Improved Flame Retardancy and Thermal Stability of P- and N-containing Diphenol Epoxy Resins from Lignin Oxidation Degraded Derivatives

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Diphenols with structures similar to bisphenol A (BPA) were designed and synthesized from three kinds of lignin oxidative depolymerized derivatives (LODD) to investigate the substitution possibility of BPA by LODD as raw material. The chemical shift and integral area of nuclear magnetic resonance spectra and the X-ray photoelectron spectroscopy analysis results showed that phosphorus- and nitrogen-containing diphenols were successfully formed. The cone calorimeter test and thermogravimetric analysis exhibited that the epoxy resin from diphenols were typical intumescent flame retardancy systems. These results showed drastically improved flame retardancy compared with traditional epoxy resin. Among them, the epoxy resin derived from vanillin presented the best flame retardancy properties. Due to a phosphorus-rich carbon layer being formed and accumulated at the surface of the epoxy resins from diphenols, the thermal degradation showed great enhancement of the char residues.

Keywords: Lignin oxidation degraded derivatives (LODD); Bio-based epoxy resin; Intumescent flame retardancy (IFR)

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INTRODUCTION

Epoxy resin, one of the most important industrial thermosets that is widely used in electrical appliances, aeronautics, coatings, adhesives, flooring, and paving (Yang *et al.* 2020; Yang *et al.* 2021), exhibits excellent properties, such as high chemical resistance, low shrinkage, superior thermo-stability, good mechanical strength, and good dielectric properties. Unfortunately, epoxy resins are highly flammable, which seriously threats the safety of people’s life and property (Hou *et al.* 2019; Gu *et al.* 2012, 2017). The most commercially available epoxy resin comes from the synthesis of bisphenol A (BPA) with epichlorohydrin, which represents 90% of the epoxy precursor in the world (Asada *et al.* 2015). The compound BPA is undesirable as a raw material for epoxy resin production because the use of fossil-based resources is no longer justifiable for practical, ecological, and socio-economic reasons. Moreover, BPA is an environmental hormone that mimics human estrogen, and can therefore cause impotency as well as cancer (Flint *et al.* 2012). With the growth of global environmental crisis and the shortage of fossil resources, the utilization of renewable biomass as substitute resources for production of epoxy resins has attracted considerable attention in recent years due to their biodegradability, availability, and renewable nature (Huo *et al.* 2014).

As a three-dimensional amorphous biopolymer composed of phenylpropanoid units linked together by ether and carbon-carbon bonds, lignin is considered to be one of the most promising resources not only because it is renewable, but also because it is second only to cellulose in abundance among naturally occurring aromatic polymers (Asada *et al.* 2015). Due to its phenolic ether structure, the preparation of lignin or lignin-based epoxy resin to improve the heat-resistance of the polymers is one of its most promising potential applications (Kong *et al.* 2014). In the past years, the study of lignin-based epoxy resin has focused on blending lignin with epoxy resin directly; modifying lignin derivatives by epoxide directly, which has been done by modifying lignin derivatives to improve their reactional ability followed by epoxidization (Zhao *et al.* 2001). The chemical modification during the preparation of lignin-based epoxy resins adds to the cost of preparation. At the same time, its heterogeneous molecules, insolubility in many organic solvents, and the indefinite structure depending on its origin and the extraction method, make the task of quality control very difficult, resulting in limited use of lignin for such purposes (Feng and Chen 2012; Upton and Kasko 2016). The direct and efficient conversion of lignin to discrete molecules or lower-molecular aromatic, monomeric building blocks for polymer productions is a very interesting future opportunity for lignin utilization.

Recently, researchers have paid more attention to lignin oxidative degraded derivatives (LODD). Koike described an interesting diepoxy monomer synthesis of diaromatic epoxy monomer from vanillin, pentaetythritol, and epichlorohydrin. An epoxide equivalent weight of 270 g/eq, synthesized by crosslinking reaction with diaminodiphenyl methane, exhibited good impact strength, tensile strength, and elongation of the final material (Koike 2011). Aouf *et al.* (2012) reported a synthesis of epoxy monomers from the chemo-enzymatic functionalization of vanillic acids. The enzymatically catalyzed epoxidation reaction is an interesting alternative to the use of epichlorohydrin. Fache *et al.* prepared diepoxy monomers from three vanillin derivatives *via* different oxidized reduction derivatives (Fache *et al.* 2014). These diepoxy monomers were used to prepare bio-based epoxy thermosets and displayed excellent thermo-mechanical properties. Wang *et al.* (2017) reported high performance flame retardant and thermostability epoxy resins synthesized by one-pot reaction containing Schiff base formation and phosphorus-hydrogen addition between vanillin, diamines, and diethyl phosphite, followed by reacting with epichlorohydrin. After curing, the vanillin-based epoxy resin showed excellent flame retardancy and thermostability.

Lignin is a natural aromatic polymer resulting from radical polymerization of three phenylpropanoid monomers including p-hydroxyl-phenyl, guaiacyl, and syringyl propanol (Li *et al.* 2016). The LODD are mainly p-hydroxybenzaldehyde (H), vanillin (V), and syringaldehyde (S), which contain a phenolic hydroxy group with different methoxyl groups on an aromatic ring. This study designed and synthesized phosphorus- and nitrogen-containing diphenols with structures similar to BPA from three kinds of LODD, namely H, V, and S, to investigate the substitution possibility of BPA by LODD as raw material. The influence of methoxy group, the typical functional group of lignin, on the reactivity of LODD, and flame retardancy, thermostability, and mechanical properties of cured epoxy resin were intensively studied.

EXPERIMENTAL

Materials

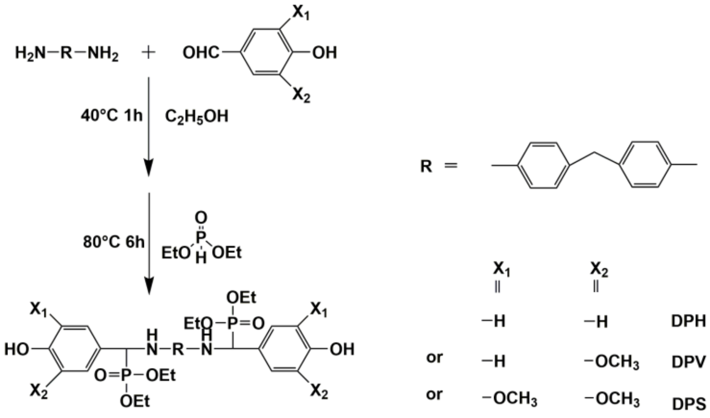
The p-hydroxybenzaldehyde (H), vanillin (V), syringaldehyde (S), 4,4-diamino-diphenylmethane (DDM), tetrabutylammonium bromide, diethyl phosphite, and zinc chloride were purchased from Aladdin Chemistry Co., Ltd., Shanghai, China.

Epichlorohydrin (ECH), ethanol, petroleum ether (boiling range: 60 to 90 °C), dichloromethane (DCM), and sodium hydroxide were supplied by Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Epoxy resin (DGEBA, trade name E51, epoxy value 0.48 to 0.54) was obtained from Nantong Xingchen Synthetic Material Co., Ltd., Nantong, China.

Methods

Synthesis diphenols (DPH, DPV, and DPS)

Diphenol H (DPH), diphenol V (DPV), and diphenol S (DPS) were synthesized from H, V, and S, respectively according to the Wang *et al.* (2017) method. The 40 g (0.33 mol) of p-hydroxybenzaldehyde (H) and 300 mL of ethanol were poured into a 1,000 mL three-neck flask, equipped with a reflux condenser and a magnetic stirrer. Then, the solution of 31.73 g (0.16 mol) of DDM dissolved in 100 mL of ethanol was added into the flask dropwise at 25 °C over 30 min and reacted at 40 °C for 1 h. After that, 63.10 g (0.45 mol) of diethyl phosphite and the catalyst of zinc chloride (0.5 g) were added into the flask. Meanwhile, the air was replaced using nitrogen (N_2) in the system, and the reaction temperature was kept at 80 °C for 8 h. Subsequently, the synthesized crude product was poured slowly into 1,000 mL of petroleum ether and stirred vigorously at room temperature until a yellow solid appeared that was separated by filtration. Finally, the purified product (DPH) was obtained by being washed with ethanol three times and dried at 50 °C for 24 h in a vacuum oven. According to the same synthetic route described above, a light yellow solid (DPV) was obtained by using vanillin and a deep yellow solid (DPS) was obtained by using syringaldehyde. The synthesis reaction route is shown in Scheme 1.

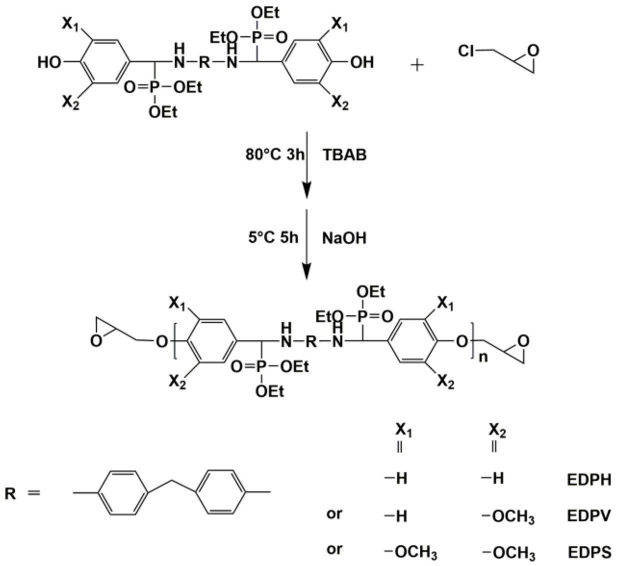


Scheme 1. Synthetic routes of DPH, DPV, and DPS

Synthesis epoxy resin from diphenols (EDPH, EDPV, and EDPS)

The 40 g (0.059 mol) of DPH was dissolved in 542.4 g (5.86 mol) epichlorohydrin (ECH) in a 1,000 mL three-neck flask, equipped with a reflux condenser and a magnetic stirrer. Then, 4.0 g (10 wt% of DPH) of tetrabutylammonium bromide (TBAB) as the catalyst was charged into the mixture, heated from room temperature to 80 °C, and reacted under nitrogen atmosphere for 3 h. After that, the environmental temperature was cooled and kept at approximately 5 °C. Next, 58.4 g of 40 wt% aqueous sodium hydroxide solution (0.59 mol NaOH) was added dropwise into the system for 30 min, and then the reaction was maintained for 5 h. The obtained mixture was diluted with dichloromethane (DCM) and washed with distilled water three times to remove impurities. Eventually, a brown solid

(EDPH) was obtained by removing DCM and ECH, followed by being washed twice with petroleum ether and then dried in a vacuum oven at 50 ℃ for 24 h to remove all volatile components. According to the same synthetic route described above, a yellow solid (EDPV) was obtained by using vanillin, and a brown solid (EDPS) was obtained by using syringaldehyde. The synthetic route is illustrated in Scheme 2.



Scheme 2. Epoxy resin synthesis routes of EDPH, EDPV, and EDPS

Preparation of cured epoxy resins

The curing agent 4,4-diaminodiphenylmethane (DDM) was melted at 90 ℃ previously, and then stirred with the epoxy resins prepared above to produce a uniform mix in 1:1 molar ratio of epoxy group to hydroxyl equivalent groups. After being degassed at 80 °C for 15 min in a vacuum oven, the mixture was poured into preheated polytetrafluoroethylene molds, cured at 100 °C for 3 h, and then cured at 160 °C for 2 h. Neat epoxy resin was prepared following the same method mentioned above for comparison.

Characterization

Fourier transform infrared (FTIR) spectra were obtained with a Nicolet 6700 infrared spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) using the KBr pellet technique in the wavenumber range of 400 to 4,000 cm^{-1}. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were performed on a Bruker AV400 NMR spectrometer (Bruker, Billerica, MA, USA) with DMSO-d6 as solvents. Thermogravimetric analysis (TGA) was performed on a NETZSCH STA449F3 (NETZSCH-Gerätebau GmbH, Freistaat Bayern, Germany) by scanning the cured resins from 100 to 700 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. Tensile properties were measured with CMT6104 universal testing machine (MTS Systems Co., Ltd., Shanghai, China) and the standard distance of dumbbell spline was 25 mm according to the GB/T 1040.2 (2006) standard. The tensile properties of each sample were reported as the average of at least 5 specimens. The limited oxygen index (LOI) measurement was obtained using a JF-3 oxygen index meter (Jiangning Analysis Instrument Company, Nanjing, China) according to ASTM D2863-10 (2010). The dimensions of the specimens were 100 mm × 6.5 mm × 3 mm. The morphology of the residue chars after LOI test were observed using a TM3030 scanning electron microscope (Hitachi High-Tech, Tokyo, Japan) with a voltage of 20 kV. Combustion behaviors were recorded with a cone calorimeter device (Fire Testing Technology, East Grinstead, UK) according to ISO 5660-1 (2015) under an external heat flux of 50 kW/m^2. The dimensions of the specimen were 100 mm × 100 mm × 3 mm. X-ray photoelectron spectroscopy (XPS) was used to record the spectra of the residue chars on an Escalab 250Xi apparatus (Thermo Fisher Scientific, Waltham, MA, USA).

RESULTS AND DISCUSSION

Characterization of Synthesized Diphenols and Cured Epoxy Resins

Lignin is a macromolecule derived from three monolignol units, p-hydroxyphenyl, guaiacyl, and syringyl.

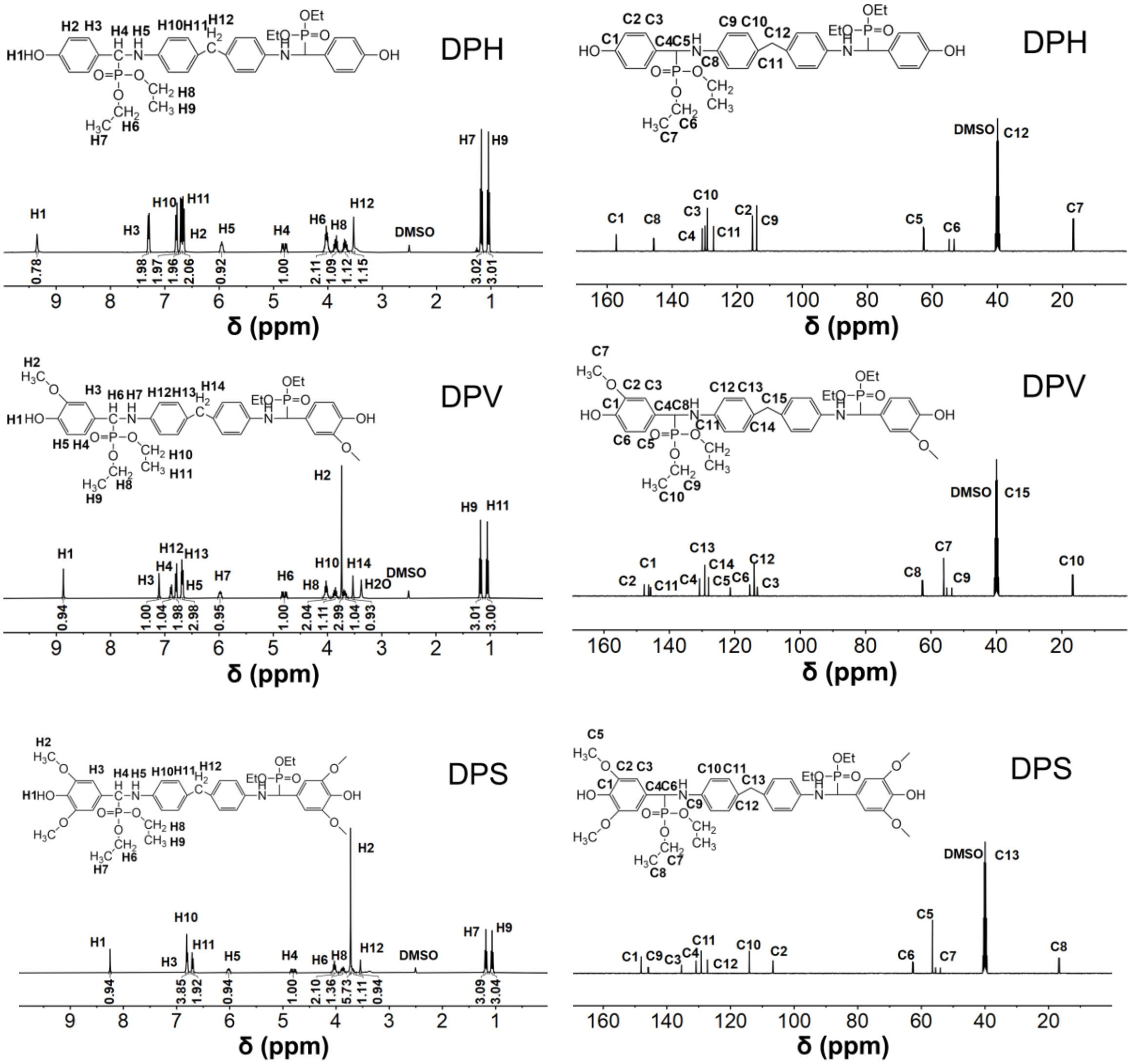


Fig. 1. ^{1}H NMR and ^{13}C NMR spectra of DPH, DHV, and DVS

Lignin's oxidation degraded derivatives (LODD) are mainly p-hydroxybenzaldehyde (H), vanillin (V), and syringaldehyde (S). The H, V, and S with different methoxyl groups on its aromatic ring were used to synthesize phosphorus- and nitrogen-containing diphenols, namely diphenol H (DPH), diphenol V (DPV), and diphenol S (DPS), respectively, in which the structure was similar to BPA. The ^{1}H NMR and ^{13}C NMR spectra showed the chemical shift and integral area of all the peaks matched well with the protons and carbons of chemical structure for DPH, DPV, and DPS (Fig. 1). These results are in accordance with that reported by Wang *et al.* (2017).

The XPS was measured to evaluate diverse information and relative content about elemental compositions. The corresponding P_{2p}, C_{1s}, N_{1s}, and O_{1s} peaks appeared at 133.3, 284.4, 400.0, and 531.8 eV, respectively (Pethsangave *et al.* 2017; Fang *et al.* 2019). As shown in Fig. 2, the XPS spectra of the char residues of EDPH, EDPV, and EDPS showed the presence of phosphorus and nitrogen, besides carbon and oxygen, indicating that diaminodiphenylmethane and diethyl phosphite reacted with H, V, and S completely. The nitrogen content of EDPS showed the highest value of 8.17%, followed by epoxy resin of DPV and DPH. In contrast, the phosphorus content of epoxy resin from DPS gave the lowest value of 4.83%, while the value of the phosphorus content was over 7% in EDPH and EDPV (Fig. 2). The XPS results quantitatively supported that nitrogen- and phosphorus-containing H-, V-, and S-based diphenols, implying that the target compounds of DPH, DPV, and DPS, were synthesized successfully.

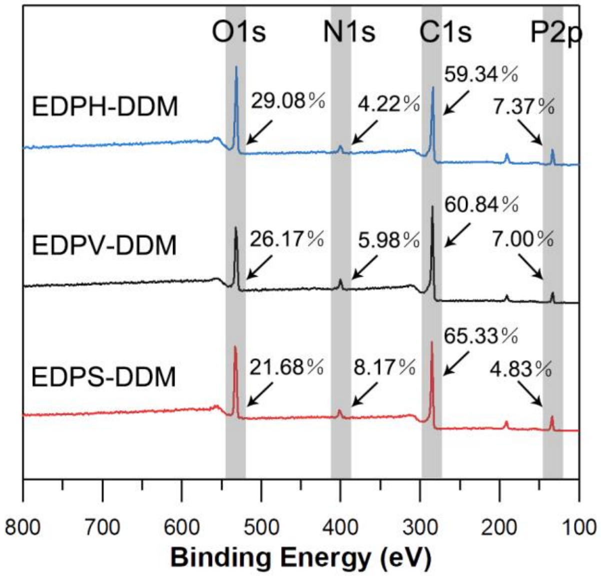


Fig. 2. XPS spectra of the char residues of cured epoxy resins from diphenols

Epoxy resins were obtained by the reaction of DPH, DPV, and DPS with epichlorohydrin. The chemical structures of EDPH, EDPV, and EDPS were confirmed by FTIR. As shown in the FTIR spectra (Fig. 3), the absorption peak at 3300 to 3600 cm^{-1} corresponds to O-H and N-H, the characteristic peak around 1250 cm^{-1} ascribed to P=O and the absorption peak around 1030 cm^{-1} belongs to P–O. These results indicated that diphenols of DPH, DPV, and DPS were synthesized successfully. Moreover, the peak at 910 cm^{-1} corresponding to the epoxy groups appeared in the spectra of EDPH, EDPV, and EDPS, indicating that the epoxidation reaction was completed.

With the curing reaction of epoxy resins, to explore the extent of reaction, the FTIR spectrum of cured epoxy resins are presented in Fig. 4. Compared with the spectra of EDPH, EDPV, and EDPS, the peaks for epoxy groups around 910 cm^{-1} disappeared, meaning that the epoxy was cured well with DDM.

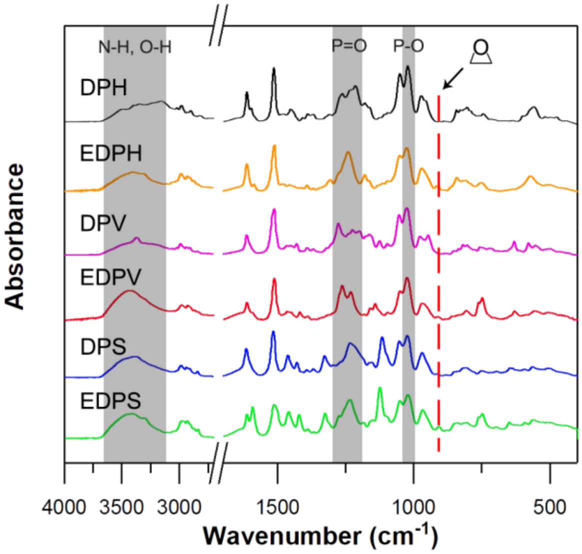


Fig. 3. FTIR spectra of diphenols (DPH, DPV, and DPS) and epoxy resins from diphenols (EDPH, EDPV, and EDPS)

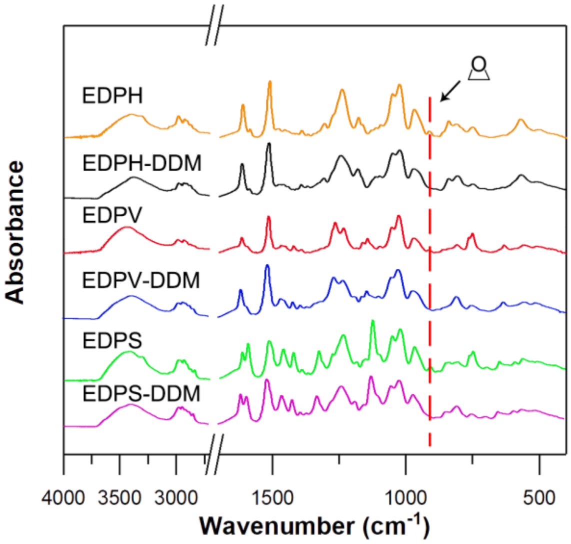


Fig. 4. FTIR spectra of cured epoxy resins from diphenols

Flame-retardant Properties

The LOI measures the minimum oxygen concentration (in a flowing mixture of oxygen and nitrogen gas) required to support candle-like downward flame combustion. The LOI value is an important parameter for comparing the flammability of polymeric materials, and the results are listed in Fig. 5. The epoxy resin from diphenols exhibited a better performance in LOI tests. The LOI values of EDPH, EDPV, and EDPS were higher compared to E51 epoxy resin, which was synthesized from BPA, suggesting that diphenols exhibited outstanding flame-retardant effects. The EDPV, synthesized from vanillin, gave the highest LOI value of 31.6%, the value of EDPS was 26.1%. These results demonstrated that a methoxy group on the aromatic ring of lignin unit could affect flame retardancy of the cured epoxy resins. The LOI is a semi-qualitative indicator of the effectiveness of flame retardants. Flame-retardant properties were further confirmed by cone calorimetry.

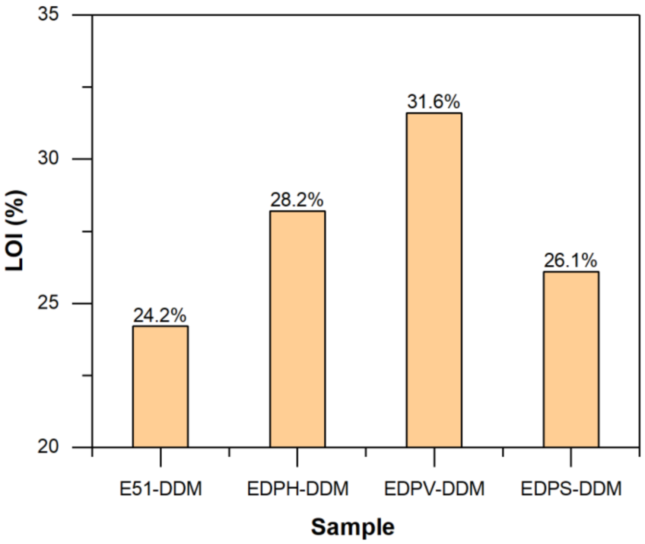


Fig. 5. LOI and UL-94 rating of the cured epoxy resins

Combustion Behavior of Biphenol Epoxy Resins

The cone calorimetry test, one of the most effective methods to study the combustion behaviors, evaluates the flammability and potential fire safety of various polymer materials under a simulated real fire condition (Schartel and Hull 2007). The cone calorimeter test was performed to further evaluate the combustion behavior and flame-retardant performances of epoxy resins in a realistic fire environment.

The heat release rate (HRR) is one of the key parameters used to evaluate flame retardancy of materials. In Fig. 6, the HRR curves of the epoxy resin (EDPH, EDPV, and EDPS) from diphenols exhibited two peaks, which was typical of intumescent fire-retardant (IFR) systems. The IFR containing polymer shows the HRR curve of typical insulating intumescent layer, which stays relatively constant and slowly decreases towards the end of combustion (Dogan *et al.* 2010). The first peak occurred around 40 s and could be assigned to the ignition and O-P linkages broken at relatively low temperature, resulting in the formation of an expanded protective shield. Moreover, the intumescent char, which has excellent thermal stability and insulation of heat, can prevent the substrate materials from further burning in a fire (Wu *et al.* 2011). This is why the second maximum HRR value of EDPH, EDPV, and EDPS was 439.2 kW/m^2, 240.5 kW/m^2, and 430.7 kW/ m^2, respectively, which was much lower than the value (954.4 kW·m^{-2}) of E51. The second peak is explained by the destruction of the intumescent structure and the formation of a carbonaceous residue. By comparing to epoxy resins from diphenols, the epoxy resin from E-51 showed one sharp HRR peak around 140 s after ignition, and the maximum HRR value was four times higher than that of EDPV (Fig. 6, Table 1).

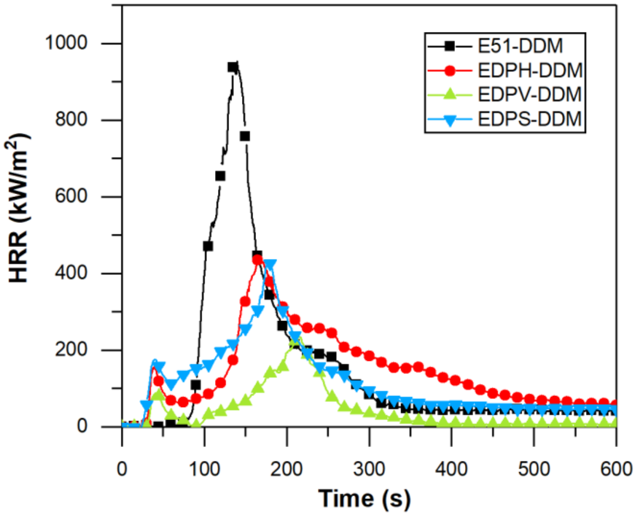


Fig. 6. HRR curves of epoxy thermosets

Table 1. Combustion Parameters of Epoxy Resins

Sample	p-HRR (kW·m^{-2})	THR (MJ·m^{-2})	av-EHC (MJ·kg^{-1})	TSP (m^2)	FGRI (kW·m^{-2}· s^{-1})	R_{600s} (wt%)
E51-DDM	954.4	89.5	20.4	22.5	6.8	1.6
EDPH-DDM	439.2	87.4	35.9	11.4	2.6	53.7
EDPV-DDM	240.5	25.3	15.1	9.3	1.1	63.3
EDPS-DDM	430.7	69.2	28.3	10.4	2.4	48.7

The peak of heat release rate (p-HRR) is the most important parameter of a given fire scenario that reflects the tendency of a flame-retardant system towards fire propagation. A higher value of p-HRR results in a greater danger of fire hazard encounter (Ruban and Zaikov 2001; Dogan *et al.* 2010). The p-HRR value of epoxy resin from diphenols was much lower than that of E51, indicating the fire retardancy of epoxy resins from diphenols was superior to that of E-51.

The total heat release (THR) is another parameter used in fire retardancy study that can be obtained by calculating the area under HRR curve and depends on total mass loss, effective heat released by burning volatiles, and effectiveness of combustion at the flame zone (Parsell *et al.* 2013). The THR value of epoxy resin EDPV from vanillin derivative was the lowest recorded at 25.3 MJ·m^{-2}, which was a reduction of 71.7% compared with that of E-51 (Table 1). The results of THP agreed with the conclusion shown by p-HRR.

In general, effectiveness of a flame-retardant system depends on carbon char formed during the combustion, as cone calorimetry specifies (Yuan *et al.* 2018). It was clear that there was almost no residue left at the end of the cone calorimeter test for E-51 (Table 1). In contrast, at the end of the cone calorimeter test, EDPH, DPV, and EDPS retained almost 50% residue, and the surface of EDPH, EDPV, and EDPS was covered with a thick black expanded char network, which provides further evidence for flame retardancy of epoxy resin from diphenols (Table 1). The excellent flame retardancy of epoxy resins from EDPH, EDPV, and EDPS compared to E51, would be due to the outstanding intumescence, which further proved the effect of protection and barrier in the condensed phase for EDPH, EDPV, and EDPS epoxy resins. The epoxy resin of EDPV, derived from vanillin, showed the highest char content of 63.3%, suggesting that one methoxyl group on aromatic ring could be superior to those with no or two methoxyl groups.

The total smoke production (TSP) and average effective heat combustion (av-EHC) were used to investigate the flame-retardant effect of epoxy resin in the gaseous phase. The TSP values of cured epoxy resins from diphenols was one half of E51. With the formation of phosphorus-rich char layers, there were more internal matrix materials that remained instead of being burned and less combustible volatiles released, corresponding to the records of lower TSP values and elevated residual weight compared with that of E51 epoxy resin (Qiu *et al.* 2018). The TSP value of epoxy resin from EDPV decreased to 9.3 m^2, a reduction of 58.7% compared with that of E51, indicating that epoxy resin from vanillin derivative can effectively suppress smoke and volatile gases production (Table 1). The conclusions of smoke suppression and volatile gases production were also supported by av-EHC, which indicates the efficiency of combustion of the volatile compounds produced from thermal degradation of materials, which can be used to understand mechanism of fire degradation of materials (Upton and Kasko 2016). The av-EHC value of epoxy resins from diphenols were lower compared with the epoxy resin from E-51, which represented the less amount of volatile gases decomposed from diphenol epoxy resins.

The fire growth rate index (FGRI) is calculated by dividing pHRR by tpHRR, and it can be used to estimate both the predicted fire spread rate and the size of a fire. The higher the FGRI value, the faster assumed flame spread and flame growth (Upton and Kasko 2016; Liu *et al*. 2020). Epoxy resins from diphenols performed good flame-retardant behaviors. The FGRI values of epoxy resin from EDPH, EDPV, and EDPS decreased 61.7%, 83.8%, and 64.7%, respectively, compared to the value of E-51 epoxy resin (Table 1), suggesting that epoxy resins from diphenols presented high-performance flame-retardant effects. The FGRI values of epoxy resin from EDPV was the lowest, at 1.1 $kW{\cdot}m^{-2}{\cdot}\ s^{-1}$. Meanwhile, due to the formation of expansive char layers, more internal matrix materials remained instead of being burned and less combustible volatiles were released, corresponding to the records of lower TSP values and elevated residual weight compared with that of E51 epoxy resin (Qiu *et al.* 2018).

Morphological Characterization

The morphology of the char residues after cone calorimeter test exhibited that the E51 was almost burnt out, leaving minimal char residue with a fragmentized and flat structure, which could not block the heat and oxygen transfer and prevent the release of volatile gas (Fig. 7). However, the char residue of cured epoxy resins from diphenols exhibited a continuous and intumescent structure. An effective intumescent char layer with good thermal stability can insulate the transfer of heat and substance and protect the underlying materials from further combustion in a fire (Wu *et al.* 2011). The intumescent char layer was formed gradually after the ignition of diphenol resins, which hindered the transfer of heat and prevented the internal materials from further burning to achieve the effect of suppression of flame combustion (Cheng *et al.* 2019). This stable and compact char layer could slow down heat and mass transfer between gas and the condensed phases and prevent the underlying polymeric substrate from being further attacked by heat flux (Zhu *et al.* 2014).

The SEM images of char residues of EDPH, EDPV, and EDPS showed continuous and spongy structures with honeycomb-like structure (Fig. 8). Undoubtedly, this kind of char structure was conducive to preventing the release of combustible gas and retarding the heat and oxygen exchange between the burning surface and the inner matrix (Cheng *et al.*

2019). In contrast, the surface of E51 exhibited craquelures resembling the cracks present in dry soil, and these could not provide a good flame shield for the underlying polymeric substrate. The presence of the smooth and featureless fracture surface of E51 indicated the rapid crack propagation due to the lack of energy dissipation (Xu *et al.* 2019).

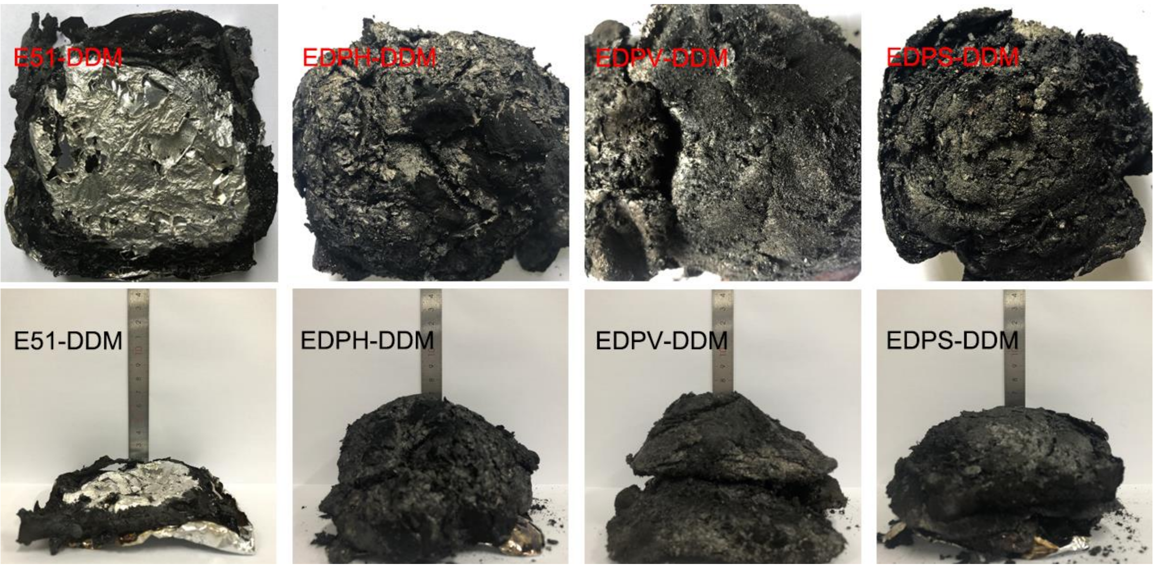


Fig. 7. Digital photos of residues after cone calorimeter test

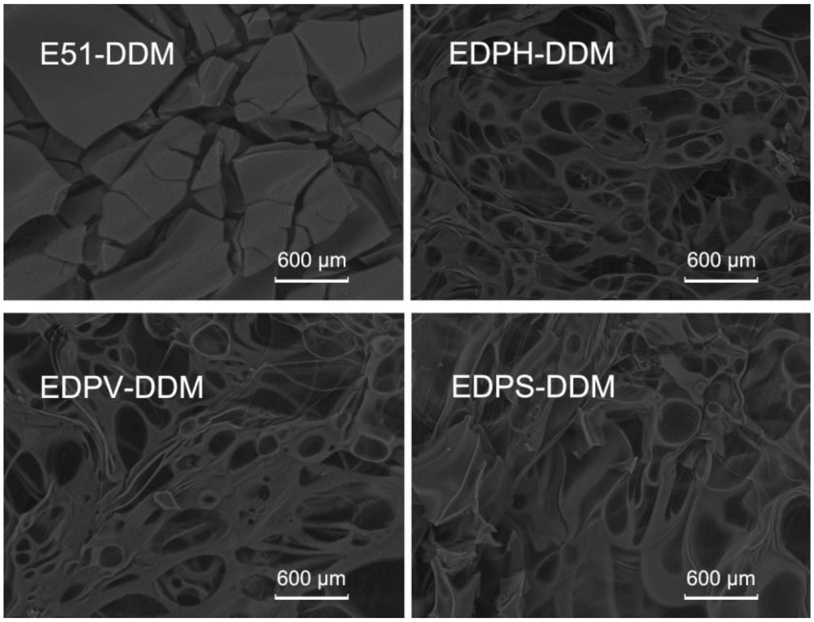


Fig. 8. SEM photographs of the residues after LOI test

Thermal Stability

Thermal stability of cured epoxy resins from diphenols (EDPH, EDPV, and EDPS) and E51 was assessed by thermogravimetric analysis under nitrogen atmosphere. The TGA and derivative thermogravimetric (DTG) curves are shown in Figs. 9 and 10. The corresponding characteristic thermal decomposition parameters are listed in Table 2.

Table 2. Thermal Parameters of Cured Epoxy Resins from Diphenols and E51

Sample	T_{max1} (°C)	Mass Loss 1 (wt%)	T_{max2} (°C)	Mass Loss 2 (wt%)	$R_{700\ °C}$ (wt%)
E51-DDM	387.8	77.6	-	-	17.0
EDPH-DDM	328.0	17.6	450.1	26.4	45.8
EDPV-DDM	308.2	27.7	457.2	18.5	43.9
EDPS-DDM	310.0	23.7	418.5	24.9	43.1

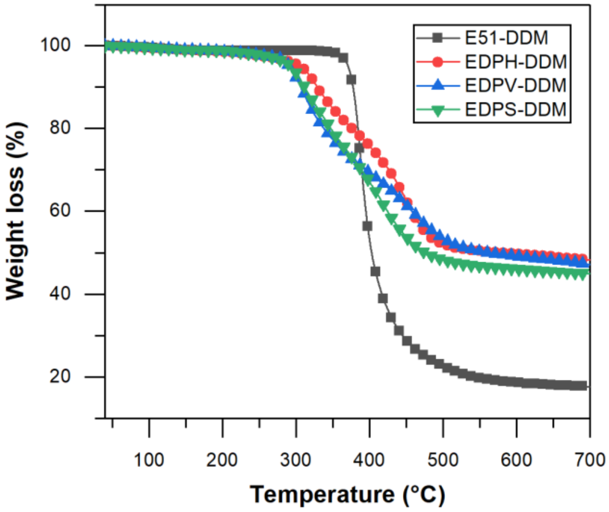


Fig. 9. TG curves of the cured epoxy resins from diphenols and E51

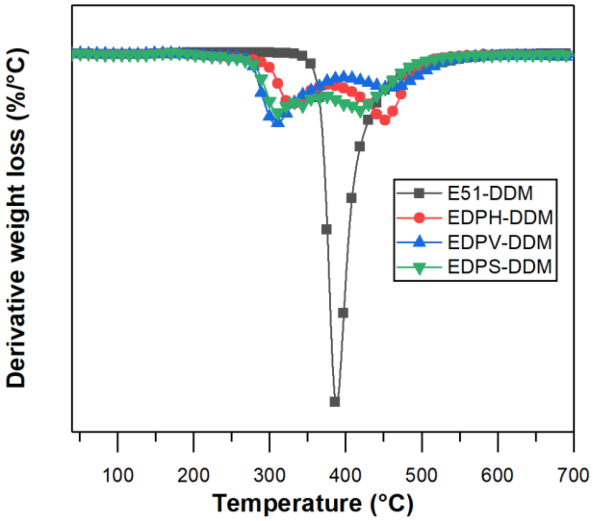


Fig. 10. DTG curves of the cured epoxy resins from diphenols and E51

The DTG curves of the cured epoxy resins from diphenols showed two peaks, suggesting that EDPH, EDPV, and EDPS underwent two-step thermal degradation. The two DTG peaks would correspond to two exothermic peaks of the HRR curves, one of the characteristics of typical of IFR systems. The first stage was in the temperature range of 274 to 399 °C with weight loss of 17.6 to 27.7%. The second stage was in the temperature range of 373 to 505 °C with weight loss of 18.5 to 26.4%. In contrast, the E51 epoxy resin exhibited one step thermal degradation at 390 °C. The two steps of thermal degradation of EDPH, EDPV, and EDPS epoxy resins would be due to the thermal degradation of O=P-O bond. Wang *et al.* (2017) also reported that the O=P−O bond exhibited in the structure of epoxy resin was more easily degradable than C−C bond. The residue after thermal degradation is a critical factor in thermal stability performance of materials. The residue yield from cured epoxy resins of EDPH, EDPV, and EDPS was much higher than that of E51, suggesting that a phosphorus-rich carbon layer was formed and accumulated at the surface of the samples. It played a superior thermal insulating role and prevented heat from reaching the interior of the remaining polymer (Xu *et al.* 2019), resulting in a higher residue at 700 °C ($R_{700\ °C}$). Moreover, EDPH exhibited higher T_{max1} and $R_{700\ °C}$ than EDPV and EDPS (Table 2), which would be due to higher phosphorus content. The conclusion was also quantitatively supported by the XPS result that contained higher phosphorus content than that of EDPV and EDPS (Fig. 2).

Mechanical Properties

The performance of elongations at break and tensile moduli showed a similar trend in which the epoxy resins from diphenols of EDPH, EDPV, and EDPS increased relative to E51 (Fig. 11). The obvious improvements in the elongations at break and tensile modulus was ascribed to the introduction of rigid diphenylphosphinyl structure and the enhancement in the cross-linking density (Zhu *et al.* 2014). Among epoxy resins from diphenols, EDPH presented the best elongation at break, which was increased 36.8% compared with E51. For tensile modulus properties, EDPV showed highest property that increased 10.63% related to E51.

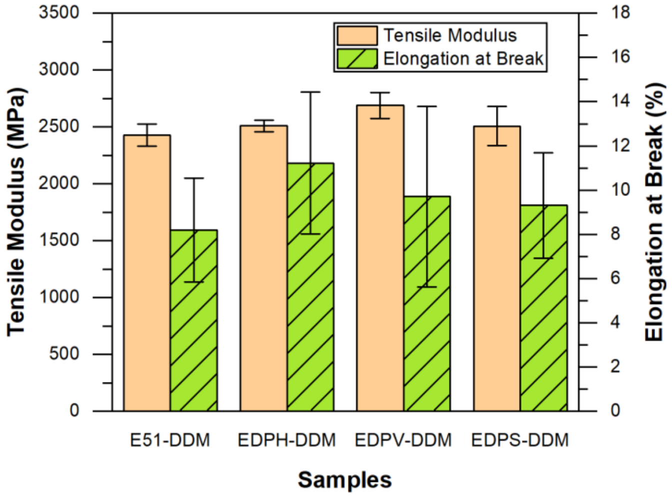


Fig. 11. Elongations at break and tensile modulus properties of epoxy resins

CONCLUSIONS

1. The chemical shift and integral area of ^{1}H NMR and ^{13}C NMR spectra and the XPS analysis results showed that phosphorus- and nitrogen-containing diphenols, namely DPH, DPV, and DPS from H, V, and S, were successfully synthesized. Subsequently,

three kinds of diphenols with different methoxy group were epoxied by reaction with epichlorohydrin.

2. The HRR curves, DTG analysis, and digital photos of residues after cone calorimeter test exhibited that the epoxy resin from diphenols were typical IFR systems, which demonstrated outstanding intumescent flame suppression performance caused by the synergistic effect of phosphorus and nitrogen, indicating that diaminodiphenylmethane and diethyl phosphite were reacted with H, V, and S completely.

3. The cured epoxy resins from diphenols exhibited enhancements in flame retardancy. The flammability of cured epoxy resins revealed that EDPH, EDPV, and EDPS could increase the LOI value and decrease the p-HRR, THR, av-EHC, TSP, and FGRI, which showed drastically improved flame retardancy compared to E51. Among the epoxy resins from diphenols, EDPV derived from vanillin presented the best flame retardancy properties.

4. Due to a phosphorus-rich carbon layer that formed and accumulated at the surface of the epoxy resins from diphenols, the thermal degradation of EDPH, EDPV, and EDPS greatly enhanced the char residues.

5. The epoxy resins from diphenols exhibited obvious improvements in the elongations at break and tensile moduli compared with E51, due to the introduction of rigid diphenylphosphinyl structure and the enhancement in the cross-linking density.

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