Available online at www.sciencedirect.com
ScienceDirect

Thermochimica Acta 453 (2007) 97–104

thermochimica acta

www.elsevier.com/locate/tca

Review

Thermal stability and degradation kinetics of novel organic/inorganic epoxy hybrid containing nitrogen/silicon/phosphorus by sol–gel method

Chin-Lung Chiang*, Ri-Cheng Chang, Yie-Chan Chiu

Department of Industrial Safety and Health, Hung-Kuang University, Sha-Lu 433, Taiwan, ROC

Received 3 August 2006; received in revised form 17 November 2006; accepted 17 November 2006
Available online 24 November 2006

Abstract

Hybrids containing silicon, phosphorous and nitrogen were prepared by the sol–gel method and compared with pure epoxy. The silicon, phosphorous and nitrogen components were successfully incorporated into the networks of polymer. Thermogravimetric analysis (TGA) was used for rapid evaluation of the thermal stability of different materials. The integral procedure decomposition temperature (IPDT) has been correlated the volatile parts of polymeric materials and used for estimating the inherent thermal stability of polymeric materials. The IPDT of pure epoxy was 464 °C and the IPDTs of hybrids were higher than that of pure epoxy. The thermal stability of hybrids increased with the contents of inorganic components. The inorganic components can improve the thermal stability of pure epoxy.

Two methods have been used to study the degradation of hybrids containing silicon, phosphorous and nitrogen hybrid during thermal analysis. These investigated methods are Kissenger, Ozawa's methods. The activation energies (E_a) were obtained from these methods and compared. It is found that the values of E_a for modified epoxy hybrids are higher than that of pure epoxy. The hybrids of high activation energy possess high thermal stability.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Epoxy; Sol–gel; Degradation; Thermal stability; Activation energy; Silicon; Phosphorous; Nitrogen

Contents

1. Introduction 97
2. Experimental 98
    2.1. Materials 98
    2.2. Preparation of IPTS-epoxy/SM-IATE 15/DPPETES hybrid materials 98
    2.3. Reaction schemes 99
    2.4. Thermogravimetric analysis (TGA) 99
3. Results and discussion 100
    3.1. Thermal stability 100
    3.2. Kinetics of thermal degradation in nitrogen atmosphere 102
4. Conclusions 103
Acknowledgements 104
References 104

1. Introduction

Inorganic/organic hybrid materials are of increasing interest as constituents of coating materials for a wide variety of applications since they offer the prospect of combining the mechanical toughness and flexibility of organic component with the hardness and thermal stability of the inorganic component. Improvement of thermal stability of polymer materials is a lasting challenge. Formation of stable char is one of the desirable mechanisms of flame retardation in polymers, since the char layer acts both as a thermal insulator and as a barrier to oxygen

---

* Corresponding author.
E-mail address: dragon@sunrise.hk.edu.tw (C.-L. Chiang).

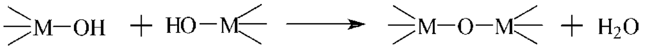
0040-6031/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2006.11.013

diffusion. A good way to augment char formation is by addition of inorganic fillers, since the presence of inherently stable inorganic phase makes char more mechanically stronger, consequently improving its insulating and barrier properties [1]. The organic/inorganic hybrid materials could also be called nanocomposites, as the inorganic phase is dispersed in the polymer matrix at a molecular (nanometric) level. But unlike the nanocomposites prepared by mixing pre-existing nano-sized filler into the matrix, in hybrids the inorganic phase is formed in situ by hydrolysis and condensation of metal alkoxides. The technique is called the sol–gel reaction. The sol–gel process [2–10] has provided promising opportunities for the preparation of a variety of organic/inorganic hybrid materials at the molecular level. The in situ development of a three-dimensional cross-linked inorganic network structure using an organic precursor such as an alkoxide, $M(OR)_4$, can be carried out within the polymer matrix. The hydrolysis and condensation reactions involved in the process may proceed as follows [11]:

Hydrolysis:

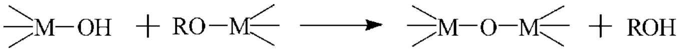
$$M(OR)_4 + H_2O \rightarrow (RO)_3M\text{–}OH + ROH \quad (1)$$

Condensation:



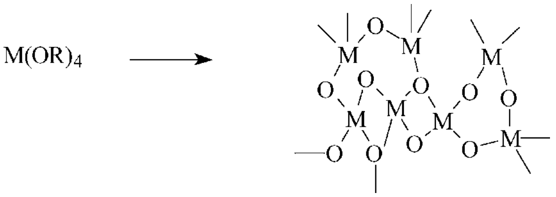
(2)

and/or



(3)

Net reaction:



(4)

M = Si or Ti, etc.

In this work, thermal properties and degradation kinetics of novel organic/inorganic epoxy hybrid containing nitrogen/silicon/phosphorus were studied by means of thermogravimetric analysis (TGA). Two analytical methods, Kissinger's [12], Ozawa's [13] methods were used to obtain the kinetic parameters of thermal degradation for comparison.

2. Experimental

2.1. Materials

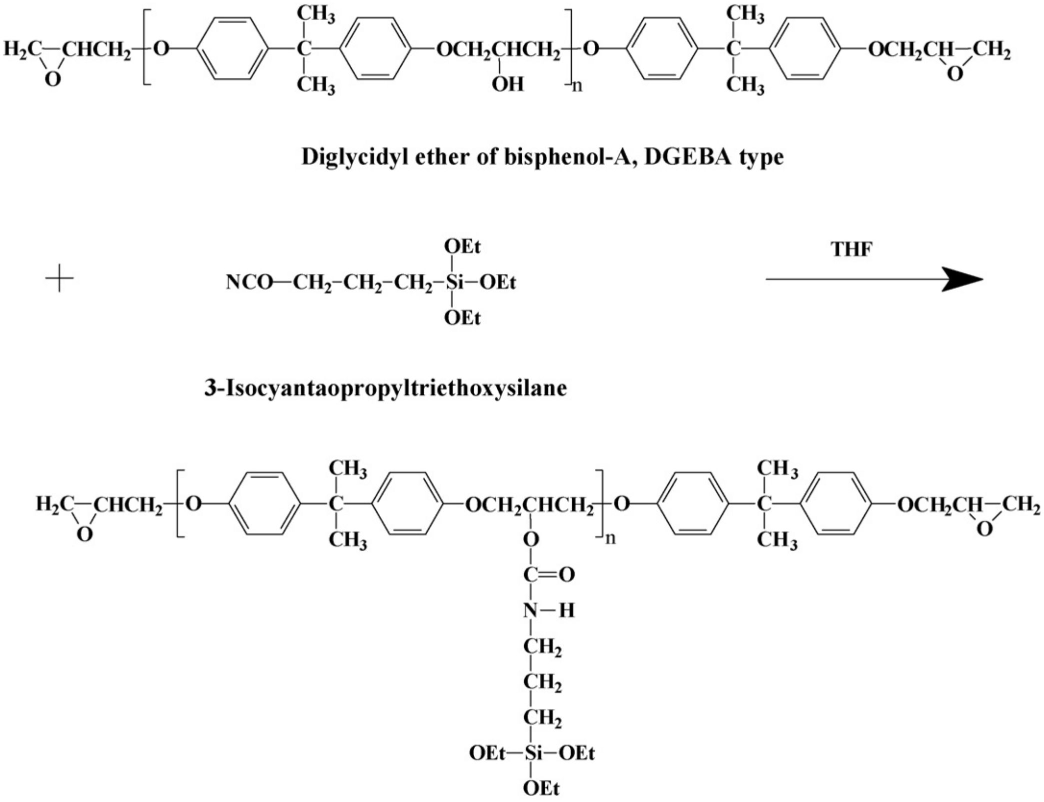
The epoxy resin used was the diglycidyl ether of bisphenol A (DEGBA, NPEL-128) which was generously provided by Nan Ya Plastics Corporation, Taiwan. 3-Isocyanatopropyltriethoxysilane (IPTS) was purchased from United Chemical Technologies, Inc., USA. 2-(Diphenylphosphino)ethyltriethoxysilane (DPPETES) was obtained from United Chemical Technologies, Inc., Bristol, PA, USA. Isocyanuric acid triglycidyl ester (IATE) was obtained from TCI, Tokyo Chemical Industry Co., Ltd, Tokyo, Japan. 3-Aminopropyltriethoxysilane (APTS) was supplied from ACROS Organics Co., Janssens Pharmaceuticalaan, 3A2440 Geel. Poly(oxypropylene)diamine (Jeffamine D400) was from the Huntsman Corporation, Salt Lake City, Utah 84108, USA. *N*,*N*-Dimethyl acetamide (DMAc) was from TEDIA Co. Farfield, Ohio, USA. Tetrahydrofuran (THF) was reagent grade and supplied by Echo Chemical Co. Ltd., Taiwan. Concentrated hydrochloric acid used was obtained from the Union Chemical Works Ltd, Taiwan. Isopropyl alcohol (IP) was purchased from the Tedia Company, Inc, Farfield, Ohio, and USA.

2.2. Preparation of IPTS-epoxy/SM-IATE 15/DPPETES hybrid materials

The hybrid ceramers were prepared by mixing two solutions, A and B and then added 5 wt.%, 10 wt.%, 15 wt.% DPPETES into the mixture. Solution A consisted of modified epoxy resin and THF. The modified epoxy resin was synthesized as follows: 4 g IPTS (equivalent weight 247 g) was added to 10 g DGEBA type epoxy resin (equivalent weight 180 g) at 60 °C, and was then stirred for 4 h until the characteristic peak of the NCO group disappeared. IPTS reacted with epoxy to form IPTS-epoxy. Solution B, was composed of IATE/APTS, in a molar ratio 3:1. IATE was dissolved into DMAc and its solid content was 20 wt.%. APTS was then slowly poured into IATE solution and mixed at 50 °C for 12 h. APTS was incorporated into IATE to form silane modified IATE (SM-IATE). HCl was used as the catalyst for hydrolysis. D400 was used as the curing agent of the modified epoxy resin. The IPTS-epoxy/SM-IATE hybrid materials were prepared with various SM-IATE feed ratios (Table 1). The mixtures were stirred until the solution became clear. The solutions were cast into aluminum dishes to gel at room temperature. The wet gels were aged at room temperature for 48 h, and was then dried at 80 °C for 2 h in a vacuum oven. The samples

Table 1
Compositions of epoxy/SM-IATE hybrid systems with different DPPETES contents

Sample no.	IPTS-epoxy (wt.%)	SM-IATE (wt.%)	DPPETES (wt.%)	Si content (wt.%)	N content (wt.%)	P content (wt.%)	Si + N + P Content (wt.%)
Epoxy/SM-IATE 15	85	15	0	3.82	4.14	0.00	7.96
Epoxy/SM-IATE 15/DPPETES 5	80	15	5	4.05	3.98	0.41	8.44
Epoxy/SM-IATE 15/DPPETES 10	75	15	10	4.27	3.81	0.82	8.90
Epoxy/SM-IATE 15/DPPETES 15	70	15	15	4.49	3.64	1.23	9.36



Scheme 1. Reaction process and structure of IPTS-epoxy.

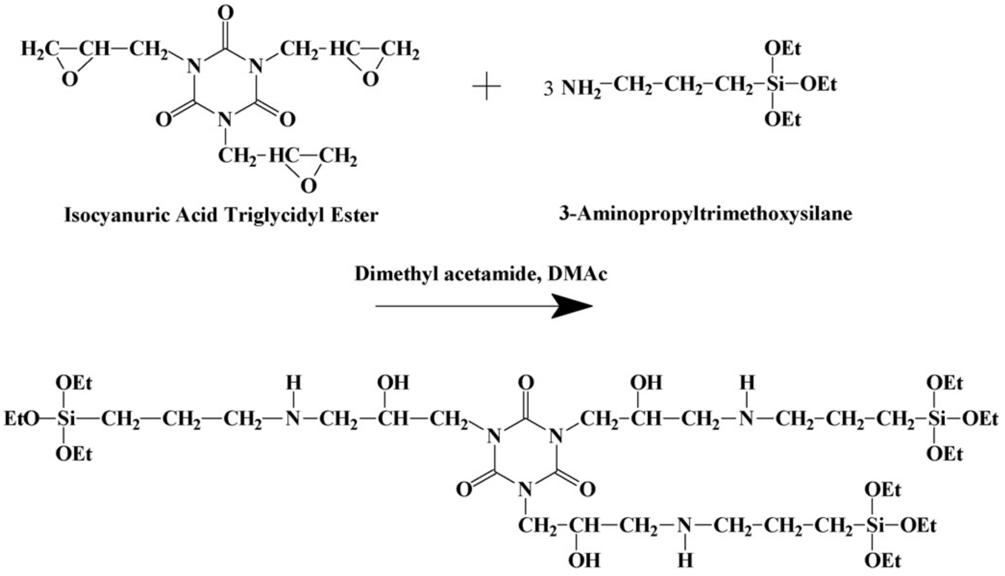
were placed in a vacuum oven at 150 °C for 4 h, then was cured at 160 °C for 24 h. Table 1 shows compositions of epoxy/SM-IATE hybrid systems with different DPPETES contents.

2.3. Reaction schemes

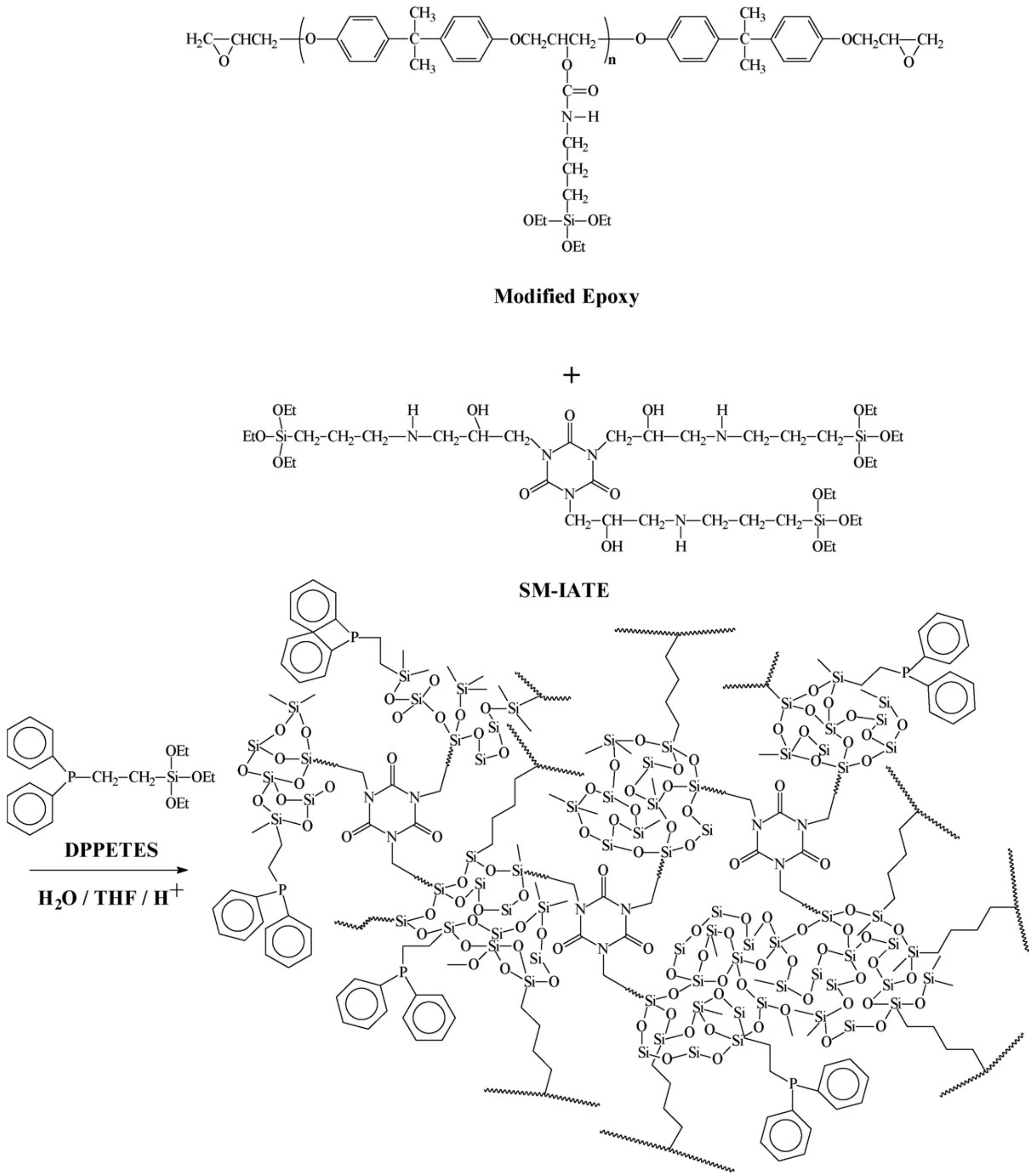
See Schemes 1–3.

2.4. Thermogravimetric analysis (TGA)

Thermal degradation of hybrid was investigated by a thermogravimetric analyzer (Perkin Elmer TGA 7) from room temperature to 800 °C with various heating rates (i.e., 5, 10, 20, 40 °C/min) under nitrogen atmosphere. The measurements were conducted using 6–10 mg samples. Weight-loss/temperature curves were recorded.



Scheme 2. Reaction process and structure of SM-IATE.



Scheme 3. Reaction process and structure of epoxy/SM-IATE/DPPETS hybrids.

3. Results and discussion

3.1. Thermal stability

Thermogravimetric analysis is one of the commonly used techniques for rapid evaluation of the thermal stability of different materials, and also indicates the decomposition of polymers at various temperatures. Fig. 1 shows the TGA thermograms of epoxy resin with various contents, from room temperature to 800 °C, in nitrogen atmosphere. Fig. 2 presents DTG curves with various contents at 10 °C/min. The slope of the curve indicates the rate of the weight loss of material. The rate of weight loss decreases with decreasing value of the slope for the curve. The value of derivative for pure epoxy is higher than those of hybrids in Fig. 2. It presents the inorganic components can restrain polymer from thermal degradation. From Figs. 1 and 2, the addition of nitrogen/silicon/phosphorus can slow down the rate of degradation of epoxy. Table 1 shows weight loss characteristics of the epoxy resin with various contents of SM-IATE/DPPTTES. Fig. 3 shows the weight loss temperature versus weight loss for epoxy resin with various SM-IATE/DPPETS contents. The thermal stability of hybrids was lower than pure epoxy when the thermal degradation just occurred. Owing to the less strength of phosphorus bonds, phosphorus-containing groups in poly-

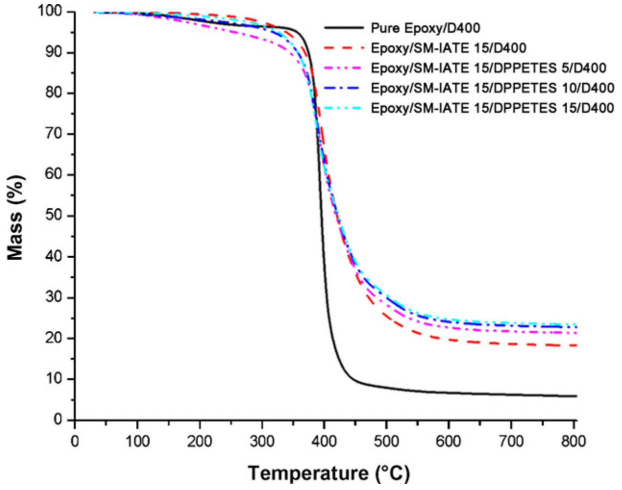


Fig. 1. TGA thermograms of epoxy resin with various contents.

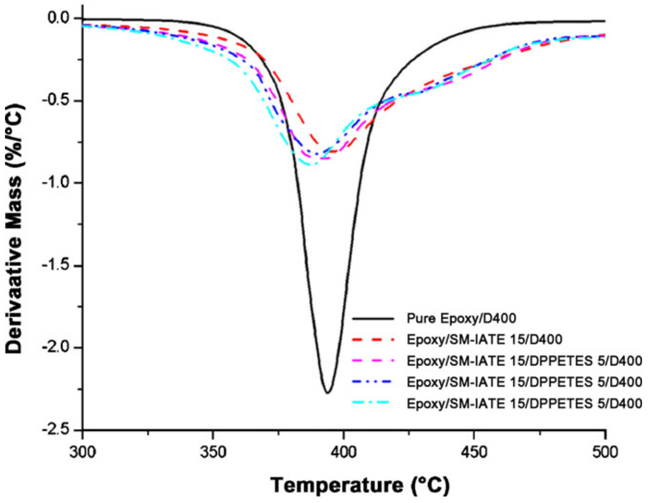


Fig. 2. DTG curves with various contents at 10 °C/min.

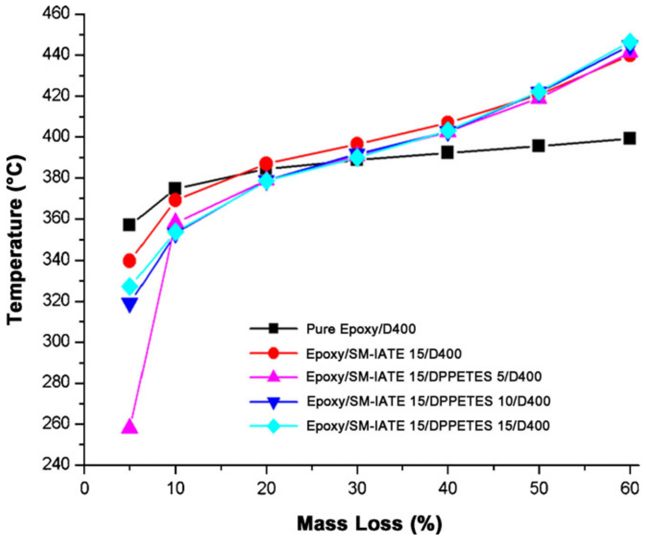


Fig. 3. The weight loss temperature vs. weight loss for epoxy resin with various SM-IATE/DPPETS contents.

mers decomposed at relatively low temperature region than the ordinary polymer chains [14]. They form a surface layer of protective char during fire before the unburned structure materials begin to decompose [15–18]. The char yields of hybrids are higher than pure epoxy during high temperature. The char yield of the hybrid containing SM-IATE 15% was higher than pure epoxy at 800 °C. High temperature thermal stability can be increased with the addition of silicon-containing compounds because their products are silicon dioxide, which cannot be degraded further. The char yields of hybrids containing DPPETS increased with the increasing of the contents of DPPETS contents at 800 °C. The phenomena revealed the thermal stability of hybrids increased with the contents of inorganic components. Apparently, enhancement of thermal stability of hybrids has been achieved by incorporation of silicon, phosphorus and nitrogen into epoxy resins with bringing a Si/P/N synergistic effect [19].

The integral procedure decomposition temperature (IPDT) proposed by Doyle [20] has been correlated the volatile parts of polymeric materials and used for estimating the inherent thermal stability of polymeric materials [21,22]. IPDT was calculated from

$$\mathrm{IPDT}\ (^{\circ}\mathrm{C}) = A^{*}K^{*}(T_{\mathrm{f}} - T_{\mathrm{i}}) + T_{\mathrm{i}} \tag{1}$$

$$A^{*} = \frac{S_1 + S_2}{S_1 + S_2 + S_3} \tag{2}$$

$$K^{*} = \frac{S_1 + S_2}{S_1} \tag{3}$$

where A^{*} is the area ratio of total experimental curve defined by the total TGA thermogram, T_{i} the initial experimental temperature, T_{f} the final the initial experimental temperature. Fig. 4 shows a representation of S_1, S_2 and S_3 for calculating A^{*} and K^{*}. From Table 2, the IPDT of pure epoxy was 464 °C and the IPDT of hybrids were higher than that of pure epoxy. The thermal stability of hybrids increased with the contents of inorganic components. The inorganic components can improve the ther-

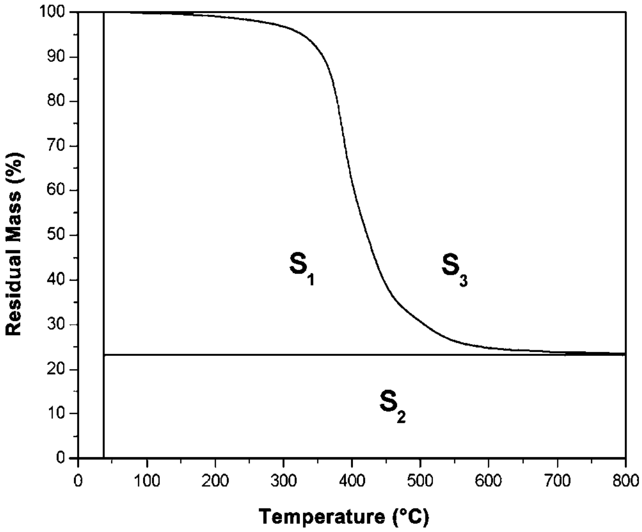


Fig. 4. Schematic representation of S_1, S_2 and S_3 for A^{*} and K^{*}.

Table 2
Weight loss characteristics of the epoxy resin with various contents of SM-IATE/DPPTTES

Sample no.	Td10 (°C)	C.Y. at 800 °C	IPDT (°C)
Pure epoxy	375	6	464
Epoxy/SM-IATE 15	369	18	689
Epoxy/SM-IATE 15/DPPETES 5	358	21	737
Epoxy/SM-IATE 15/DPPETES 10	353	23	793
Epoxy/SM-IATE 15/DPPETES 15	354	24	795

mal stability of pure epoxy. Fig. 5 shows that the value of IPDT was found to increase linearly with Si + N + P content in hybrid materials, which confirms improved thermal stability of hybrid materials.

3.2. Kinetics of thermal degradation in nitrogen atmosphere

The degree of conversion, α, is defined as the ratio of the actual weight loss to the total weight loss, $\alpha = m_0 - m/m_0 - m_\infty$, where m is the actual weight at time t (or at temperature T); m_0 the initial weight, and m_∞ is the weight at the end of isothermal or non-isothermal experiments. Consequently, the rate of degradation dα/dt, depends on the temperature and the weight of sample, as given by Eq. (1)

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)\ f(\alpha) \tag{1}$$

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 follows

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\ \exp\left(\frac{-E_a}{RT}\right)(1-\alpha)^n \tag{2}$$

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

$$\frac{\mathrm{d}\alpha}{(1-\alpha)^n} = \left[\frac{A\ \exp(-E_a/RT)}{\beta}\right]\mathrm{d}T \tag{3}$$

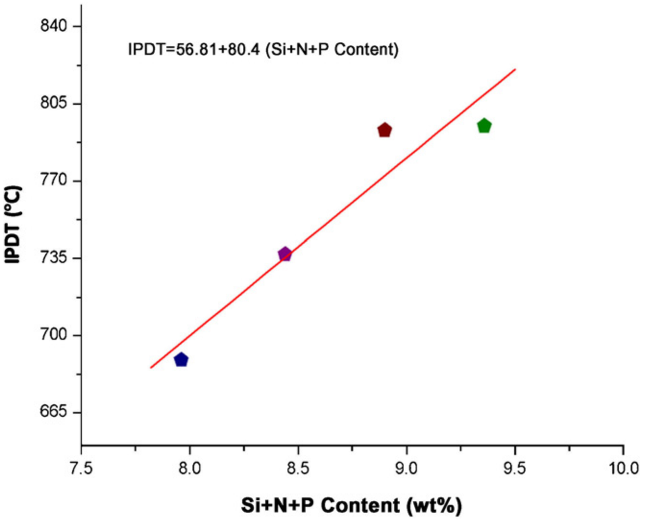


Fig. 5. The plot of IPDT vs. Si + N + P content.

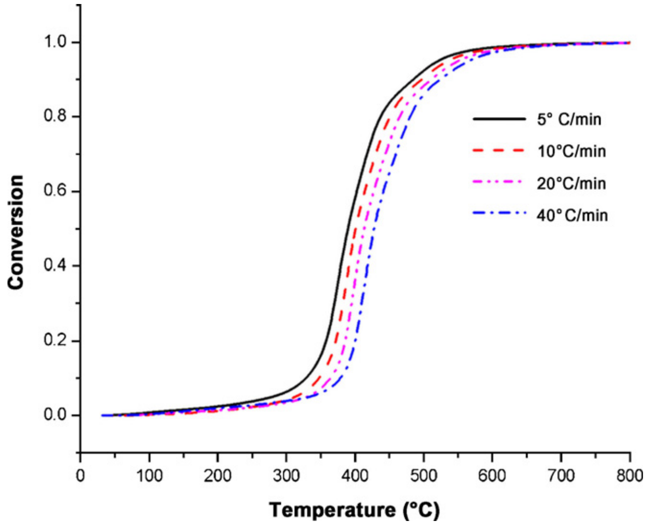


Fig. 6. Typical conversion curves for hybrid (epoxy/SM-IATE 15 wt.%/DPPETS 15%).

where β = heating rate Ozawa's method considers several TGA curves obtained at various heating rates (β). Fig. 6 shows the relationships between the conversions and temperature at various heating rates. Fig. 7 presents Ozawa plots of log β versus 1/T for each value of α, which displays excellent linearity. The degree of conversion α is defined as the ratio of actual weight loss to total weight loss. From the isoconversation curve, appar-

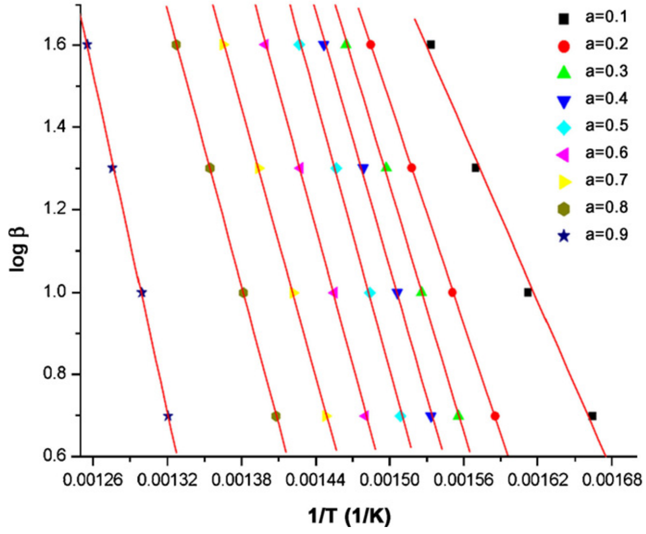


Fig. 7. Typical Ozawa plots for the thermal degradation for hybrid (epoxy/SM-IATE 15 wt.%/DPPETS 15%).

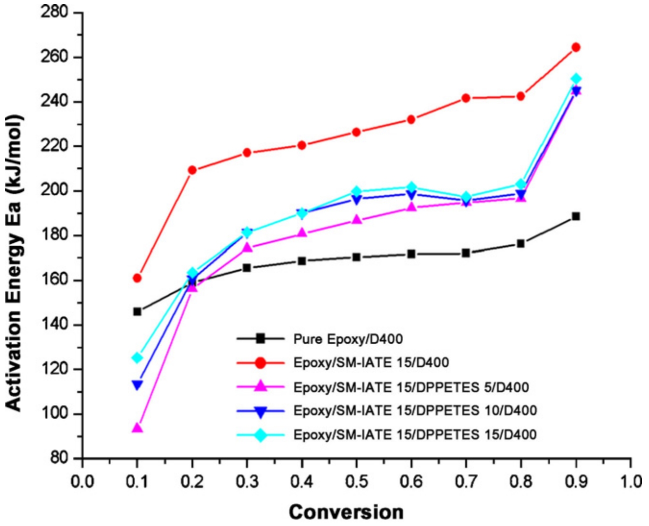


Fig. 8. The plot of the thermal degradation activation energy, ΔE (kJ/mol), with various conversions by Ozawa's method.

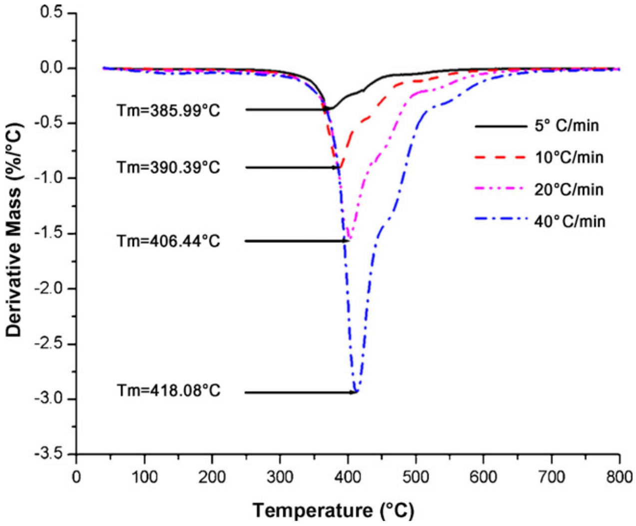


Fig. 9. Typical DTG curves for hybrid (epoxy/SM-IATE 15 wt.%/DPPETS 15%).

Table 3
The calculated activation energy of thermal degradation (ΔE, kJ/mol) by Kissinger's method

Sample no.	Kissinger's method	Ozawa's method
Pure epoxy	173	169
Epoxy/SM-IATE 15	241	224
Epoxy/SM-IATE 15/DPPETES 5	199	180
Epoxy/SM-IATE 15/DPPETES 10	201	187
Epoxy/SM-IATE 15/DPPETES 15	213	190

ent activation energies are calculated from the slopes of the lines using the expression,

$$E_{\mathrm{a}} = -\mathrm{slope} \times \frac{R}{0.457} \tag{4}$$

Fig. 8 illustrates the relationship between the activation energies of the hybrid and the degree of conversion, due to continuous change of degradation mechanisms. The activation energy of thermal degradation generally increases with the extent conversion for different contents of SM-IATE/DPPETS. Increasing dependencies of the activation energy on conversion are quite typical for degradation of polymers, including epoxy materials [23]. The thermal stability of hybrid increases with the degree of conversion. The formed char protects the polymer from further degradation. The activation energy of hybrid containing 15 wt.% IATE was higher than those of other hybrids containing phosphorus. The average activation energies of hybrids were higher than that of pure epoxy. The phenomena revealed the incorporation of SM-IATE and DPPETS into the networks of hybrids would promote the thermal stability of hybrids. In the hybrid materials, phosphorus and silicon might change their thermal degradation process. An opposite effect of phosphorus and silicon on the activation energy was observed for the hybrids degrading in nitrogen. Introducing silicon into the epoxy resin leveled up their activation energies of degradation and phosphorus depressed the activation energies. The enhancing effect of silica was understood with the thermal resistance of silica. Owing to the low surface energy of silica, it would result in migration to the surface of resins to form a heat-resistant layer. The low activation energy of hybrid containing phosphorus was due to the weakness of P–O bonds [16].

In Kissinger's method, it was assumed that the temperature of maximum deflection in differential thermal analysis is also the temperature at which the reaction rate is a maximum. The maximum rate occurs when the derivative of Eq. (3) is zero [12]. Kissinger's method considers the maximum temperatures (T_{m}) of the first derivative weight loss curves. Therefore, Eq. (3) is differentiated with respect to T and the resulting expression set to zero. With some rearrangement and using β = heating rate, the following expression,

$$\frac{\mathrm{d}[\ln(\beta/T_{\mathrm{m}}^2)]}{\mathrm{d}(1/T_{\mathrm{m}}^2)} = \frac{-E}{R} \tag{5}$$

was derived. Therefore, the activation energy can be determined from a plot of $\ln(\beta/T_{\mathrm{m}}^2)$ against $1/T_{\mathrm{m}}$. Fig. 9 displays the DTG curves for pure epoxy and hybrids, from which T_{m} can be obtained. Table 3 showed the activation energies of degradation calculated from the slope for pure epoxy and hybrids. The activation energy of pure epoxy was 173 kJ/mol. The activation energies of hybrids containing different contents of inorganic fillers were 241, 199, 201, 213 kJ/mol, respectively. The activation energies of hybrids were higher than that of pure resin. The incorporation of nitrogen, silicon and phosphorus into epoxy would promote the thermal stability of epoxy resin.

Kissinger's method and Ozawa's method yield similar calculation results, which are therefore reasonable.

4. Conclusions

From TGA, the char yields of hybrids containing DPPETS increased with the increasing of the contents of DPPETS contents at 800 °C. Apparently, enhancement of thermal stability of hybrids has been achieved by incorporation of silicon, phosphorus and nitrogen into epoxy resins with bringing a Si/P/N synergistic effect. The IPDTs of hybrids were higher than that of pure epoxy. The thermal stability of hybrids increased with the contents of inorganic components. The inorganic components can improve the thermal stability of pure epoxy.

It is also found that the values of E_a for modified epoxy hybrid are higher than that of pure epoxy. The incorporation of nitrogen, silicon and phosphorus into epoxy would promote the thermal stability of epoxy resin. Kissinger's method and Ozawa's method yield similar calculation results, which are therefore reasonable.

Acknowledgements

The authors would like to express their appreciation to the National Science Council of the Republic of China for financial support of this study under grant NSC 94-2211-e-241-003.

References

[1] R.P. Kambour, W.V. Ligon, R.R. Russel, J. Polym. Sci., Polym. Lett. Ed. 16 (1978) 327.
[2] J.E. Mark, J. Appl. Polym. Sci.: Appl. Polym. Symp. 50 (1992) 273.
[3] J.E. Mark, J. Inorg. Organomet. Polym. 1 (1993) 431.
[4] H. Schmidt, J. Sol-Gel Sci. Technol. 1 (1994) 217.
[5] S.C. Betrabet, G.L. Wilkes, J. Inorg. Organomet. Polym. 4 (1994) 343.
[6] H. Schmidt, R. Kasemann, T. Burkhart, G. Wangner, E. Arpac, E. Geiter, ASC Symp. Ser. on Hybrid Organic-Inorganic Composites 585, 1995, p. 331.
[7] L. Mascia, Trends Polym. Sci. 3 (1995) 61.
[8] K. Gaw, H. Suzuki, M. Kakimoto, Y. Imai, J. Photopolym. Sci. Technol. 8 (1995) 307.
[9] H. Kita, H. Saiki, K. Tanaka, K. Okamoto, J. Photopolym. Sci. Technol. 8 (1995) 315.
[10] J.E. Mark, S. Wang, Z. Ahmad, Macromol. Chem. Symp. 98 (1995) 731.
[11] M.I. Sarwar, Z. Ahmad, Eur. Polym. J. 36 (2000) 89.
[12] H.H.E. Kissinger, Anal. Chem. 29 (1957) 1702.
[13] T. Ozawa, Bull. Chem. Soc. Jpn. 38 (1965) 1881.
[14] C.L. Chiang, C.C. Ma, Eur. Polym. J. 38 (2002) 2219.
[15] C.P.R. Nair, G. Clouet, Y. Gulbert, Polym. Dedra. Stab. 26 (1989) 305.
[16] C.S. Wu, Y.L. Liu, Y.S. Chiu, Polymer 43 (2002) 4277.
[17] S.Y. Lu, I. Hamerton, Prog. Polym. Sci. 27 (2002) 1661.
[18] Y.L. Liu, J. Polym. Sci. Part A: Polym. Chem. 40 (2002) 359.
[19] Y.L. Liu, C.I. Chou, Polym. Dedra. Stab. 90 (2005) 515.
[20] C.D. Doyle, Anal. Chem. 33 (1961) 77.
[21] M. Jelena, B. Ivan, O. Sebastijan, I. Hrvoje, I. Marica, Polym. Dedra. Stab. 91 (2006) 122.
[22] S.J. Park, H.C. Kim, H.I. Lee, D.H. Suh, Macromolecules 34 (2001) 7573.
[23] S. Vyazovkin, N. Sbirrazzuoli, Macromol. Rapid Commun. 27 (2006) 1515.