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Flame retardance and thermal degradation of new epoxy containing silicon and phosphorous hybrid ceramers prepared by the sol-gel method

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Abstract

An epoxy containing silicon and phosphorous hybrid (modified epoxy hybrid) was prepared and compared with pure epoxy. Four methods have been used to study the degradation of the hybrid during thermal analysis. These investigated methods are Van Krevelen, Horowitz–Metzger, Coats–Redfern, and MacCallum–Tanner. The activation energies (E_a) were obtained from these methods and compared. It is found that the value of E_a for modified epoxy hybrid is smaller than that of pure epoxy. The low activation energy is probably due to the presence of phosphorous–carbon (P–C) bonds which are susceptible to chain scission during thermal degradation and which act as a weak link. The thermal stability of modified epoxy hybrid ceramer is not superior to that of the pure epoxy, however the char yield of modified epoxy hybrid is higher than that of the pure epoxy at 800 °C. The limiting oxygen indices (LOI) of pure epoxy and modified epoxy hybrid are 24 and 32, respectively. This indicates that modified epoxy hybrid possesses better flame retardance. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Epoxy; Hybrid ceramers; Degradation; Flame retardance; Activation energy; Silicon; Phosphorous

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1. Introduction

Organic/inorganic hybrid ceramers fabricated through sol-gel methods have become a new type of composite, which has attracted much interest in the past decade. This material combines the advantages of both organic and inorganic materials and is expected to possess new properties that individual organic and inorganic materials could be not achieved [1]. From the interactions between organic and inorganic phases, hybrid ceramers can be divided into two major classes. In the first class, the inorganic precursors directly bond to the organic polymers and form covalent bonds between them. The most common system of this type is the polydimethylsilane/tetraethoxysilane (PDMS/TEOS) system [2,3]. In the second class, only physical interactions, such as hydrogen bonding or interpenetrating networks (IPN) may be formed between organic and inorganic phases. Polyimide is a typical organic polymer that is found in this class [4,5].

Epoxy resins are used worldwide on a large scale for adhesive, lamination, coating, casting applications, and so forth. To meet some application requirements, several approaches have been used to enhance the thermal properties of epoxy resins [6–8]. Apart from that, a further requirement that has recently gained in importance is the requirement for flame resistance. Therefore, imparting flame retardancy into epoxy resins has received a lot of attention [9–12]. In order to improve the flame retardancy of pure epoxy, diethylphosphatoethyltriethoxysilane was used in this study.

The main objective of this work was to study the kinetics of thermal degradation of epoxy containing silicon and phosphorous hybrid and of pure epoxy by means of thermogravimetric analysis. Four analytical methods, Van Krevelen [13], Horowitz–Metzger [14], Coats–Redfern [15], and MacCallum–Tanner [16] methods were used to obtain the kinetic parameters of thermal degradation for comparison

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2. Experimental

2.1. Materials

The epoxy resin used was the diglycidyl ether of bisphenol A(DEGBA,NPEL-128) which was generously provided by Nan Ya Plastics Corporation, Taiwan. 3-Isocyanatopropyltriethoxysilane was purchased from United Chemical Technologies, Inc., USA. Diethylphosphatoethyltriethoxysilane was obtained from Gelest, Inc., USA. Tetraethoxysilane was purchased from Acros Organics Co., USA.

2.2. Preparation of hybrid ceramers

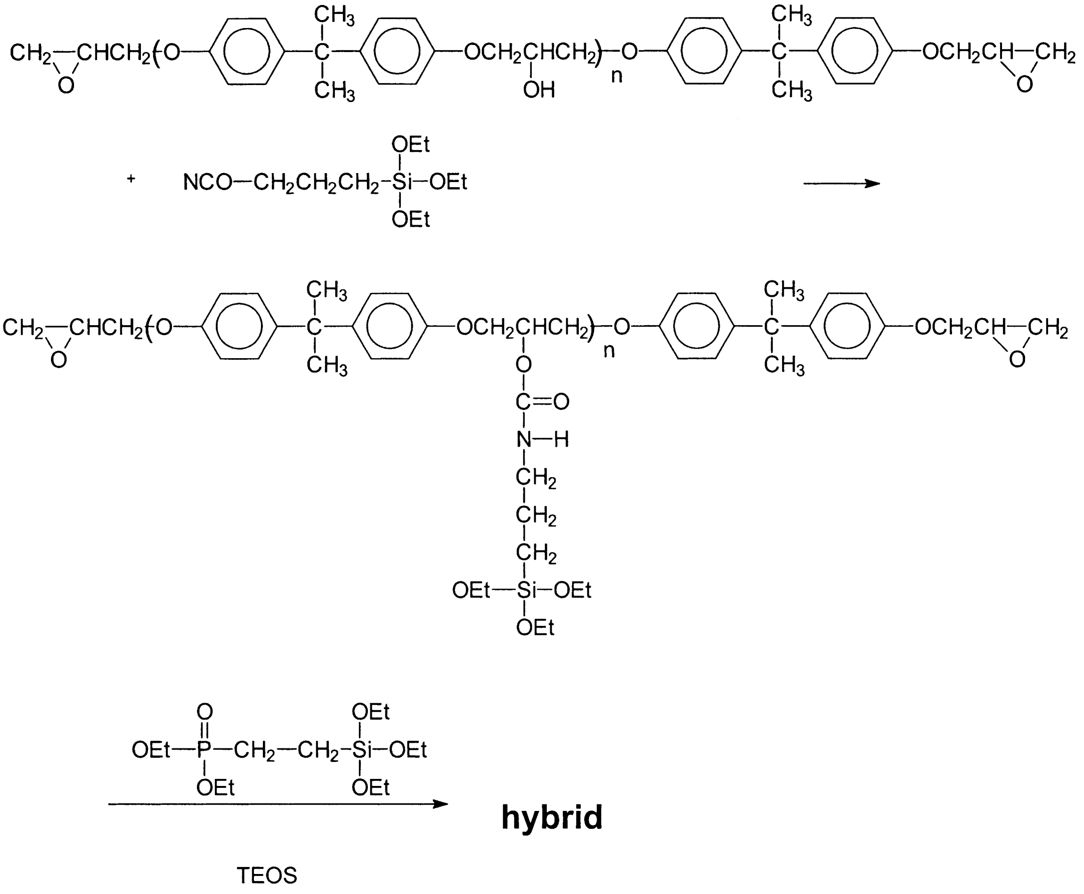
Preparation of the hybrid ceramers involved mixing of two solutions, A and B. Solution A consisted of modified epoxy and THF. The modified epoxy was synthesized as follows: 4 g 3-isocyanatopropyltriethoxysilane (equivalent weight 247 g) was added into 10g DGEBA type epoxy (equivalent weight 180 g) at 60 °C, then it was stirred for 4 h until the peak characteristic of the NCO group disappeared. Solution B was composed of H_2O/diethylphosphatoethyltriethoxysilane/HCl/TEOS with the molar ratio 9:1:0.63:1. HCl was used as the catalyst for hydrolysis. 3.4 g 4,4′-diaminodiphenylsulfone (equivalent weight 62 g) was poured into the mixture of solution A and B. 4,4′-diaminodiphenylsulfone was used as the curing agent of the modified epoxy. For 3-Isocyanatopropyltriethoxysilane/epoxy/4,4′-diaminodiphenylsulfone the equivalent ratio is 0.3:1:1. The mixture was stirred until the solution became clear. The solution was cast into aluminum dishes to gel at room temperature. The wet gel was aged at room temperature for 48 h, then dried at 80 °C for 24 h. The samples was put in a vacuum oven at 150 °C for 24 h.

2.3. Reaction scheme

Epoxy containing silicon and phosphorous hybrid was prepared as described in Scheme 1.

2.4. Thermogravimetric analysis (TGA)

Thermal degradation of the modified epoxy hybrid ceramer was measured by TGA (DU-Pont-951) from room temperature to 800 °C with a heating rate of 10 °C/min under nitrogen atmosphere. The measurements were conducted using 6–10 mg samples. Weight-loss/temperature curves were recorded.



Scheme. 1.

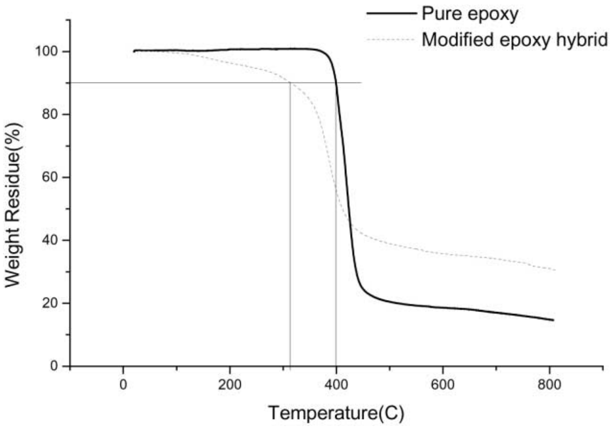


Fig. 1. Thermogravimetric analysis (TGA) curves of pure epoxy and modified epoxy hybrid.

2.5. Limiting oxygen index (LOI) test

The LOI is defined as the minimum fraction of O_2 in a mixture of O_2 and N_2 that will just support flaming combustion. The LOI test was performed according to the procedure of ASTM D 2836 Oxygen Index Method with test specimen bar of 7–15 cm in length, 6.5±0.5 mm in width, and 3.0±0.5 mm in thickness. The vertically suspended sample bars were ignited by a Bunsen burner. The flame was removed and the timer was started. The concentration of oxygen was raised if the specimen extinguished before burning 3 min or 5 cm. The oxygen content was adjusted until the limiting concentration was determined.

3. Results and discussion

3.1. Thermal stability and flame retardance

Fig. 1 shows TGA curves of pure epoxy and modified epoxy hybrid. Table 1 describes the thermal properties of pure epoxy and modified epoxy hybrid ceramer. The values of T_{d10} (the temperature of degradation at which weight loss is 10%) for pure epoxy and modified epoxy hybrid are 399 and 313 °C, respectively. The thermal stability of the modified epoxy hybrid is not better than that of the pure epoxy, however, the char yield of the modified epoxy hybrid is higher than that of the pure epoxy at 800 °C. The char yield of pure epoxy is 14.8 wt.% and that of modified epoxy hybrid is 31 wt.% at 800 °C. Flame resistance can be evaluated from the char residue on pyrolysis. A linear relationship between LOI and char residue for halogen-free polymers has been established by Van Krevelen [18]. Increasing char formation can limit the production of combustible carbon-containing gases, decreases the exothermicity due to pyrolysis reactions, as well as decreasing the thermal conductivity of the surface of burning materials [19]. A higher char yield will enhance the flame retardance. The LOI of pure epoxy and modified epoxy hybrid are 24 and 32, respectively. This indicates that the modified epoxy hybrid ceramer possesses better flame retardance.

Table 1
Thermal properties of pure epoxy and modified epoxy hybrid

	Temperature of weight loss at 10% (°C)	Char yield at 800 °C (%)	LOI[a]
Pure epoxy	399	14.8	24
Modified epoxy hybrid	313	31	32

[a] LOI, limiting oxygen index.

3.2. Kinetics of thermal degradation in nitrogen atmosphere

The degree of conversion, α, is defined as the ratio of actual weight loss to the total weight loss, i.e.$\alpha = \frac{m_0 - m}{m_0 - m_\infty}$, where m is an actual weight at time t (or at temperature T), m_0 the initial weight and m_∞ the weight at the end of isothermal or non-isothermal experiments.

Therefore, the rate of degradation $d\alpha/dt$, dependent on temperature and weight of sample, is given by Eq. (1)

$$d\alpha/dt = k(T) \times f(\alpha) \tag{1}$$

where $k(T)$ is the rate constant and $f(\alpha)$ is a function of conversion. If $k(T) = A \exp(-E_a/RT)$ and $f(\alpha) = (1-\alpha)^n$, then Eq. (1) can be expressed as:

$$d\alpha/dt = A\exp(-E_a/RT)(1-\alpha)^n \tag{2}$$

where A represents the preexponential factor; E_a, activation energy; R, gas constant; T, absolute temperature, and n, reaction order, respectively.

The integrated form of Eq. (2), introducing the initial condition of $\alpha = 0$ at $T = T_0$ is expressed as follows:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{q}\int_{T_0}^{T} \exp\left(\frac{-E_a}{RT}\right)dT \tag{3}$$

where q is the heating rate (dT/dt). For the special case, $n = 1$,

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = -\ln(1-\alpha) \tag{4}$$

For n does not equal to zero or unity, then

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = -\frac{1-(1-\alpha)^{1-n}}{1-n} \tag{5}$$

Several techniques have been developed for solving the integration of Eq. (3). The four methods used in this

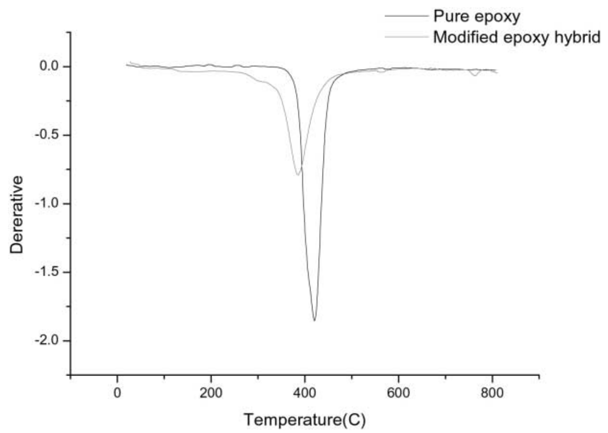


Fig. 2. Differential thermogravimetric curve of pure epoxy and modified epoxy hybrid.

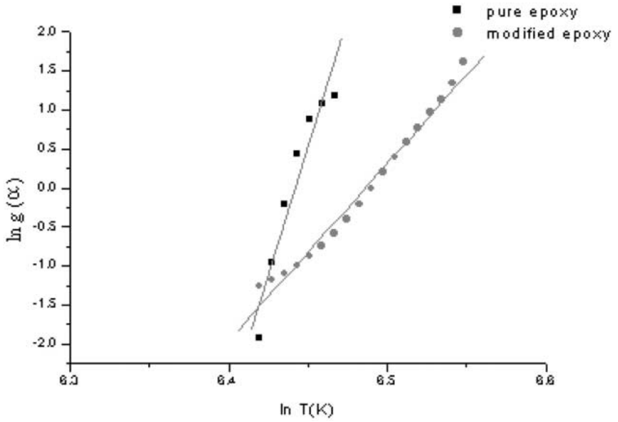


Fig. 3. The plot of ln $g(\alpha)$ versus ln T for pure epoxy and epoxy hybrid at 10 K/min.

study include the van Krevelen [13], Horowitz–Metzger [14], Coats–Redfern [15] and MacCallum–Tanner [16] methods. These methods are based on a single heating rate of 10 K/min.

Reactions of solid decomposition may take place by one of a number of elementary mechanisims, as well as the combinations of these mechanisms. However, it is difficult to find a meaning for the reaction order of a thermoset polymer in thermal degradation. The reaction order of thermal degradation is generally determined by Kissingers' equation [17]:

$$n = 1.26\sqrt{S} \tag{6}$$

where S is the shape index of the differential thermal analysis. The shape index is defined as the absolute value of the ratio of the slopes of tangents to the curve of differential thermal analysis at the inflection points [17]. From Fig. 2, the values of S in thermal degradation of pure epoxy and modified epoxy hybrid are 1 and 0.79, respectively. The values of n which are calculated from Eq. (6) of pure epoxy and modified epoxy hybrid are 1.26 and 1.12, respectively. The van Krevelen method for $n \neq 1$ introduced the following expression [13]:

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{1-n}\right] = \ln[A(0.368/T_{\mathrm{m}})^x/q(x+1)] + (x+1)\ln T \tag{7}$$

$$\text{for } n = 1 \ln[(1-\alpha)] = (x-1)\ln T \tag{8}$$

where $x = E_{\mathrm{a}}/RT_{\mathrm{m}}$, T_{m} is defined the temperature at which the peak differential thermal analysis deflection occurs.

A plot of ln $g(\alpha)$ versus ln T gives two straight lines for chosen n, as shown in Fig. 3. The activation energies of degradation calculated from the slopes are 270 and 119 kJ/mol for pure epoxy and epoxy hybrid, respectively.

In the case of the Horowitz–Metzger method, approximation is made regarding the exponential integral to derive the following equation [14], for $n \neq 1$:

$$\ln[-\ln(1-\alpha)] = \ln(A\mathrm{E}_{\mathrm{a}}/qR) - 5.33 - 1.052/T_{\mathrm{s}} + 1.052E_{\mathrm{a}}\theta/RT_{\mathrm{s}}^{2} \tag{9}$$

$$\text{for } n = 1, \ln(1-\alpha) = \frac{A}{q}\int_{T_0}^{T}\exp\left(\frac{-E_{\mathrm{a}}}{RT}\right)\mathrm{d}T = -\exp\left(-E_{\mathrm{a}}\theta/RT_{\mathrm{s}}^{2}\right) \tag{10}$$

Finally,

$$\ln[1/(1-\alpha)] = E_{\mathrm{a}}\theta/RT^2 \tag{11}$$

where

$$\theta = T - T_{\mathrm{s}}$$

and T_{s} is defined as a parameter and a characteristic temperature, respectively. T_{s} is the temperature at which $(1-\alpha) = 1/\mathrm{e}$.

Fig. 4 shows T_{s} are 427 and 396 °C for pure epoxy and modified epoxy hybrid ceramer, respectively. From this method, there is a linear relationship existed between ln $g(\alpha)$ and θ, as shown in Fig. 5. The activation energies of pure epoxy and modified epoxy hybrid are 295 and 91 kJ/mol.

The Coats and Redfern method provides an alternative calculation of E_{a}, and the rate of degradation is expressed as [15]:

$$\frac{A}{q}\int_{T_{\mathrm{o}}}^{T}\exp\left(\frac{-E_{\mathrm{a}}}{RT}\right)\mathrm{d}T = \frac{ART^2}{qE_{\mathrm{a}}} \times \left(1 - \frac{2RT}{E_{\mathrm{a}}}\right)\exp\left(\frac{-E_{\mathrm{a}}}{RT}\right) \tag{12}$$

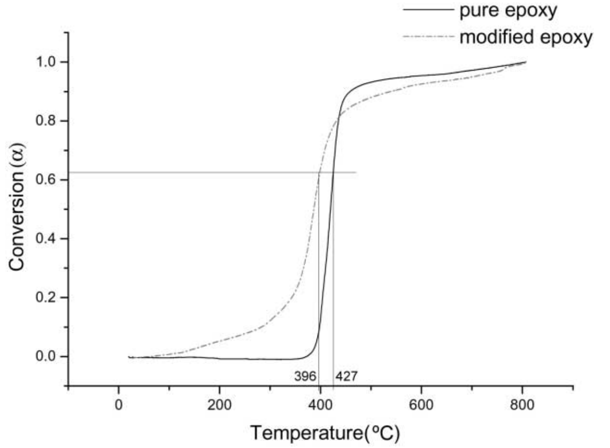


Fig. 4. Curves of conversion versus temperature for pure epoxy and epoxy hybrid.

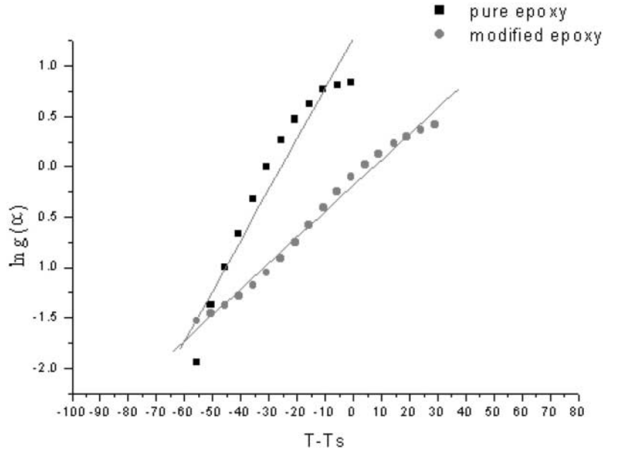


Fig. 5. The plot of ln $g(\alpha)$ versus θ for pure epoxy and epoxy hybrid at 10 K/min.

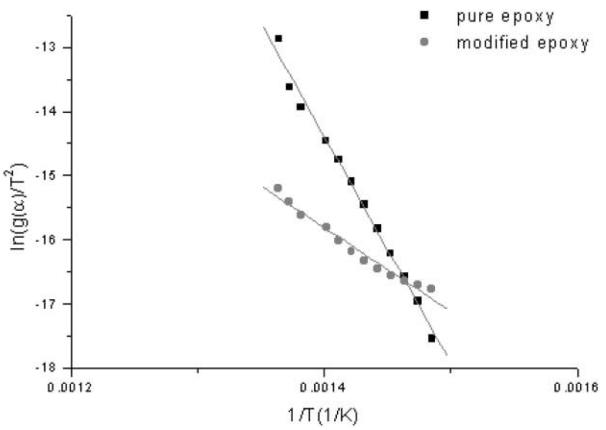


Fig. 6. The plot of ln $(g(\alpha)/T^2)$ versus $1/T$ for epoxy and epoxy hybrid at 10 K/min.

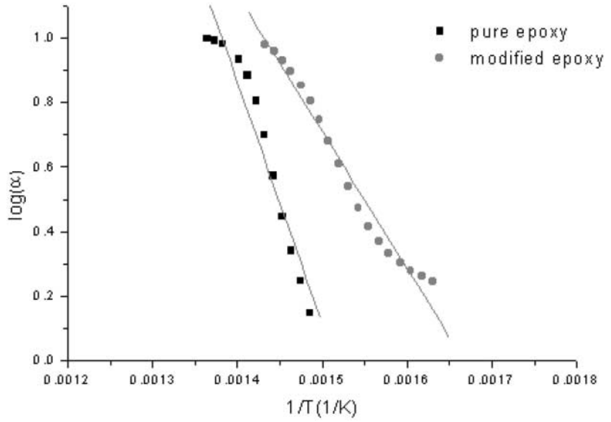


Fig. 7. The plot of log $g(\alpha)$ versus $1/T$ for pure epoxy and modified epoxy hybrid.

after taking logarithms the following equation can be obtained:

$$\text{for } n \neq 1 \ \ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln\frac{AR}{qE_a}\left(1-\frac{2RT}{E_a}\right)-\frac{E_a}{RT} \tag{13}$$

$$\text{for } n = 1 \ \ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\frac{AR}{qE_a}\left(1-\frac{2RT}{E_a}\right)-\frac{E_a}{RT} \tag{14}$$

according to this method, the plot of ln $(g(\alpha))$ versus $1/T$ gives straight lines with slopes equal to $-E_a/R$ as shown in Fig. 6. The activation energies of pure epoxy and modified epoxy hybrid are 293 and 108 kJ/mol, respectively.

The MacCallum–Tanner method provides an approximated integrated form of the rate of degradation as a function of temperature. The rate of degradation can be expressed as [16]:

$$\log g(\alpha) = \log\frac{AE_a}{qR} - 0.4828{E_a}^{0.4351} - \left(\frac{0.449+0.217E_a}{T\times 10^{-3}}\right) \tag{15}$$

Fig. 7 is a plot of log $g(\alpha)$ against $1/T$. From this method, the activation energies of pure epoxy and modified epoxy hybrid are 270 and 145 kJ/mol, respectively. Table 2 summarizes the characteristic parameters of thermal degradation of pure epoxy and modified epoxy hybrid at a heating rate of 10 °C/min

Table 3 summarizes the activation energies of thermal degradation for pure epoxy and modified epoxy hybrid. It is found that the values of E_a for modified epoxy hybrid are approximately 116 kJ/mol, and this value is smaller than that of pure epoxy, 282 kJ/mol. Typical bond energies of P–C, C–C, C–O, C–H are 260, 347,

Table 2
The characteristic parameters of thermal degradation of pure epoxy and modified epoxy hybrid at a heating rate of 10 °C/min

	S	n	T_m (°C)	T_s (°C)
Pure epoxy	1	1.26	421	427
Modified epoxy hybrid	0.79	1.12	388	396

S, shape index; n, reaction order; T_m, temperature at which the peak differential thermal analysis deflection occurs; T_s, the temperature at which $(1-\alpha)$ is 1/e.

Table 3
Activation energies E_a (kJ/mol) of thermal degradation for pure epoxy and modified epoxy hybrid at heating rate of 10 °C/min

Compound	Van Krevelen	Horowitz–Metger	Coats–Redfern	MacCallum–Tanner	Average
Pure epoxy	271	295	293	270	282
Modified epoxy hybrid	119	91	108	145	116

284, 368 kJ/mol, respectively [20,21]. The low activation energy is probably due to the presence of the phosphorous–carbon bonding (P–C) which is susceptible to chain scission during thermal degradation and acts as a weak link [22,23].

4. Conclusions

The thermal stability of the modified epoxy hybrid ceramer is not better than that of the pure epoxy, however, the char yield of modified epoxy hybrid is higher than that of the pure epoxy at 800 °C. The values of the LOI of pure epoxy and modified epoxy hybrid are 24, 32, respectively. The LOI of modified epoxy hybrid is higher than that of pure epoxy. This indicates that modified epoxy hybrid possesses the better flame retardance.

It is also found that the value of E_a (116 kJ/mol) for modified epoxy hybrid is smaller than that of pure epoxy (282 kJ/mol). The low activation energy is probably due to the presence of phosphorous–carbon bonding bond (P–C) which is susceptible to chain scission during thermal degradation and acts as a weak link.

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