a positive effect on flame-retarding EP in vapor phase during combustion. Combining the aforementioned results, the significant improvement on the LOI value and vertical burning test level of IDOP/EP was owed to the dominating vapor phase flame-retardant effect and a certain degree of condensed phase activity.

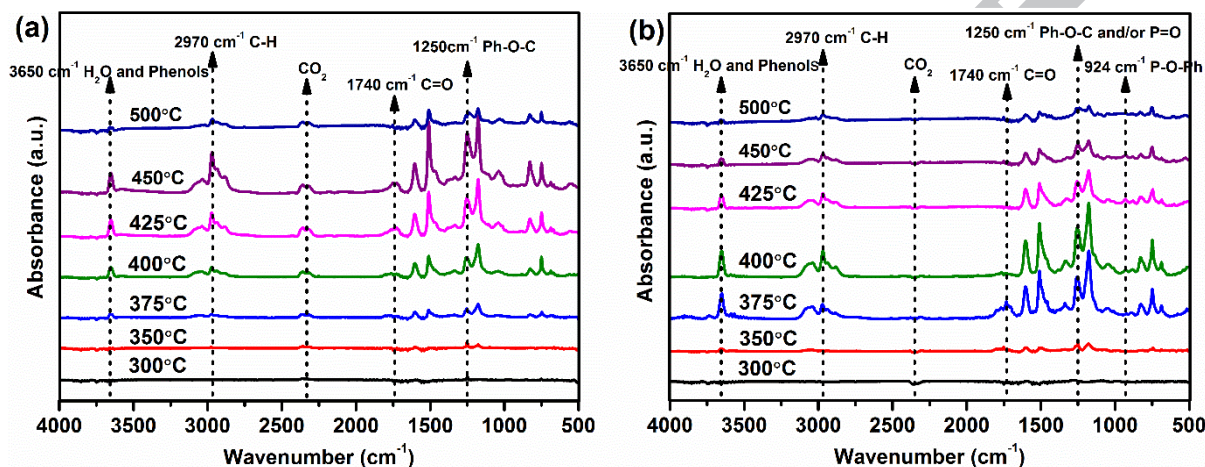


Figure 7. IR spectra of the volatile products for MZ/EP (a) and IDOP/EP (b) decomposed at different temperatures.

3.4. Thermal mechanical property

The thermal mechanical properties of the cured resins were studied by DMA. G' , G'' and loss factor ($\tan \delta$) versus temperature for MZ/EP and IDOP/EP were presented in **Fig. 8**. Notably, all thermosets showed a so-called “rubbery plateau” beyond their glass transition temperature (T_g , defined as the peak of $\tan \delta$). In general, the rubbery state modulus provides the information about the crosslink density, which can be used to further understand the architecture of the resins. Particularly, the rubbery state modulus of 5% MZ/EP was 15.6 MPa and T_g of the resins was as high as 175.0 °C, indicating a network with a highly crosslinking network. As for IDOP/EP, they all presented a lower T_g and a smaller rubbery state modulus compared with the reference sample. Moreover, as the content of the flame-retardant curing agent

increased, T_g of IDOP/EP then got higher but the rubbery state modulus became even smaller. e.g. 15% IDOP/EP had a T_g about 143.8 °C, near to the one cured by alicyclic amines (according to our previous work [47]); comparatively it showed a rubbery state modulus as low as 5.6 MPa, indicating a very low crosslinking density. This is because the formation of the phosphonate ester and/or ring-opening product from DOPO consumed excessive epoxy groups, and the phosphonate ester further acted as the end-capping agent, which resulted in poorer crosslinking networks. Nevertheless, such a big pendent group with steric hindrance inhibited the movement of polymer chains, thus the cured resins obtained a very low crosslinking density while kept a relatively high T_g finally [56, 57].

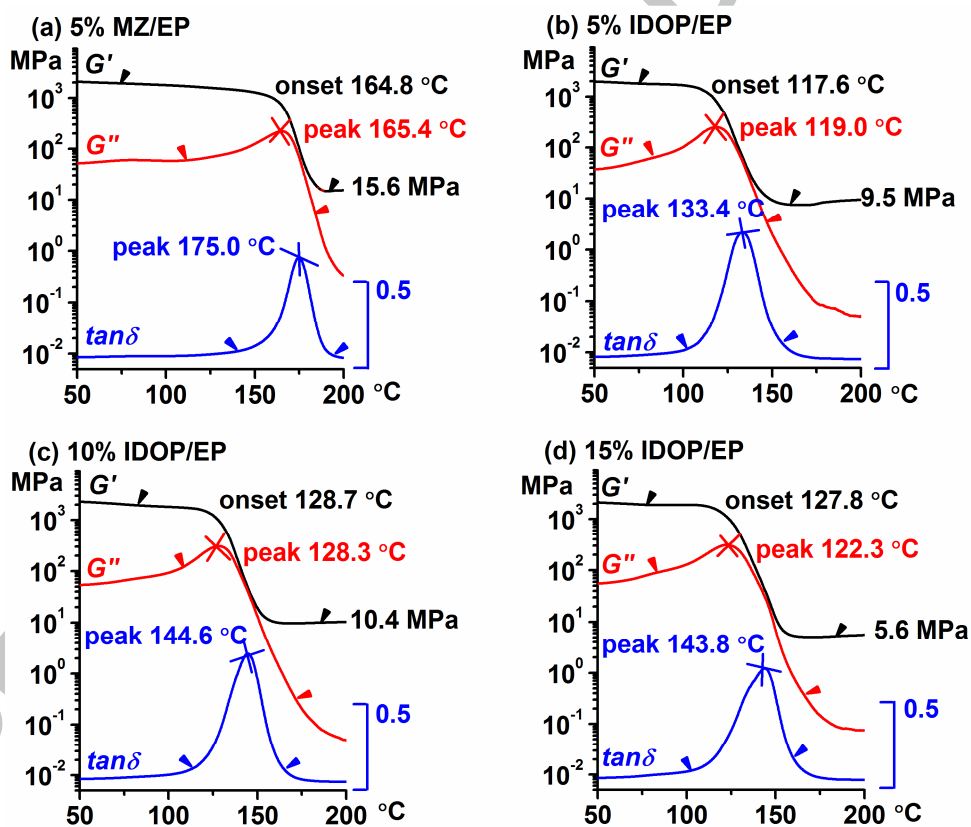


Figure 8. G' , G'' and $\tan \delta$ versus temperature curves of the cured resins.

3.5. Dielectric property

As the working frequency of electronic devices continually increases, low dielectric constant and

dissipation energy in electric fields are necessary for electronic materials to guarantee the velocity of signal propagation. Herein, the dielectric constant (ϵ) and loss ($\tan \delta$) versus frequency of the final resins were measured by a broadband dielectric spectrometer, and the resulting plots were shown in **Fig. 9**. The dielectric constant actually reflects the charge storage ability of a material on each surface. It's noteworthy that the dielectric constant of IDOP/EP remained stable over a wide frequency range from 1 to 10^6 Hz (< 4.75 within the scope) similarly as MZ/EP did. Besides, the dielectric constant of the flame-retardant samples slightly increased with the increase of the IDOP content. In general, the dielectric constant can be increased by reducing free volume and/or improving polarization of the matrix [58, 59]. Herein, the higher content of IDOP was added to the epoxy system, the more polar groups such as the hydroxyl group and ionic bond were incorporated into the molecular networks; moreover, the free volume was gradually occupied by the bulky DOPO-based pendants. Thus, the cured resins possessed a higher dielectric constant finally. Moreover, compared with the reference sample, all IDOP/EP samples exhibited a lower dielectric loss from 1 to 10^6 Hz (< 0.02 within the range). Architecturally, phosphaphenanthrene pendent group with large steric hindrance in epoxy networks restricted the polarization and movement of polymer chains after curing, thus resulted in a lower dielectric loss in the alternated electric field (1- 10^6 Hz). Notably, the dielectric loss refers to a phenomenon that the dielectric consumes electric energy as heat in the alternating electric field, and a lower dielectric loss is preferred for an insulating material [60, 61]. Accordingly, the incorporation of the flame-retardant groups didn't deteriorate the insulating performance of the final resins, suggesting the potential application in the electric/electronic fields.

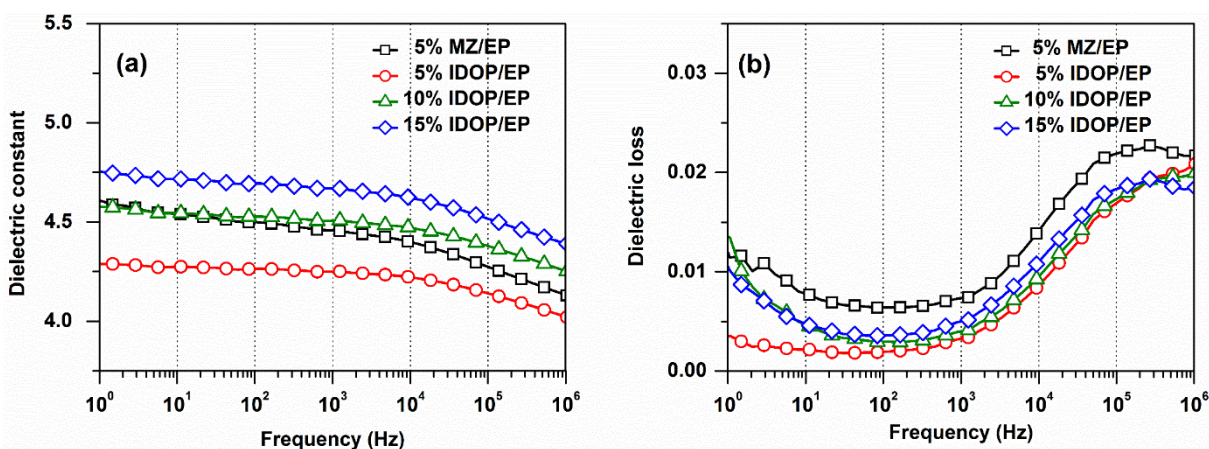


Figure 9. The frequency dependence of the dielectric constant (a) and loss (b) of the cured resins.

4. Conclusion

Concerning the stability of storage and ease of operation, one-pack epoxy materials containing the latent curing agent are always acclaimed in electrical/electronic field. Up to now, unfortunately, the traditional epoxy system is still hard to meet the demand for such versatile properties, especially to have high-standard thermal stability, suitable dielectric property and satisfactory flame retardance simultaneously. In this work, an imidazole derivative named IDOP was designed and synthesized as a latent flame-retardant curing agent, endowing the resulting materials with excellent comprehensive performance. It was confirmed that the IDOP/EP system kept stable in the liquid state at room temperature, besides cured efficiently with a moderate heat release under heating. The curing route was explored by XPS and it indicated that the flame-retardant group was incorporated into the epoxy chains by the ionic and/or covalent bonds. As a consequence, IDOP/EP had a lower crosslinking density with a slightly decreased T_g (> 133 °C), as demonstrated in DMA results. The results of TGA revealed that IDOP/EP had excellent thermal stability with a minor reduction on $T_{5\%}$ compared with MZ/EP. The LOI value of IDOP/EP dramatically improved and the sample easily achieved the UL-94 V-0 rating within 15% IDOP addition. The flame-retardant samples presented a longer TTI and showed a few reductions on p-HRR and THR owing to a dominating vapor-phase flame-retardant effect, which was further confirmed by TG-IR

results. IDOP/EP showed a stable tendency on dielectric constant as the reference sample did and had a lower dielectric loss than MZ/EP over a wide frequency range from 1 to 10^6 Hz. Taking these advantages, IDOP/EP system exhibited great potential to be a latent curing flame-retardant material for large batch production in electrical/electronic applications such as bonding, coating and encapsulating, where reliable electric insulation, excellent thermal stability and defined flame-retardant standards are all required.

ASSOCIATED CONTENT

Supporting Information

Electronic Supplementary Information (ESI) available: [the characterizations of IDOP and the comparison between this work and our group's previous works].

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HIGHLIGHTS

for

Latent Curing Epoxy System with Excellent Thermal Stability, Flame Retardance and Dielectric Property

Ying-Jun Xu, Li Chen*, Wen-Hui Rao, Min Qi, De-Ming Guo, Wang Liao and Yu-Zhong Wang*

Highlights

A novel imidazole salt was applied as a latent flame-retardant curing agent for EP.

This EP system showed long pot life as storing and fast curing while operating.

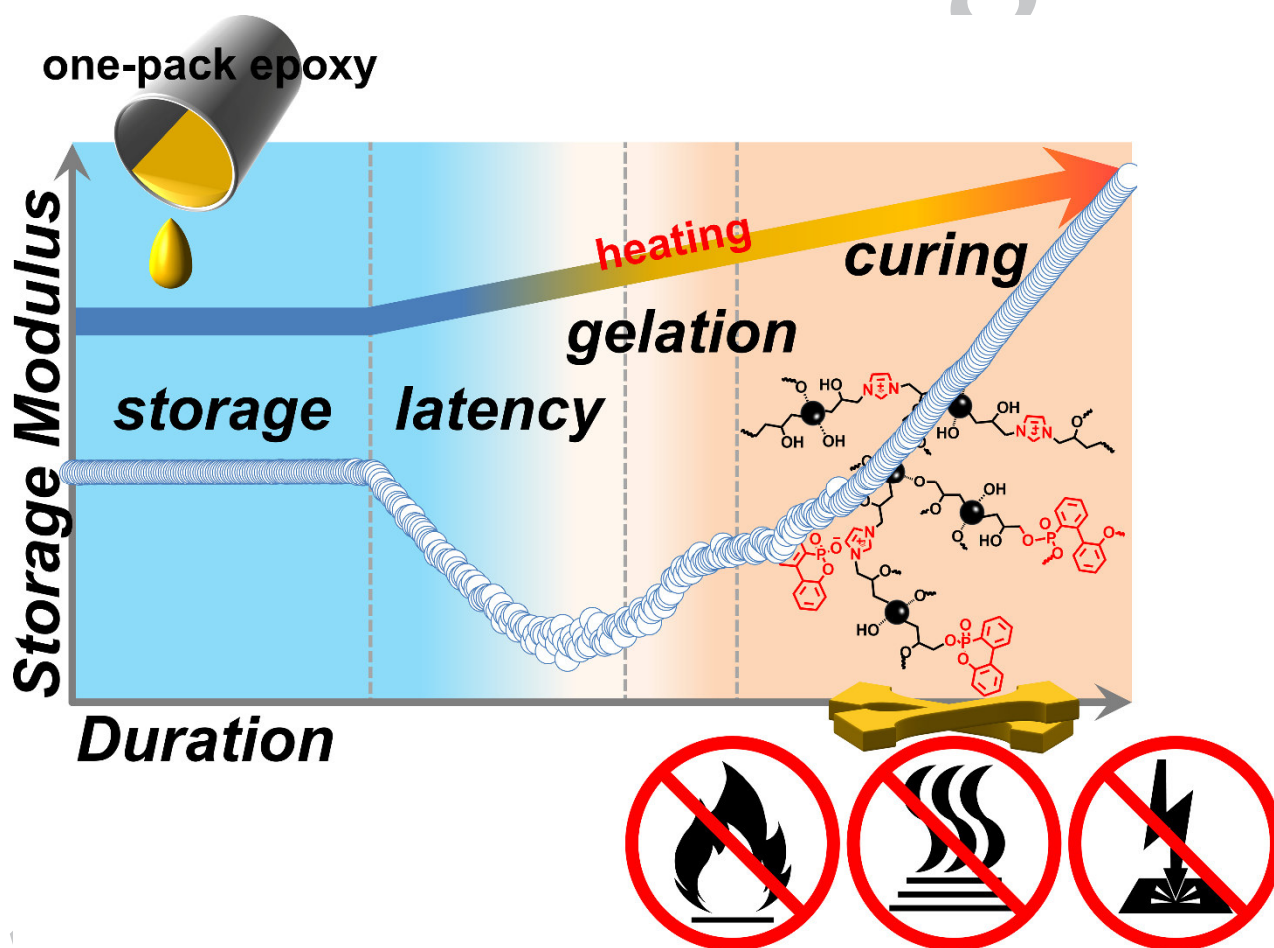
The cured resin with superb properties is applicable to electronic/electrical fields.

GRAPHIC ABSTRACT

for

Latent Curing Epoxy System with Excellent Thermal Stability, Flame Retardance and Dielectric Property

Ying-Jun Xu, Li Chen, Wen-Hui Rao, Min Qi, De-Ming Guo, Wang Liao and Yu-Zhong Wang



A latent curing epoxy system with excellent thermal stability, flame retardance and dielectric properties for versatile applications was reported for the first time.