

## Flame retardancy and thermal properties of organoclay and phosphorous compound synergistically modified epoxy resin

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**ABSTRACT:** Phosphorous flame retardants (PFRs) are common halogen-free flame retardants. However, the flame retardancy of PFRs has not been fully exploited. Herein, the synergistic flame retardant effect of a typical phosphorous compound, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), and organoclay on epoxy is studied. Results show that the peak of heat release rate (pHRR) and smoke production rate of modified epoxy resin (EP) with both 2.0 wt % phosphorus and 4.0 wt % organoclay are only 40% and 46% of that of neat EP resin, respectively, while the sole use of 2.0 wt % phosphorus only decrease the pHRR to 59% of that of neat EP resin. The structure and thermal decomposition behavior of as-prepared nanocomposites are analyzed, and a synergistic flame retardant mechanism is proposed. This investigation opens a new approach to obtain halogen-free EPs with higher flame retardancy and better overall properties than the EPs loaded with DOPO only. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43367.

**KEYWORDS:** clay; flame retardance; nanostructured polymers; resins; thermogravimetric analysis

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### INTRODUCTION

Epoxy resins (EPs) are widely used in the field of coating, construction, adhesive, electronic, and aerospace etc.<sup>1,2</sup> owing to their excellent electrical properties,<sup>3,4</sup> heat resistance,<sup>5</sup> cohesiveness, mechanical properties<sup>6</sup> and chemical stability.<sup>7</sup> However, one of major drawbacks of epoxies is their inflammability, which limits the applications of epoxies and their composites.

Although halogenated flame retardants can effectively inhibit the flammability of EPs, their environmental problems are always a concern. Moreover, during their combustion, harsh, and corrosive poisonous gases, such as dioxin and polybrominated dibenzofurans, are produced, which can be hazardous to health. Thus, the flame retardants are encouraged or enforced to be used by many countries.

Phosphorus forms a large category of halogen-free flame retardants, which can effectively decelerate the spread of fire with a minimal release of toxic gases. As an additive, phosphorus is economic but easily leaches out from the matrix, which can induce negative effects on the processability and mechanical properties.<sup>8</sup> These negative effects can be mitigated by the use

of functionalized phosphorous. Functionalized phosphorous compounds are able to react with the hydroxyl and epoxide groups in EPs, and thus to incorporate the phosphorus units into backbones or side chains of polymer. However, the phosphorus loading in resin is limited as the mechanical properties of resin often deteriorate upon high loading. To date, the use of phosphorous compounds such as 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), as flame retardants in polymer especially the EP, has been widely studied. With an active hydrogen, the phosphaphenanthrene group of DOPO can be easily induced into backbone structure of epoxy through the reaction between P-H bond and other function groups,<sup>9</sup> such as unsaturated C=C bond.<sup>10</sup> DOPO and its derivatives, such as DOPO-MAH,<sup>11</sup> can be used in various polymers. Liu<sup>11</sup> found that the limiting oxygen index (LOI) increased from 20.9 to 25.7, and UL-94 V-0 rating was achieved. Generally, the LOI represents the minimum concentration of oxygen in air that supports combustion of a polymer, moreover, the UL-94 V-0 illustrates the burning stops within 10 secs on a vertical specimen and drips of particles allowed as long as they are not inflamed. Perrt<sup>12</sup> further studied the degradation behavior of EP

and amine curing agent modified by DOPO. It was found that DOPO could exhibit excellent flame retardancy only when it was grafted onto EP backbone, else, it would volatilize before the combustion. During the process of combustion, the phosphaphenanthrene group decomposed into phenyl phosphate and glassy state phosphorous compounds, and then formed a phosphorous-rich char. The phosphorous-rich char could inhibit the degradation of EP, thus the polymeric material exhibit much better flame retardancy. However, a DOPO molecule only contains 14.4% of phosphorous element, which limits the maximum possible phosphorous loading grafted onto the epoxy backbone. Moreover, since the phosphorous compounds are introduced into the polymer matrix through chemical reaction, the smoke production rate (SPR) and smoke density of the developed material will be high.<sup>13</sup>

The synergistic effects of the phosphorus and inorganic fillers, such as metallic oxides<sup>14</sup> and nitrogen intumescent,<sup>15</sup> on reducing the smoke emission has been reported. However, their synergistic effects on the flame retardancy were not obvious. Recently, polymer/layered silicate nanocomposites have attracted great interests, because the composites exhibit remarkable improvement in several properties over the virgin polymer. With the addition of organoclay, the nanocomposites can not only exhibit better mechanical properties, including dynamic mechanical,<sup>16</sup> tensile,<sup>17</sup> and flexural properties,<sup>18</sup> but also improved flame retardant properties, such as low heat release rate (HRR), and low SPR.<sup>19–25</sup> Also, the thermal stability of the materials can be greatly improved.<sup>26,27</sup> Therefore, it would be interesting if DOPO and organoclay are simultaneously loaded into EP for the improvement of flame retardant properties of EP.

In this study, novel organoclay/DOPO modified EP nanocomposites were prepared. The dispersion of organoclay was characterized by small-angle XRD and TEM. The flame retardancy of the nanocomposites were studied by cone calorimeter and the char residue was studied by scanning electron microscope (SEM) with energy dispersive spectrometer (EDS) attached with it. In addition, the flame retarding mechanism is studied in detail by non-isothermal kinetic theory and Arrhenius equation. These investigations might lead to obtain a novel halogen-free EPs with excellent flame retardancy and overall properties.

## EXPERIMENTAL PROCEDURE

### Materials

DOPO was purchased from Sanko Organoclay, Nanomer I.30P were purchased from Nanocor. Its organic modifying agent is octadecan-1-aminium salt, and the molecular formulation is  $\text{CH}_3(\text{CH}_2)_{17}\text{NH}_3^+$ . The cation exchange capacity is 145 meq/100 g. Diglycidylether bisphenol-A, DGEBA was purchased from Shanghai Resin Factory, which has a trade code 618 and its epoxy equivalent weight is 188. The amine hardener, diamino diphenyl sulfone (DDS), was purchased from Aladdin Industrial. In this study, 7 samples have been prepared. In which, EP represent neat EP, which is the control sample. EP-DOPO-2 means the EP with 2 wt % of DOPO added. As for organoclay and DOPO modified nanocomposites, we used ED2-*x* to indicate. In which, the *x* means the weight of organoclay in DOPO

**Table I.** Components of Organoclay/DOPO Modification Nanocomposite Formulations

	DGEBA (g)	DDS (g)	DOPO (g)	I.30P (g)
Neat EP	100.00	31.66	0	0
EP-DOPO-2	100.00	28.23	16.13	0
ED2-2	100.00	28.23	16.13	2
ED2-4	100.00	28.23	16.13	4
ED2-6	100.00	28.23	16.13	6
Organoclay only (4 wt %)	100.00	31.66	0	4
EP with 20.13 g DOPO	100.00	27.38	20.13	0

modified EP. All the detailed formulation can be seen in Table I.

### Preparation of Reference Samples

One hundred grams of DGEBA was introduced into a beaker with a stirring equipment and heated to 80 °C; 31.66g of amine curing agent DDS was added into this EP and stirred continuously until DDS was dissolved in the EP, thus a transparent mixture of DGEBA and DDS was obtained. After defoaming by a vacuum oven for 20 min, the mixture was poured into the die coated with Teflon past on its surface and put into an oven for curing. The curing procedure was as follows: 160 °C for 2 h, 180 °C for 4 h.

### Preparation of DOPO Modified EP

The formulation of preparing DOPO modified EP is listed in Scheme 1. The weight percent of phosphorus in DGEBA was 2 wt %. The weight percent of phosphorus in DOPO was 14.4 wt %. The epoxy value of DGEBA is 0.51–0.53. The computational formula is in eq. (1):

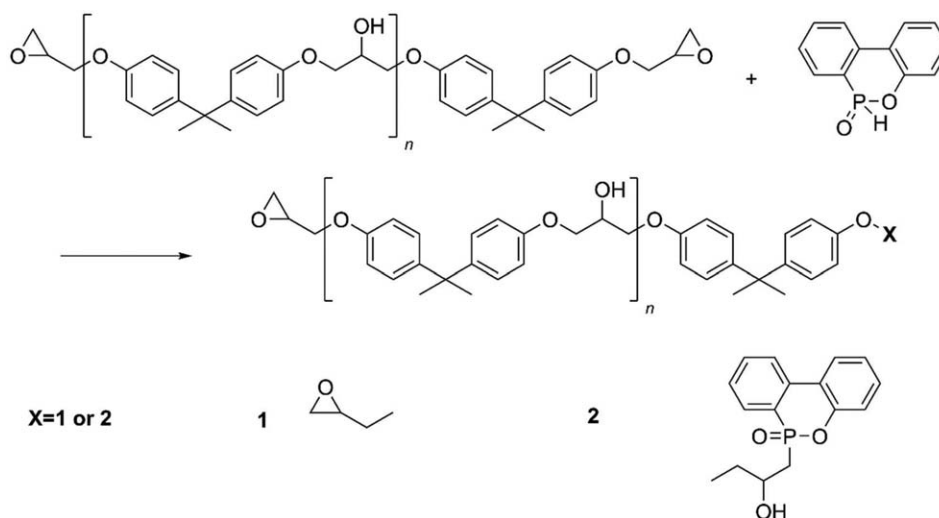
$$P\% = \frac{14.4\%X}{X+100} \quad (1)$$

in which the *P* represents the weight percentage of phosphorus in the DGEBA, *X* represents the mass of DOPO per 100 g of DGEBA.

DOPO was added into 100 g of DGEBA stoichiometrically and the mixture was heated to 160 °C while stirring. The reaction time was 5 h, and transparent faint yellow liquid EP was obtained. When the temperature of the EP was fallen to 120 °C, stoichiometric ratio of DDS was added and stirred until it dissolved completely. The DOPO modified EP was poured into preheated die for curing, the curing procedure was same as described above.

### Preparation of Organoclay/DOPO-Modified EP Nanocomposites

Predetermined amounts of organoclay were added into DOPO modified EP and stirred at 120 °C for 2 h. To obtain well dispersed organoclay nanocomposite, the mixture was subjected to ultrasonic before mixing with DDS. Prior to curing treatment, the mixture was put into vacuum oven to remove the bubble away at 120 °C for 20 min. The curing procedure was as follows: 160 °C for 2 h, 180 °C for 4 h.



**Scheme 1.** The reaction of EP and DOPO.

### Measurements and Characterization

The chemical structure of DOPO-modified EP was analyzed by Fourier transform infrared spectroscopy (FTIR, Thermo Nicolet 5700 coupled with an ATR accessory) in the range of 500–4000  $\text{cm}^{-1}$ .

The XRD patterns of the samples were obtained using Co-K $\alpha$  radiation ( $l = 1.78901 \text{ \AA}$ ) in an X'Pert Pro MPD (Philips), diffractometer and operating at 40 kV and 30 mA ( $2\theta$  range from 0.5° to 10° with a step size of 0.02°).

A transmission electron microscope (TEM, JEOL JEM-2010) was employed to observe the morphologies of samples. The acceleration voltage was 200 kV. All samples were made by ultrathin sectioning.

Flammability of the samples were characterized using a cone calorimeter performed in a cone calorimeter JCZ-1 (Nanjing Jiangning Analytical Instrument Factory, China). Radiation heat flux was 50  $\text{kW/m}^2$  according to ISO5660 standard procedures. The dimension of samples was  $100 \times 100 \times 3 \text{ mm}^3$ .

The SEM was performed using JSM-7500F SEM (JEOL, Japan) at an accelerating voltage of 3.0 kV.

Thermogravimetric (TG) analysis was carried out with STA449C thermal analyzer (NETZSCH, German) in the range 25–800 °C under an air atmosphere with a flow rate of 100 mL/min and heating rate was 10, 20, 30, and 40 °C/min.

## RESULTS AND DISCUSSION

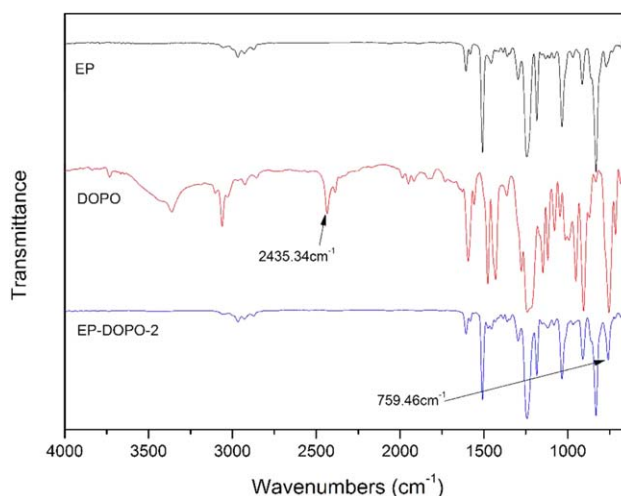
### Chemical Structure of ED2-N Nanocomposites

By the reaction between DOPO and DGEBA, EP modified by DOPO was obtained. In the synthetic process, the electrophilic active hydrogens in DOPO served as a reactive site for the epoxy group in DGEBA. As reported by Wang *et al.*,<sup>28,29</sup> the strong peaks in FTIR spectra at 2435.34 and 759.46  $\text{cm}^{-1}$  are assigned to the P—H and P—O—Ph bonds, respectively, which are also observed in the FTIR spectrum of DOPO as shown in Figure 1. Nevertheless, after the reaction with DGEBA, the peak of P—H bond disappears. Compared with neat EP, the peak of

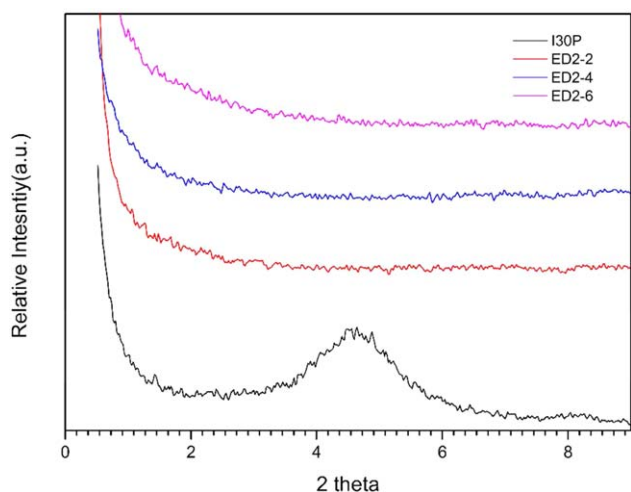
P—O—Ph appears in the spectrum of DOPO-EP-2, indicating that DOPO has successfully grafted into the backbone structure of DGEBA.

The properties of organoclay/polymer nanocomposites are highly dependent on the dispersion of organoclay in the polymer matrix. If there is a cross-linking reaction between the galleries of the clay layer, the intercalated or exfoliated structure of PLS will be formed. Thus, the dispersion of organoclay will be significantly improved.

For the EP cured by an amine hardener, the extent of exfoliation of organoclay decreased along with the decreasing Brønsted acidity of organic modifier in the order of  $\text{CH}_3(\text{CH}_2)_{17}\text{NH}_3^+ > \text{CH}_3(\text{CH}_2)_{17}\text{N}(\text{CH}_3)\text{H}_2^+ > \text{CH}_3(\text{CH}_2)_{17}\text{N}(\text{CH}_3)_2\text{H}^+ > \text{CH}_3(\text{CH}_2)_{17}\text{N}(\text{CH}_3)_3^+$ .<sup>30</sup> On the basis of Gibbs free energy formulation  $\Delta G = \Delta H - T\Delta S$ , since intercalation reaction can lead to an entropy reduction, the reaction between the galleries should be an exothermic reaction, thus making the Gibbs free energy  $\Delta G$



**Figure 1.** FTIR spectra of DOPO and EP modified by DOPO. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



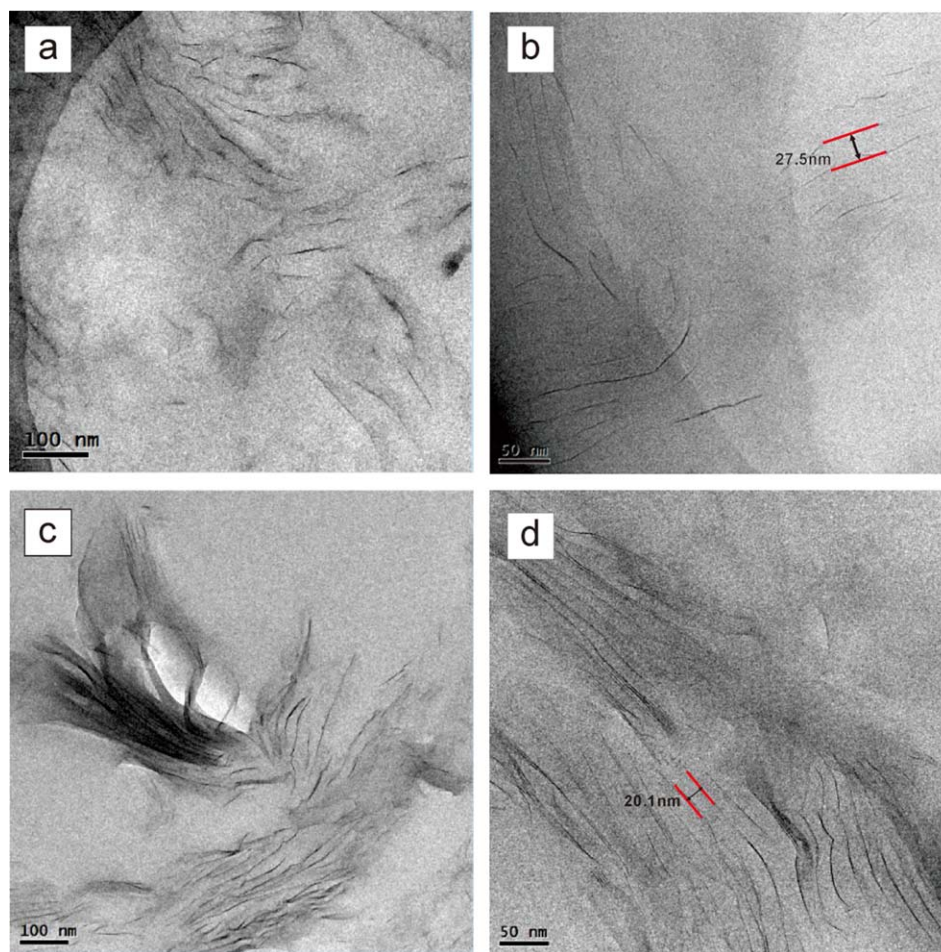
**Figure 2.** X-ray diffraction patterns for I30P organoclay and EP nanocomposites modified by DOPO and organoclay. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

minus. The reaction heat  $|\Delta H|$  between EP and organic modifier increased in accordance with the Brønsted acidity of organic modifier, making the reaction towards the direction of intercala-

tion. In this study, organoclay containing primary amine salt is chosen as a modifier to EP.

XRD is usually used to determine the microstructure of the clay in the nanocomposites. The XRD patterns of organoclay and its nanocomposites are shown in Figure 2. In the patterns of organoclay, the prominent peak corresponding to the basal spacing of organoclay is seen at 4.6, corresponding basal spacing of organoclay is 2.21 nm according to Bragg equation ( $2d\sin\theta = n\lambda$ ). In contrast to the organoclay, the prominent peaks are absent in the patterns of all nanocomposites, which indicate the basal spacing of organoclay is more than 4 nm.<sup>31</sup>

The morphologies of the nanocomposites were examined using TEM, and the representative images of ED2-4 and ED2-6 are shown in Figure 3. When the content of organoclay was 4 wt %, the image with lower magnification [Figure 3(a)] indicates that the organoclay layers are well dispersed in the epoxy matrix. The dark lines, which represent the layers of organoclay distributed in the epoxy matrix, and the exfoliated structure is formed. The image with higher magnification [Figure 3(b)] confirms that the interlayer spacing is about 30 nm. In the TEM image with low magnification, although some agglomerates of organoclay is observed, most of the organoclay are infiltrated by EP, and the



**Figure 3.** TEM images of EP organoclay nanocomposites. (a) ED2-4 with lower magnification, (b) ED2-4 with higher magnification, (c) ED2-6 with lower magnification, and (d) ED2-6 with higher magnification. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table II.** Cone Calorimeter Data for the Flame Retarded EP Composites

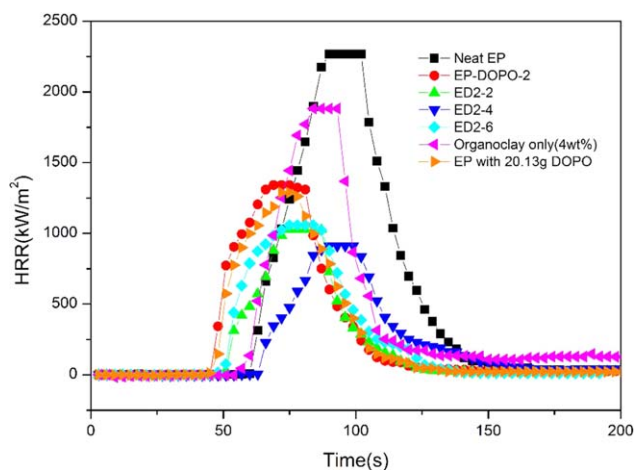
Sample	TTI (s)	Peak of HRR (kW/m <sup>2</sup> )	Peak of SPR (M <sup>2</sup> /s)	Total heat evolved (MJ/m <sup>2</sup> )	Residue yield (%)
Neat EP	60	2266.9	313.6	166.2	6.9
EP-DOPO-2	35	1341.2	350.6	92.8	11.4
ED2-2	50	1026.1	229.1	84.9	13.8
ED2-4	65	911.1	143.9	80.9	13.9
ED2-6	50	1056.0	230.0	75.3	14.3
Organoclay only(4 wt %)	55	1881.1	200.6	135.3	14.0
EP with 20.13g DOPO	35	1288.7	355.7	91.7	12.1

intercalated structure of nanocomposite is obtained. Apparently, when the content of organoclay increased to 6 wt % [Figure 3(c,d)], the extent of exfoliation is worse than that at 4 wt %. With higher magnification, the interlayer spacing is evaluated, which is about 20 nm.

As the curing progresses, the resin transformed from a reactive fluid to a crosslinking solid. At the meantime, the viscosity of the system will significantly increase. This makes the intragallery diffusion more restrictive, and it becomes more difficult to achieve a complete exfoliation of the clay tactoids.<sup>32</sup> For the EP, the exfoliated extent of organoclay is not only affected by the difference in reaction speed inside and outside the gallery, but also by the size of the clusters and the distance between them.<sup>33</sup> When the content of organoclay is relatively high, the available space for exfoliation is limited by neighboring clusters of clay, and the extent of exfoliation is worse in the case.

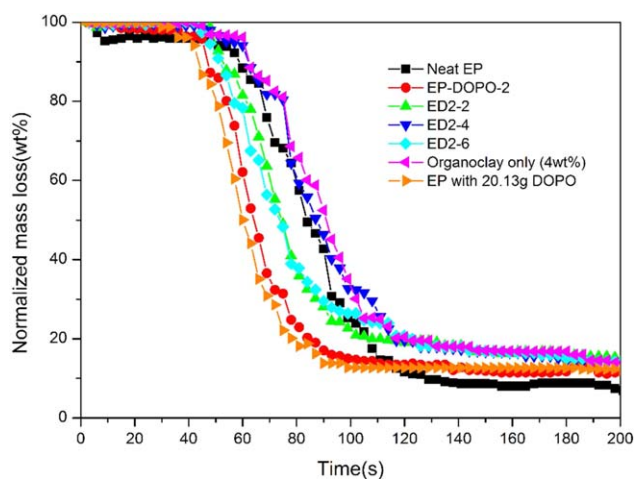
#### Flame Retardancy of DOPO/Organoclay Nanocomposites

The cone calorimeter is one of the most effective bench-scale methods for studying the fire retardant properties of polymeric materials. Fire-relevant properties such as the HRR, normalized mass loss, time to ignition (TTI), and SPR are vital to the evaluation of the fire safety of materials. These parameters are listed in Table II.

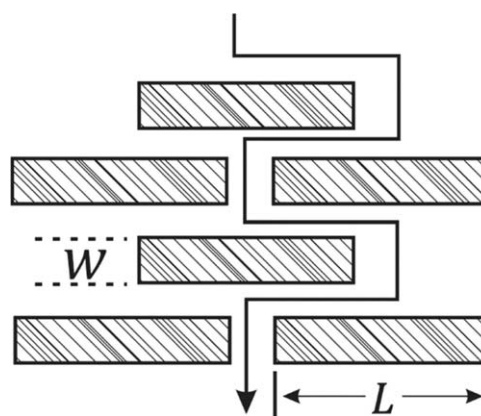


**Figure 4.** HRR curves of neat EP and EP modified by DOPO and organoclay. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

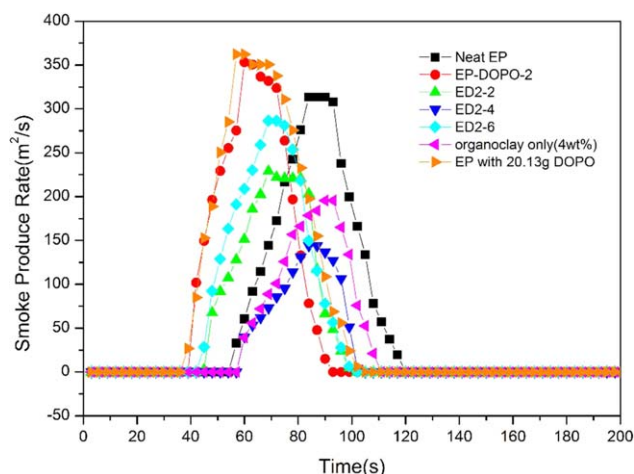
TTI represents the duration before the surface of the material is burned with luminous flame, which is used to determine the influence of flame retardant on ignitability. Higher TTI indicates that the polymer is difficult to ignite under the favorable circumstances. As shown in Table II, the TTI of epoxy decreases from 60 to 35 s after the addition of DOPO as a modifier. Such phenomenon can be due to the fact that the incorporation of flame retardant not only decomposes ahead of time themselves



**Figure 5.** Normalized mass loss on combustion time of neat EP and EP modified by DOPO and organoclay. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



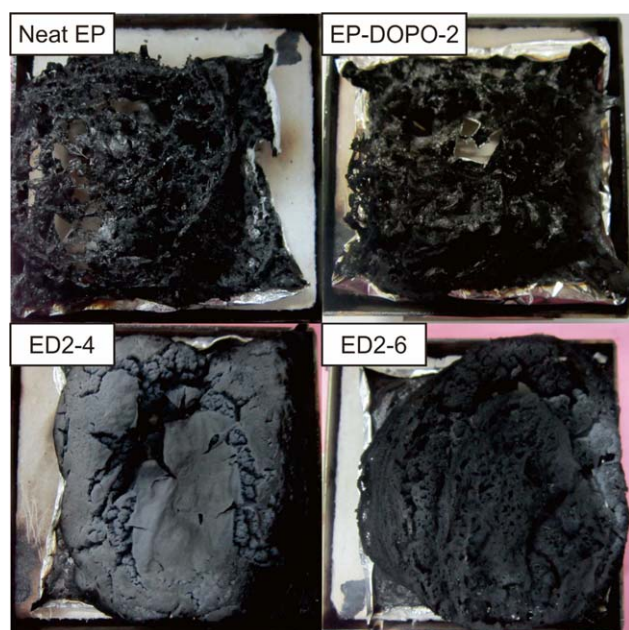
**Figure 6.** Model for the path of a diffusing molecule through a PLS.



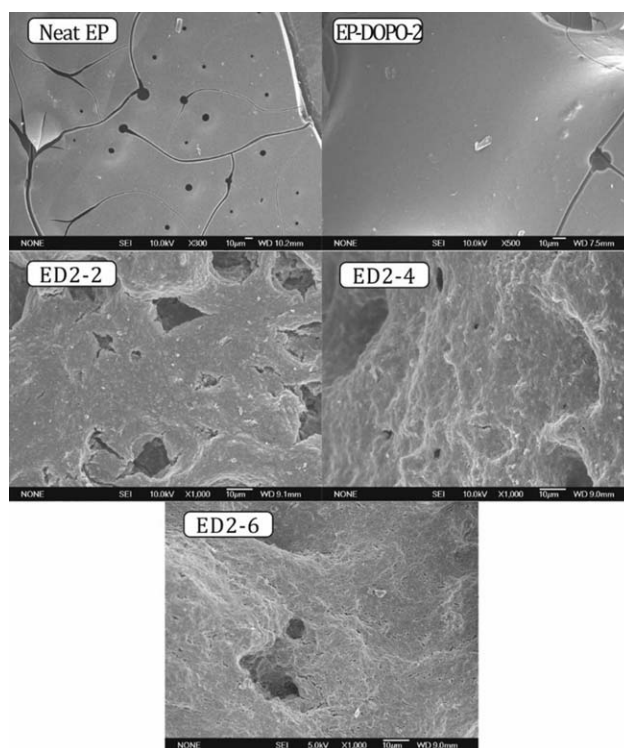
**Figure 7.** Smoke produce rate (SPR) curves of neat EP and EP modified by DOPO and organoclay nanocomposites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

but also promotes resin matrix to degrade at lower temperature.<sup>34</sup> It is worthy to note that when the organoclay is added into the matrix of polymer, the TTI of prepared nanocomposites is even longer than that of neat EP. In addition, TTI is 65 s when the weight percentage of organoclay is 4 wt %. These increase of TTI are very valuable for the enhancement of flame retardancy of EPs.<sup>35</sup>

Figure 4 stands for the HRR curves of different samples. As the curves show, neat EP burns rapidly after ignition and peak heat release rate (pHRR) reaches 2267 kW/m<sup>2</sup>. HRR of EP modified by DOPO decreases to a great extent compared to neat EP, of which pHRR reaches 1341 kW/m<sup>2</sup>. When organoclay is introduced into DOPO modified polymer matrix, the HRR of the EP is reduced further. The pHRR reaches only 911 kW/m<sup>2</sup>



**Figure 8.** Photographs of char from different samples after the cone calorimeter test. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

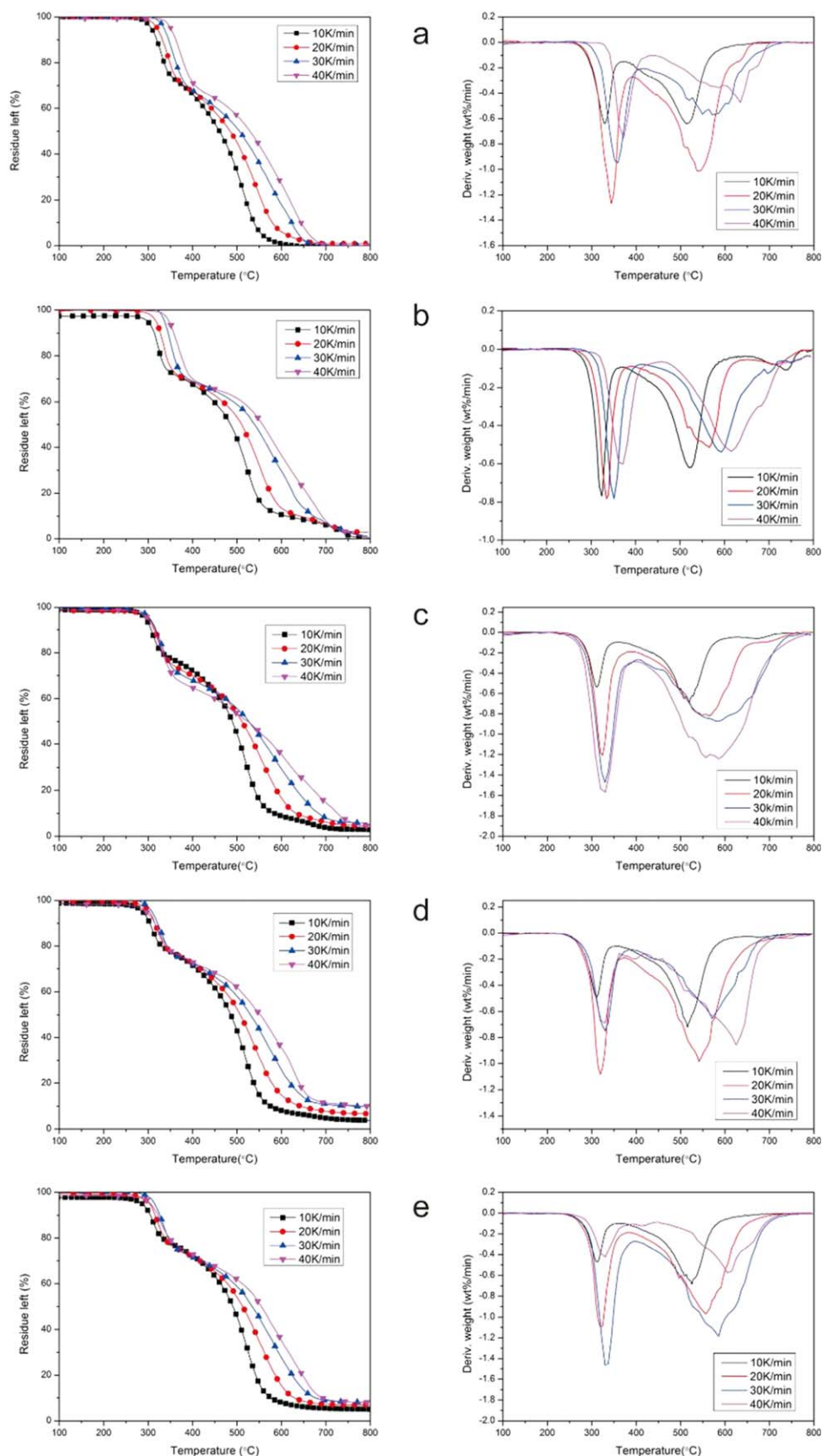


**Figure 9.** SEM micrographs of char residue after combustion.

when the content of organoclay is 4 wt %. Compared with EP-DOPO-2 system, the pHRR of EP containing 4 wt % organoclay only decreases to 1881 kW/m<sup>2</sup>. In addition, to confirm that the improvement of retardancy comes from the synergistic effect between DOPO and organoclay, the HRR test of EP composite with (16.13 + 4 g) DOPO, which has same loading of additives as the ED2-4 sample, was carried out. Figure 4 clearly shows that by introducing 20.13 g of DOPO, the pHRR does not reduced too much compared with EP-DOPO-2 and was higher than that of ED2-4. It can be concluded that under the same loading of additives, the synergistically flame retardancy brought by DOPO and organoclay was better than using DOPO or organoclay only. Moreover, the normalized mass loss (shown in Figure 5) showed that by introducing DOPO into EP matrix, the initial thermal decomposition temperature was lower compared with neat EP. However, by introducing organoclay, the initial thermal decomposition temperature was higher compared with EP-DOPO-2. In addition, the char residue increased obviously.

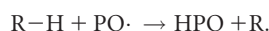
**Table III.** Elemental Compositions of the Residual Chars of Different Samples

Sample	Elemental composition (wt %)			
	C	O	Si	P
Neat EP	73.65	16.99	0	0
EP-DOPO-2	72.79	17.24	0	3.3
ED2-2	27.65	44.3	7.52	9.69
ED2-4	14.63	41.61	13.51	13.29
ED2-6	22.55	45.85	8.61	10.87

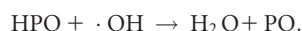
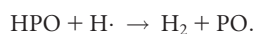


**Figure 10.** TG and DTG curves of different samples in air atmosphere with different heating rates. (a) EP, (b) EP-DOPO-2, (c) ED2-2, (d) ED2-4, and (e) ED2-6. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

These results confirm that the mixture of DOPO and organo-clay can act as an attractive flame retardant for EP.<sup>36</sup> The reduction of initial thermal decomposition temperature can be explained as the degradation of phosphate ester organic compounds present in DOPO, also decompose to phosphoric acid, metaphosphoric acid and polymetaphosphate acid while burning. Thus, produced phosphoric acids can help dehydration and promote carbonization at the surface of polymer. Moreover, such solid carbon does not take part in either evaporation combustion or decomposition combustion, making the resin loaded with DOPO with better flame retardancy. Meanwhile, PO· free radical, which is generated while burning, captures the H· and HO· free radicals and intercept the radical chain reactions in the flame, leading to a reduction of the heat production until self-extinguishment of the flame. Reaction equation is as follows:



HPO recombines with H· and HO· and regenerates PO· free radical, resulting in a catalytic flame retardant effect of species.



The improvement of flame retardancy brought by organo-clay can be explained by the model (Figure 6) created by Nielsen [eq. (2)]<sup>37,38</sup>:

$$\tau = \frac{\text{distance a molecule must travel to get through film}}{\text{thickness of film}} \quad (2)$$

$$= 1 + \left( \frac{L}{2W} \right) \phi_F$$

where,  $\tau$  is the tortuosity factor,  $L$  is length of a face of a filler particle,  $W$  is the thickness of the filler plates, and  $\phi_F$  is the volume fraction of filler. Due to its high length-diameter ( $L/W$ ) ratio, delaminated clay can prolong the permeation time of the micromolecules and blocks the diffusion of the gas. In addition, organo-clay, which is dispersed in the epoxy matrix will remain on the surface during the thermal degradation, preventing the mass transport of the polymer below or isolating the contact between flame and polymer. Moreover, the flame retarding properties of DOPO, these peculiarities of organo-clay improves the flame retardancy of the polymer.

The emission of smoke is considered as another important parameter in estimating the flame retardancy of materials. The SPR curves of different samples are depicted in Figure 7. It can be seen that the maximum SPR of neat EP is about 314 m<sup>2</sup>/s. When EP is modified by DOPO, no obvious effect of smoke suppression is observed although HRR is significantly reduced. More interestingly, the SPR is decreased when the organo-clay is introduced into DOPO/EP blend; especially when the weight percentage of organo-clay was 4 wt %, the peak of SPR is only about 144 m<sup>2</sup>/s. These results indicate that organo-clay can significantly inhibit smoke production of EP for a great extent, which is also explained by the unique properties that polymer layered silicate (PLS) have a good gas barrier effect.

#### Characterization of Char Residue

Figure 8 shows the morphologies of the residues of the different cone calorimetric samples after testing. It can be seen that

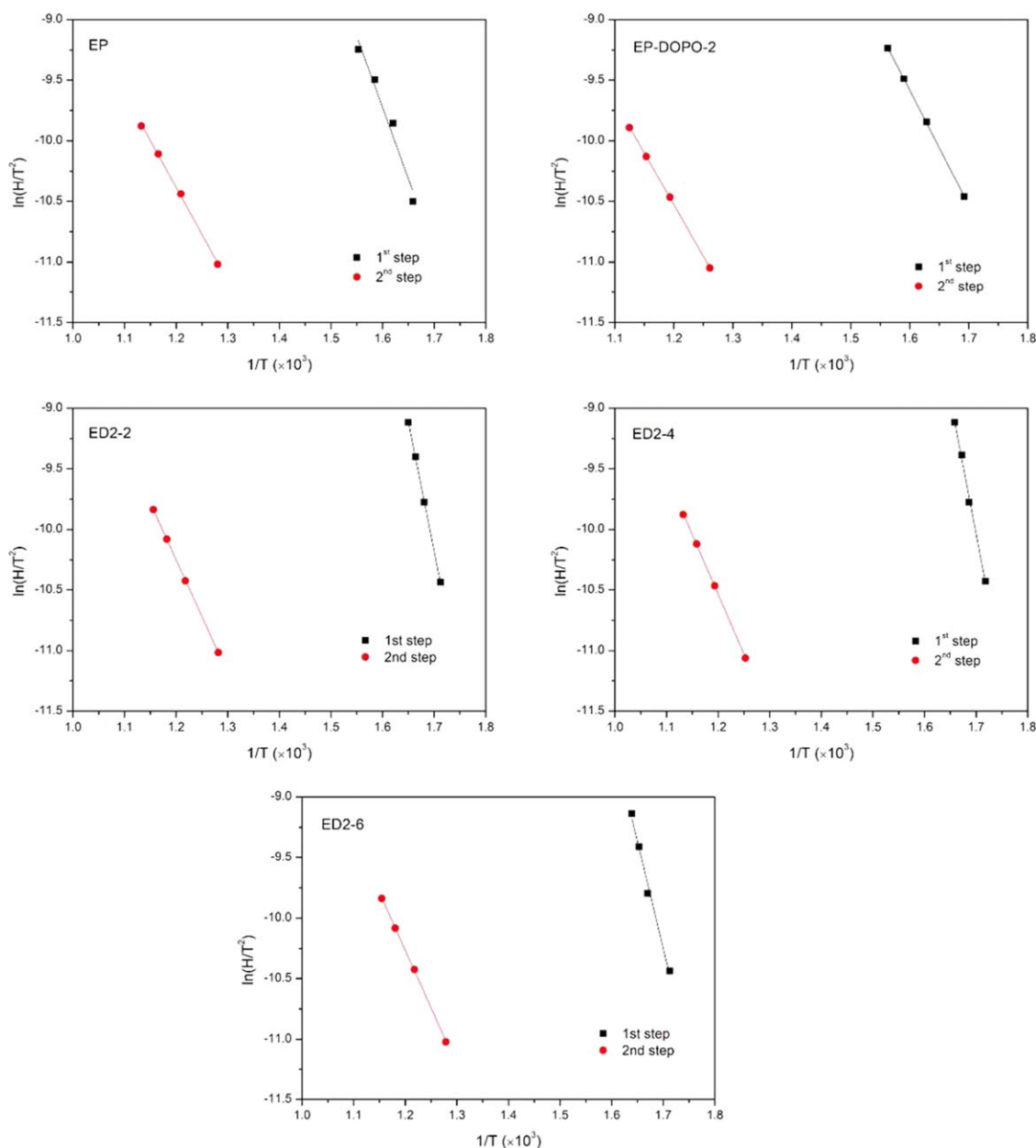
**Table IV.** Characteristic Data from TG Analyses of Different Samples in an Air Atmosphere

Sample	Heating rate (°C/min)	$T_{di}$ (°C)	$T_{max}$ (K)		$Y_c$ at 800°C (wt %)
			$T_{max1}$	$T_{max2}$	
EP	10	280	603	781	0.0
	20	290	617	827	0.8
	30	314	631	858	0.1
	40	340	644	883	0.0
EP-DOPO-2	10	294	591	793	0.0
	20	314	614	838	2.0
	30	336	629	867	1.1
	40	341	640	889	0.6
ED2-2	10	291	584	780	2.9
	20	298	595	821	4.7
	30	301	601	846	5.8
	40	303	606	865	4.6
ED2-4	10	277	582	798	3.8
	20	284	593	838	6.7
	30	295	598	863	9.7
	40	304	603	883	9.9
ED2-6	10	279	584	782	5.0
	20	300	599	821	6.9
	30	302	605	847	8.2
	40	312	610	866	8.1

DOPO-modified EP produces more char than neat EP after cone calorimeter testing. Generally, the char on the surface of the sample acts as an insulating barrier to stop the propagation of heat and oxygen. In addition, the inert gas produced during the process of the earlier formation of the char, such as carbon dioxide, diluted the flammable gases to prevent the further combustion. When organo-clay is added to the DOPO/epoxy blend, the amount of the residual char gradually increases with an increase in the loading of organo-clay, and the residual char becomes thicker, the char on the surface of the composite turns more compact and continuous, especially when the organo-clay loading reaches 6 wt %. This demonstrates that the thermal stability of the organo-clay nanocomposite has increased remarkably than neat EP and DOPO modified epoxy systems.<sup>39</sup>

To further understand how clay works in the epoxy/DOPO system, the morphology of the outer char obtained from the sample after HRR test was characterized by SEM (Figure 9). It can be seen that there exists a large amounts of porous structures on the outer surface of the neat EP and DOPO modified EP, which means a rapid volatilization on the surface of the sample.<sup>40,41</sup> Compared to the sample which is not modified by organo-clay, the outer surface of the sample modified by organo-clay is covered by continuous and protective carbon-silica layer. When organo-clay is added into the EP modified by DOPO system, it is interesting to note that the outer surface is rough and poriferous. By using EDS, mass of phosphorus and silicon elements is obtained (Table III), which accounts the fact that the unique layered





**Figure 11.** Plots of  $\ln(H_r/T^2)$  against  $1/T$  for different decomposition steps of different samples. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

structure of organoclay adsorb the volatile products<sup>42,43</sup> and make them to aggregate on the surface of the galleries while burning. Thus makes the products not only reducing the HRR, more importantly, the production of smoke is restrained greatly.

#### Kinetic Analysis

To confirm the effect of DOPO and organoclay on the flame retardancy, the thermal-oxidation stability of DOPO/organoclay modified EP were evaluated. Figure 10 shows TG and DTG curves of different samples at different heating rates, and the corresponding data were summarized in Table IV. It reveals that two distinct steps of thermal-oxidation decomposition can be observed from the appearance of two peaks in their DTG curves. According to the nonisothermal kinetic theory and

Arrhenius equation, the decomposition kinetics of a material can be calculated by eq. (3).

$$\ln\left(\frac{H_r}{T^2}\right) = \left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right) - \ln\left[\frac{AR_n(1-\alpha)^{n-1}}{E_a}\right] \quad (3)$$

where,  $H_r$  = heating rate at maximum degradation rate ( $^{\circ}\text{C}/\text{min}$ );  $T$  = temperature at maximum degradation rate (K);  $E_a$  = activation energy (J/mol);  $R$  = molar gas constant (8.314 J/mol·K);  $A$  = pre-exponential factor (1/s);  $n$  = reaction order; and  $\alpha$  = fraction of decomposition. The equation is obtained by taking the second derivative of the Arrhenius equation versus temperature and the natural log to get.<sup>36,44</sup> The activation energy ( $E_a$ ) can be obtained from the slope ( $E_a/R$ ) of  $\ln(H_r/T^2)$

**Table V.** Thermal-Oxidative Decomposition Kinetics Parameters of Different Samples

Sample	First step		Second step	
	$E_{a1}$ (kJ/mol)	$R_1$	$E_{a2}$ (kJ/mol)	$R_2$
Neat EP	97.83	0.95	64.40	0.99
EP-DOPO-2	78.74	0.99	70.74	0.98
ED2-2	177.39	0.99	77.90	0.99
ED2-4	184.89	0.99	81.93	0.99
ED2-6	147.01	0.98	79.18	0.99

versus  $1/T$  plot (Figure 11). In Figure 11, black squares and red dots represent the first and second thermal-oxidative decomposition. The calculated values of  $E_a$  are summarized in Table V.  $E_{a1}$  and  $E_{a2}$  represent the first and second step of degradation, respectively.

The thermal-oxidative decomposition of different samples can be divided into two distinct steps as in the DTG curves, which mainly correspond to the decomposition of the macromolecular chains and the oxidative degradation of char residue.<sup>45</sup> It is notable that the addition of DOPO and organoclay to EP changed the kinetic parameters of both degraded steps. In details, DOPO modified EPs show significantly decreased value of  $E_{a1}$ , which can be explained by the existence of weak P—C and P—O—C bonds in the backbone of DOPO modified EP. However, the value of  $E_{a2}$  for DOPO modified EPs are higher than those of pure epoxy. The phenomenon can be explained by the formation of a phosphorus-rich residue with strong resistance to thermo-oxidative decomposition, which can prevent further decomposition of the EP and result in the increasing of the  $E_{a2}$  value for modified EPs.

Nevertheless, more interestingly, when the organoclay are introduced into the DOPO modified EP, both  $E_{a1}$  and  $E_{a2}$  of as-prepared modified EP significantly higher than those of pure EP or DOPO modified EP. Apparently, these results can be attributed to the unique gas barrier effects of organoclay, and can well explain the reason behind the synergic effect of organoclay and DOPO on the flame retardancy of EP. Briefly, in the case of DOPO modified EP, when the EPs are heated to a certain temperature, the weak P—C and P—O—C bonds initially degrade to phosphoric acid, and before reacting with the decomposition products of EP, some phosphoric acids will be lost, while for EP modified by DOPO and organoclay, the existence of organoclay can inhibit the loss of phosphoric acids and isolates the resin from oxygen and heat through a “tortuous path” model as shown in Figure 6, and thereby increase the content of phosphorus in residual char, ultimately leading to a higher values of  $E_{a1}$  and  $E_{a2}$ . The increased content of phosphorus element can be confirmed by Table III.

It is known that phosphorous compound shows prominent effect on improving the flame retardancy of polymer. However, because its flame retarding effect can be exerted only through the reaction between its decomposed products and the decomposed products of polymer. High loading of phosphorus is usually necessary to remedy the loss of phosphoric acids. However,

such high levels of phosphorous compounds will lead to significant deterioration of strength, toughness, and processing characteristics. Herein, with the addition of organoclay to DOPO modified EP, it is so exciting that the effective content of phosphorus element significantly increases due to the gas barrier effects of organoclay, and thus the developed new flame retardant EP using the mixture of organoclay and DOPO as an additive can achieve the required flame retardancy (including lower SPR and HRR, etc.) in real time applications without significantly compromising its original properties.

## CONCLUSIONS

EPs modified by the mixture of DOPO and organoclay nanocomposites reinforced with different weight percentage of organoclay were prepared and the composite exhibit excellent flame retardancy. Specially, the pHRR and SPR of modified EP resin with 2.0 wt % phosphorus and 4.0 wt % organoclay are only 40 and 46% of that of neat EP resin respectively, while the use of 2.0 wt % phosphorus alone decreased the HRR to 59% and increased the SPR to 112% of neat EP resin. The modified EP by the mixture of DOPO and organoclay can be attributed to synergic action of the condensed phase mechanism and gas barrier effects, and they can effectively inhibit the loss of decomposed products from DOPO.

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