

Thermo-oxidative degradation of novel epoxy containing silicon and phosphorous nanocomposites

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Abstract

Modified epoxy nanocomposites containing silicon and phosphorous was prepared and compared with pure epoxy. The study of thermo-oxidative degradation of modified epoxy nanocomposites and pure epoxy has been utilized by thermal analysis. The thermal stability of modified epoxy nanocomposites is not superior to that of the pure epoxy at low temperature, however, the char yield of modified epoxy nanocomposites is higher than that of the pure epoxy at 800 °C in air atmosphere. The modified epoxy nanocomposites possess better thermal stability at high temperature range. The values of the limiting oxygen index of pure epoxy and modified epoxy nanocomposites are 24 and 32, respectively. This indicates that modified epoxy nanocomposites possesses better flame retardance.

By the Kissinger's method, the activation energies of thermo-oxidative degradation for epoxy nanocomposites are less than those of thermo-oxidative degradation for pure epoxy in first stage of thermo-oxidative degradation. However, the activation energies of thermo-oxidative degradation for epoxy nanocomposites are more than those of thermo-oxidative degradation for pure epoxy in second stage of thermo-oxidative degradation.

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1. Introduction

In recent years, preparation of hybrid organic–inorganic composites [1–5] has attracted much attention since such hybrids may show controllable properties such as optical, electrical and mechanical behaviors by combining the properties of both organic and inorganic compounds [6–9]. In the hybrids, the inorganic phase is formed within an organic polymer matrix by sol–gel process consisting in hydrolysis and condensation of alkoxy derivatives of metals such as Si, Ti, Al [10]. The most common precursor is tetraethoxysilane (TEOS)

which yields a glassy silica network that acts as a hard reinforcement in a soft polymer.

Procedures of hybrid synthesis involving either sequential type, i.e. inorganic phase formation within polymer matrix, or a simultaneous polymerization of organic and inorganic monomers. The hybrids with or without a covalent bond of the inorganic substrate to the polymer matrix may be formed. Organic monomers or polymers modified by alkoxy groups are used to provide bonding to the in-situ formed inorganic structure. Strong interaction between phases was found [11–14] to improve the mechanical properties of the hybrid.

Epoxy resins are used worldwide on a large scale for adhesive, lamination, coating, casting applications, and so forth. For meeting some application requirements, several approaches have been utilized to enhance the

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thermal properties of epoxy resins [15–17]. Apart from that; a further requirement that has recently gained in importance is the requirement for flame resistance. Therefore, imparting flame retardance into epoxy resins has received a lot of attention [18–21]. In order to improve the flame retardance of pure epoxy, diethylphosphatoethyltriethoxysilane was used in this study. The main objective of this work is to study the kinetics of thermo-oxidative degradation of modified epoxy and of pure epoxy by means of thermogravimetric analysis (TGA).

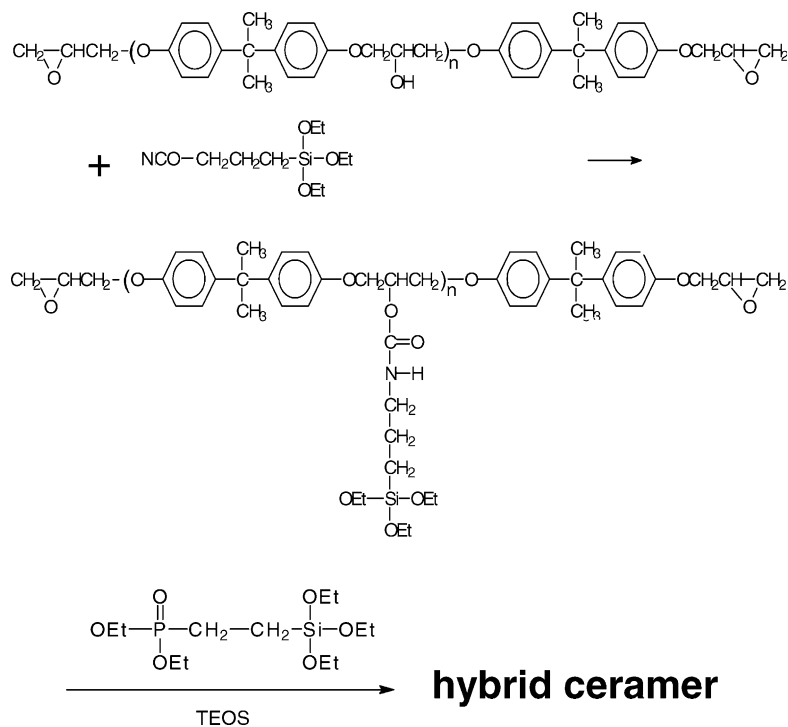
2. Experimental

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. TEOS was purchased from Acros Organics Co., USA.

2.2. Preparation of hybrid ceramers

Preparation of the nanocomposite 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 10 g DGEBA type epoxy (equivalent weight 180 g) at 60 °C, then it was stirred for 4 h until the characteristic peak of NCO group disappeared by FTIR spectra. Solution B was composed of H₂O/diethylphosphatoethyl-triethoxysilane/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. 3-Isocyanatopropyl-triethoxysilane/epoxy/4,4'-diaminodiphenylsulfone with 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. Epoxy containing silicon and phosphorous nanocomposites was prepared as described in Scheme 1.



Scheme 1.

2.3. Thermogravimetric analysis

TGA was performed with a Dupont 951 instrument coupled to a 1050 thermal analyzer. The measurements (10 ± 3 mg) were stacked in an open platinum sample pan and the experiment was conducted under air atmosphere with various heating rates (i.e., 5, 10, 20, 40 °C/min). Although machine-selected heating rates are reported and used in the calculations, the actual heating rates were determined from the appropriate plots.

Prior to multiple-heating-rate kinetics experiments, samples (10 ± 3 mg) were heated using a TGA weight curves of pure epoxy and modified epoxy nanocomposites. For the multiple-heating-rate kinetic experiments, the sample was placed into the TGA pan and heated until the sample reached thermal-oxide degradation in air atmosphere.

2.4. Limiting oxygen index test

The limiting oxygen index (LOI) is defined as the minimum fraction of O₂ in a mixture of O₂ and N₂ that will just support flaming combustion. The LOI test was performed according to the testing 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 sample bars suspended vertically 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 discussions

3.1. Thermal stability

Fig. 1 shows TGA curves of pure epoxy and modified epoxy nanocomposites. The thermo-oxidative degradation of pure epoxy and modified epoxy nanocomposites is two processes, which involves chemical reactions between degrading polymer and oxygen of air. Table 1 describes the thermal properties of pure epoxy and modified epoxy nanocomposites. The values of T_{d10} (the temperature of degradation at which weight loss is 10%) for pure epoxy and modified epoxy nanocomposites are

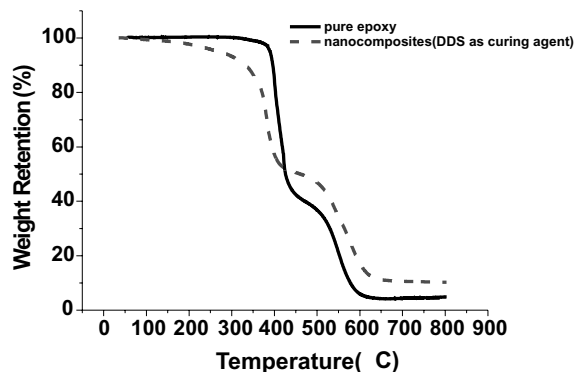


Fig. 1. TGA curves of pure epoxy and modified epoxy nanocomposites at 10 °C/min under air.

396 and 331 °C, respectively. The thermal stability of the modified epoxy nanocomposites is not superior to that of the pure epoxy at low temperature, however, the char yield of the modified epoxy nanocomposites is higher than that of the pure epoxy at 800 °C. This phenomenon reveals that the modified epoxy nanocomposites possess the better thermal stability during high temperature period. The char yield of pure epoxy is 4.8 wt.% and that of modified epoxy nanocomposites is 10 wt.% at 800 °C. This behavior characterizes all phosphorylated polymers, and may be due to the low degree of polymerization and the easy thermal degradation of the phosphorus segment [22]. Typical bond energies of P–C, C–C, C–O, C–H are 260, 349, 286, 370 kJ/mol, respectively [23,24]. The bonding of phosphorous–carbon (P–C) that is susceptible to chain scission during thermal degradation and acts as a weak link [25,26]. 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 [27]. 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 [28]. 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 nanocomposites possesses better flame retardance. One can apply the Perkin–Elmer standard program to obtain

Table 1
Thermal properties of pure epoxy and modified epoxy nanocomposite

	Temperature of weight loss at 10% (°C)	Char yield at 200 °C (%)	Char yield at 400 °C (%)	Char yield at 600 °C (%)	Char yield at 800 °C (%)	LOI
Pure epoxy	396	100	85	6	4.8	24
Epoxy nanocomposite	331	98	57	17	10	32

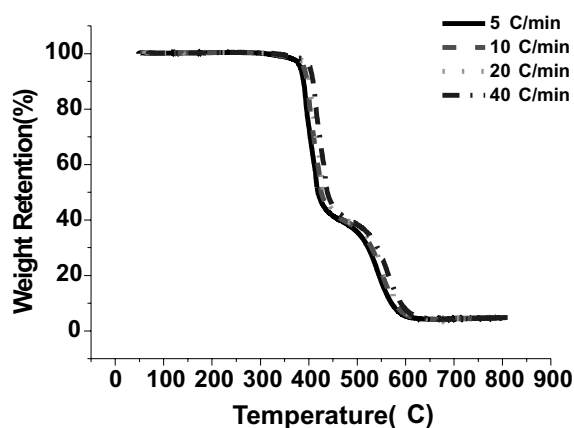


Fig. 2. TGA curves of pure epoxy hybrid at various heating rates.

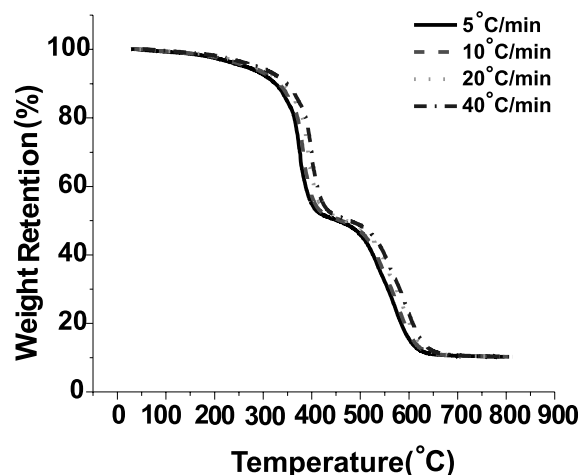


Fig. 3. TGA curves of modified epoxy nanocomposites at various heating rates.

Table 2

The activation energies (kJ/mol) of thermo-oxidative degradation for pure epoxy and modified epoxy nanocomposites by the Kissinger's method

	Pure epoxy	Epoxy nanocomposites
First stage	245	181
Second stage	338	395

the characteristics of the TGA curves as shown in Figs. 1–3. The kinetic parameters are listed in Table 2.

3.2. Kinetics of thermal degradation in air atmosphere

The degree of conversion, α , is defined as the ratio of actual weight loss to the total weight loss, i.e.,

$\alpha = (m_0 - m)/(m_0 - m_\infty)$, where m is an actual weight at time t (or at temperature T), m_0 is the initial weight and m_∞ is 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)

$$d\alpha/dt = k(T)f(\alpha) \quad (1)$$

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

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

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

$$\frac{d\alpha}{(1 - \alpha)^n} = \left[\frac{A \exp(-E_a/RT)}{\text{hr}} \right] dT \quad (3)$$

where hr = heating rate.

The Kissinger's method [29] involves the maximum temperatures (T_m) of the first derivative weight loss curves. Therefore, Eq. (3) was differentiated with respect to T and the resulting expression set to zero. With some rearrangements and β = heating rate, the expression

$$\frac{d[\ln(\beta/T_m^2)]}{d(1/T_m)} = \frac{-E}{R} \quad (4)$$

was derived. Therefore, the activation energy can be determined from a plot of $\ln(\beta/T_m^2)$ against $1/T_m$. Figs. 4 and 5 show Kissinger's plots of pure epoxy and modified epoxy nanocomposites degradation in air atmosphere. Each straight line corresponds to a degradation stage of pure epoxy and modified epoxy nanocomposites. Table 2 shows the activation energies of thermo-oxidative degradation for pure epoxy and modified epoxy nanocomposites by the Kissinger's method. The activation

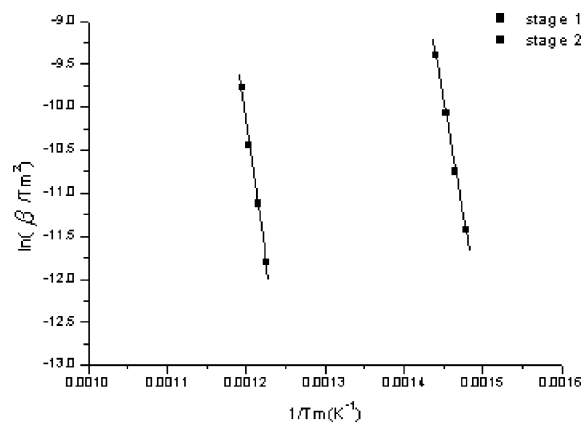


Fig. 4. The plot of $\ln(\beta/T_m^2)$ versus $1/T_m$ for pure epoxy.

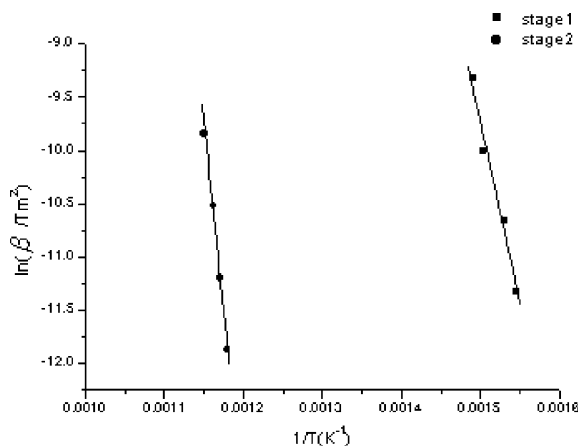


Fig. 5. The plot of $\ln(\beta/T_m^2)$ versus $1/T$ for modified epoxy nanocomposites.

energies of thermo-oxidative degradation calculated from the slopes are 245 and 338 kJ/mol in first stage and second stage of thermo-oxidative degradation for pure epoxy, respectively. The activation energies of thermo-oxidative degradation calculated from the slopes are 181 and 395 kJ/mol in first stage and second stage of thermo-oxidative degradation for modified epoxy nanocomposites, respectively. The activation energies of thermo-oxidative degradation for modified epoxy nanocomposites are less than those of thermo-oxidative degradation for pure epoxy in first stage of thermo-oxidative degradation. However, the activation energies of thermo-oxidative degradation for modified epoxy nanocomposites are more than those of thermo-oxidative degradation for pure epoxy in second stage of thermo-oxidative degradation. The phenomenon indicates an important role in improving the flame retardance of the resins. While the resin is burning, the phosphorus-containing groups first decompose, and then form a phosphorus-rich residue that prevents further decomposition of the epoxy resin and results in the increasing of the activation energies for epoxy nanocomposites.

4. Conclusions

The thermal stability of modified epoxy nanocomposites is not superior to that of the pure epoxy at low temperature, however, the char yield of modified epoxy nanocomposites is higher than that of the pure epoxy at 800 °C. The modified epoxy nanocomposites possess the better thermal stability during high temperature period. The values of the LOI of pure epoxy and modified epoxy nanocomposites are 24, 32, respectively. The LOI of modified epoxy nanocomposites is higher than that of

pure epoxy. This indicates that modified epoxy nanocomposites possesses the better flame retardance.

By the Kissinger's method, the activation energies of thermo-oxidative degradation for modified epoxy nanocomposites are less than those of thermo-oxidative degradation for pure epoxy in first stage of thermo-oxidative degradation. However, the activation energies of thermo-oxidative degradation for modified epoxy nanocomposites are more than those of thermo-oxidative degradation for pure epoxy in second stage of thermo-oxidative degradation.

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