

Thermal Degradation and Flammability of P/Si Polysilsesquioxane Epoxy Nanocomposites

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ABSTRACT: A thermal stable epoxy nanocomposite prepared from the 4,4'-diglycidylether bisphenol A (DGEBA) and the P/Si ladder-like polysilsesquioxane (PSSQ). The activation energies of thermal degradation were calculated by Kissinger's and Ozawa's methods. The higher ladder-like PSSQ content not only increase the oligomer content but also generate the steric hindrance. Which steric hindrance influence the epoxy/amine curing reaction of the

modified epoxy system was more than the pristine DGEBA epoxy system. The P-Si synergistic effect on the thermal stability of the nanocomposites was discussed. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1435–1443, 2009

Key words: resins; hybrid; nanostructures; thermal properties; nanocomposite

INTRODUCTION

The versatile properties of epoxy were widely used as surface coating, adhesive, encapsulates for semiconductors, insulating materials for electronic devices, etc.^{1–5} However, flammability is the main drawback of the epoxy resin. Polymer matrixes containing bromine atoms could enhance the flame retardance.⁶ Liu et al.⁷ indicated that the bromine-containing epoxy resins might generate hydrogen bromide and dioxin derivatives during high temperature incineration. The halogen compounds may cause toxic, halogenated gases and release the “environmental hormones” in combustion. Consequently, it is an important task to use green flame retardant in epoxy resin.⁸

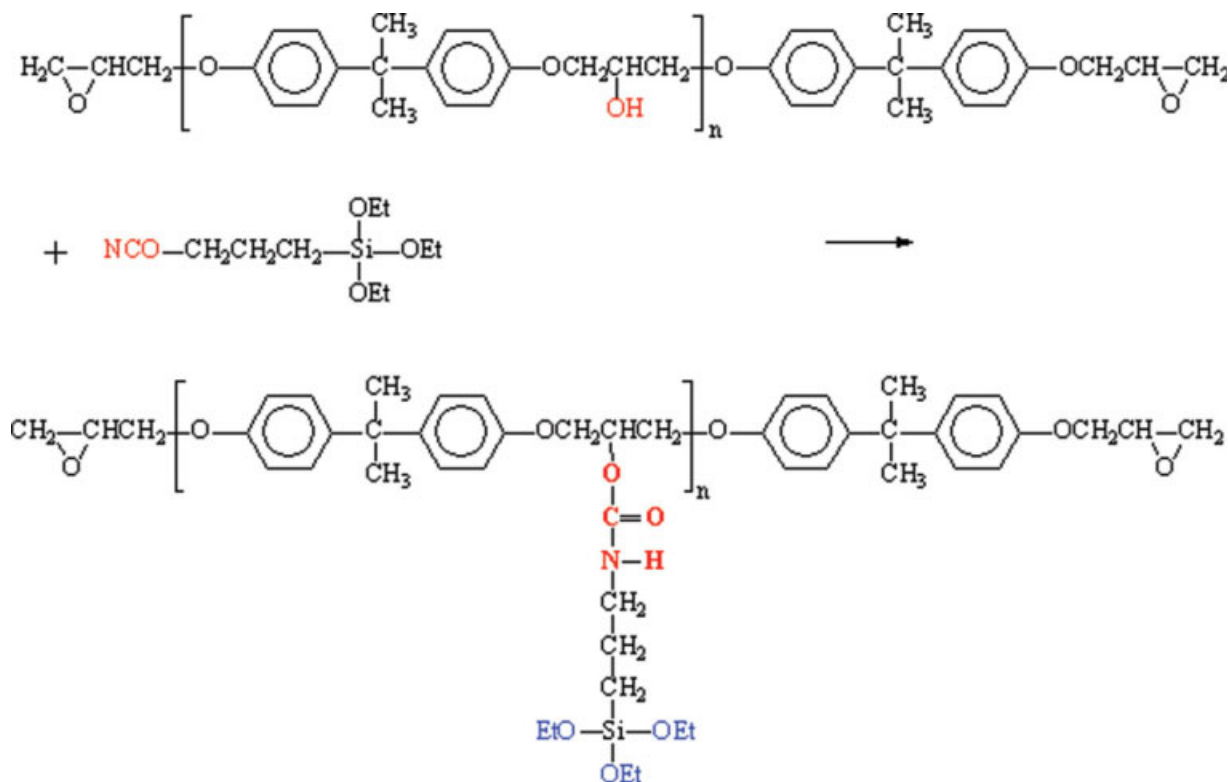
Recently, the modification of thermal stable epoxy resins with various functional groups, such as imide,¹ melamine,⁹ silicones,^{10,11} have been studied. Silicon and nitrogen compounds are mostly used as green flame retardant further to improve the thermal stability of polymer, which compounds were called “green materials.”¹¹ The phosphorus segments could be decomposed at lower temperature; meanwhile, the phosphorus-rich char could not only form a thermal insulation layer but also reduce the content of combustible gases. Additionally, the silica

compound reformed a thermal lamina in the material surface at high temperature. Which P/Si char could provide heat transfer and oxygen barrier to retard the flammability. Consequently, the excellent thermal stability of epoxy resins was due to P/Si synergistic effect of phosphorus and silicon moiety.^{12–15}

Polysilsesquioxane (PSSQ) is one of the oligomeric organo-silicon compounds. The general structural formula of PSSQ is $(\text{SiO}_{1.5})_n$. Which PSSQ possessed the ladder-like or random architectures; however, the cage-shape compound was called the polyhedral oligomeric silsesquioxane (POSS). The special structure of PSSQ could provide many unique properties, such as good thermal and oxidative stability, electrical insulating properties, and selective permeability to gas.^{16–19}

In general, various P and Si chemical reactants were added to provide the P/Si synergistic effect. In this study, a P/Si-containing polysilsesquioxane was induced into epoxy resins, furthermore, investigated the P-Si synergistic thermal properties. The morphology of nanocomposites was also investigated by scanning electron microscope (SEM), transmission electron microscope (TEM), and atomic force microscopy (AFM). Additionally, thermal stability properties of the nanocomposites was investigated by thermogravimetric analysis (TGA) and limited oxygen index (LOI). And the kinetics of thermal degradation of nanocomposites were investigated by Ozawa's and Kissinger's methods.

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Scheme 1 Preparation of IPTS-modified epoxy. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

EXPERIMENTAL

Materials

The diglycidyl ether of bisphenol A (DGEBA) epoxy used in this work was supplied by the Nan Ya Plastics, Taiwan, with an epoxide equivalent weight (EEW) of 180 g/equiv. 2-(Diphenylphosphino)ethyltriethoxysilane (DPPETES) and 3-isocyanatopropyltriethoxysilane (IPTS) were obtained from the United Chemical Technologies, Bristol, PA. Tetraethoxysilane (TEOS) and 4,4-methylene-dianiline (DDM) were supplied by the Acros Organic, Geel, Belgium. Isopropyl alcohol (IPA), tetrahydrofuran (THF), and triethylamine (TEA) were received from the Tedia, Fairfield, OH.

Preparation of the IPTS-modified epoxy precursor

DGEBA resin (10 g) and THF (10 g) were stirred in a 100 mL round-bottom flask at room temperature to obtain the DGEBA solution. After adding 3-isocyanatopropyltriethoxysilane (4 g, 16.19 mmol, IPTS) with an optimum concentration of TEA (about 0.2 g), the mixture was allowed to reflux at 60°C. Then, the IPTS-modified epoxy was obtained. The reaction of precursor is described in Scheme 1.²⁰

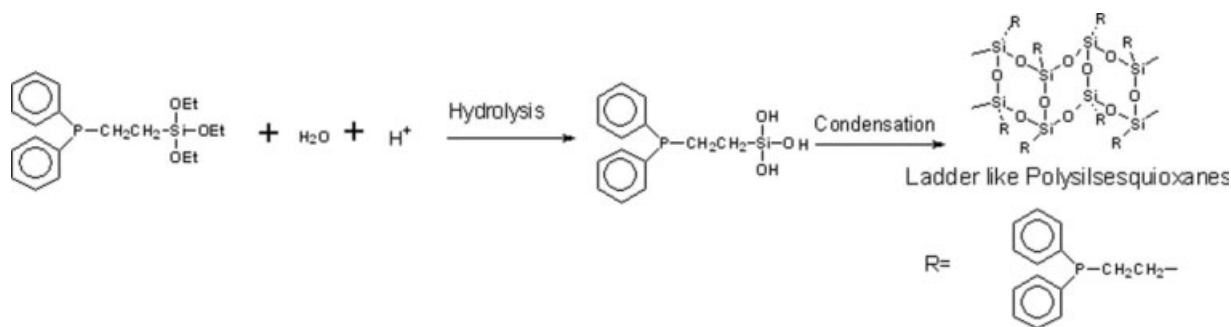
Preparation of ladder-like polysilsesquioxane

DPPETES (5 g, 13.263 mmol) was placed in a glass bottle. The molar ratio of H₂O/DPPETES was 3 : 1

and the molar ratio of DPPETES/IPA/THF was 1 : 6.23 : 1.67. Then, the two reacting systems were mixed. The wet gel was aged at room temperature for 48 h and dried at 80°C for 24 h. Finally, the reactant was kept in a vacuum oven at 200°C for 24 h. The reaction is described in Scheme 2.¹⁶

Preparation of hybrid nanocomposites

The hybrid nanocomposites prepared from the DGEBA epoxy system (EP system) and IPTS-modified epoxy system (ME system), and which nanocomposites with various DPPETES monomer or DPPETES ladder-like PSSQ ratios (0, 3, 6, 9, and 12 wt % based on 100% epoxy resin). Consequently, there two different type DPPETES compounds introduced into the DGEBA epoxy and IPTS-modified epoxy matrix, which further to form four type nanocomposite system. For DGEBA epoxy and DPPETES monomer reaction system, the nanocomposites contained various DPPETES monomer ratios (0, 3, 6, 9, and 12 wt %) were assigned as EP-DDM, EP-3M, EP-6M, EP-9M, and EP-12M. And for the DGEBA epoxy reacted with DPPETES ladder-like PSSQ system, the nanocomposites contained various DPPETES ladder-like PSSQ ratios (0, 3, 6, 9, and 12 wt %) were assigned as EP-DDM, EP-3L, EP-6L, EP-9L, and EP-12L, respectively. For the IPTS-modified epoxy system, the "EP" was change to the "ME."



Scheme 2 Preparation of P/Si ladder-like polysilsesquioxane.

TEOS and HCl were used as the coupling agent and the catalyst for all reaction systems. All mixtures were stirred for 1 h and then the homogeneous reactants were settled for 24 h at room temperature. 4, 4-Methyl-enedianiline (DDM) was used as curing agent, then the DDM/epoxy with a molar ratio of 1 : 2 was cured at 80°C for 12 h and at 160°C for 12 h.

Characterization and properties measurement

Solid-state ^{29}Si -NMR analysis was performed with a Bruker DSX 400WB (400 MHz) NMR spectrometer. TGA was conducted with a Thermal Analysis TGA-951 thermogravimetric analyzer at various heating rates (5, 10, 15, 20, and 30°C/min) under nitrogen atmosphere. The nitrogen gas flow rate was 100 mL/min. LOI values were measured with ATLAS Fire Science Products, New York. The LOI test was performed according to the testing procedure of ASTM D2836 oxygen index method. The LOI represented the lowest oxygen content for sustaining the flame. The morphology of the cross section surface of the cured hybrid resins was observed with a SEM (JEOL JSM 840A). Nanostructures of epoxy nanocomposites were investigated by a TEM (JEOL JEM-1230) and its accelerated voltage is 100 kV. The nanocomposites were microtomed with Reichert-Jung ULTRACUTE into 100-nm thick slices in a direction normal to the plane of the films. AFM measurements were carried out with an AFM of Seiko SPI3800N, series SPA-400.

Determination of thermal stability parameters

The integral procedure decomposition temperature (IPDT) was calculated from the method proposed by Park and Cho^{14,21}:

$$\text{IPDT}(\text{°C}) = AK \times (T_f - T_i) + T_i \quad (1)$$

Where A is the area ratio of total experimental curve as shown in Figure 1 as defined by the total TGA thermogram. T_i is the initial experimental tem-

perature and T_f is the final experimental temperature. In this work, the T_i and T_f were 50°C and 700°C, respectively. A and K can be calculated by eqs. (2) and (3). The S_1 , S_2 , and S_3 were the TGA illustration integral of the characteristic area and shown in Figure 1. Generally, the thermal stable materials possessed higher thermal degradation temperature and char yield. Consequently, which materials possessed higher S_1 and S_2 values, however, the S_3 was lower.

$$A = \frac{S_1 + S_2}{S_1 + S_2 + S_3} \quad (2)$$

$$K = \frac{S_1 + S_2}{S_1} \quad (3)$$

Kinetic studies of thermal degradation process

Ozawa's method²²

The degree of conversion, α , is defined in eq. (4)

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty} \quad (4)$$

where m_0 is the initial weight, m is the actual weight at temperature T and m_∞ is the weight at the end of experiment. The equation by Ozawa is expressed as:

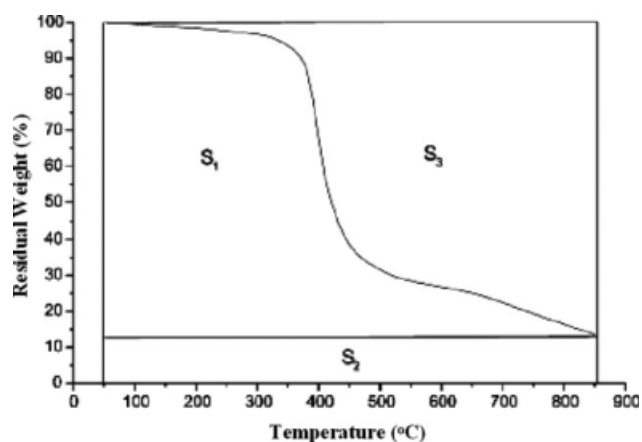


Figure 1 IPDT model curve.

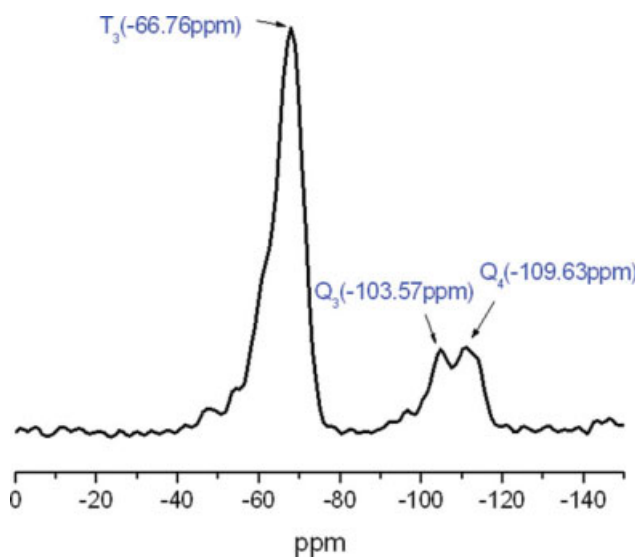


Figure 2 Solid-state ^{29}Si -NMR spectrum of ME-9M nanocomposite. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$$\log \beta = -0.4567 \left(\frac{E_a}{RT} \right) + \left[\log \frac{AE_a}{R} - 2.315 - \log F(\alpha) \right] \quad (5)$$

where E_a is the activation energy of thermal degradation, R is the ideal gas constant, T is the absolute temperature of various conversion degrees of thermal degradation, β is the heating rate. The activation energy of thermal degradation was obtained from the plot of $\log \beta$ vs. $1/T$.

Kissinger's method²³

The Kissinger's method is expressed in eq. (6)

$$\frac{d[\ln(\beta/T_m^2)]}{d(1/T_m)} = -\frac{E_a}{R} \quad (6)$$

where T_m is the maximum temperature of the first derivative weight loss curves, β is the heating rate, and R is the ideal gas constant. Activation energy of the thermal degradation (E_a) can be determined from the plot of $\ln(\beta/T_m^2)$ vs. $1/T_m$.

RESULTS AND DISCUSSION

The characterization of the structure of nanocomposites

Figure 2 illustrated that the solid-state ^{29}Si -NMR spectra of nanocomposite, which assigned to the T and Q groups of the silsesquioxane characteristic peak. The T and Q structures are shown in Scheme 3. The trisubstituted (T_3) of $\text{R}-\text{Si}-(\text{O}-\text{Si})_3-$ structure and trisubstituted (Q_3) and tetrasubstituted (Q_4)

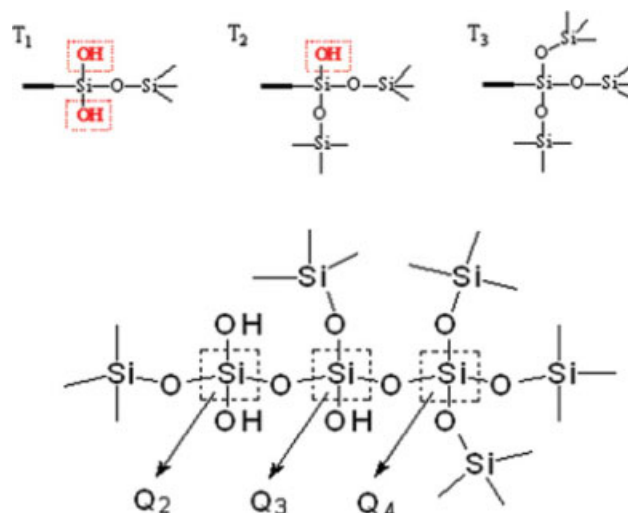
of $\text{Si}-(\text{O}-\text{Si})_4-$ structure of nanocomposite appeared. The spectra of the nanocomposite clearly possessed three peaks and appeared at about -66.76 , -103.57 , and -109.63 ppm, which peaks were corresponded to T_3 , Q_3 , and Q_4 , respectively. The absorption of peak of T_3 was stronger than Q_3 and Q_4 , since the IPTS-modified epoxy system (ME system) possessed the $\text{Si}-\text{O}-\text{Et}$ side chain, which caused more T_3 unit in the sol-gel reaction.^{24,25} The T-formation of IPTS-modified epoxy side chain could interfere the curing reaction and increase the steric hindrance effect. Meanwhile, the steric hindrance of random sol-gel reaction might inhibit the formation of Q_3 or Q_4 chemical structures, hence, increase the production of oligomer and decrease thermal stability.

Morphological properties of nanocomposites

Figure 3 was the SEM microphotography of the fractured surfaces of EP-9L nanocomposite. No aggregated inorganic particles observed in the smooth surface of the hybrid nanocomposites. This result indicated that the good miscibility between organic and inorganic phases.

Furthermore, the polysilsesquioxane domains of the nanocomposites were investigated by TEM. It can be found in Figure 4(a,b), the particles dispersed uniformly throughout the epoxy matrix. Meanwhile, this phenomenon reveals that the nanocomposites exhibited good miscibility between organic and inorganic phases, no phase separation was found. It is notably that the size of polysilsesquioxane particles was below 50 nm.

The surface topographies of the nanocomposites were characterized by AFM and shown in Figure 5.



Scheme 3 The T and Q structures of polysilsesquioxane. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

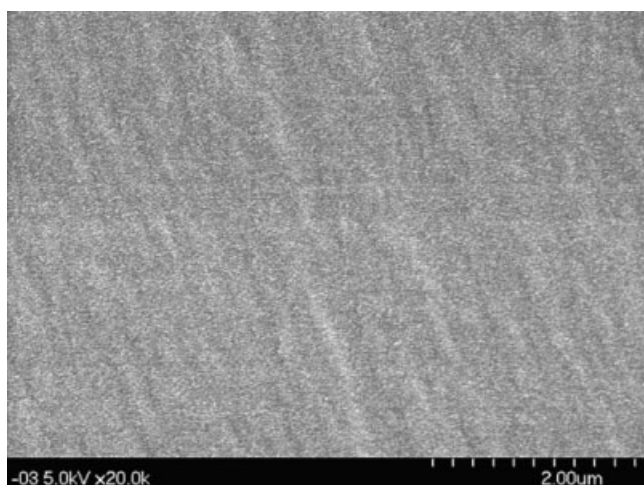


Figure 3 The SEM microphotograph of EP-9L ($\times 20K$, cross section).

From the AFM 3D microphotograph, it can be seen that the DPPETES monomer or DPPETES ladder-like polysilsesquioxan are well dispersal without any visible agglomeration. Furthermore, the excellent planarity of nanocomposites was due to well dispersion and homogeneity between the epoxy (organic moiety) and the DPPETES monomer or DPPETES ladder-like polysilsesquioxan (inorganic moiety).^{26–30}

Kinetics of thermal degradation

Various heating rates of TGA study were used to obtain the activation energy of thermal degradation. The values were calculated from TGA data according to the Ozawa's²² and Kissinger's methods.²³ The thermal degradation of the nanocomposites was a complicated process, and the calculation of activation energies of thermal decomposition from different mathematical models might show wide variation in the analysis. Ozawa's²² and Kissinger's²³ methods were applied to calculate activation energies of thermal degradation, since they are simple methods and without considering the disturbance of the heating rate or side reaction. The calculated activation energies of thermal degradation were summarized in Tables I and II.

Table I was the activation energies of thermal degradation of various nanocomposites by Kissinger's method. The P/Si synergistic effect of DPPETES monomer or DPPETES ladder-like PSSQ on the thermal stability could be observed, which increased the activation energy of thermal degradation. It indicated that the DPPETES monomer or DPPETES polysilsesquioxan addition might increase the P/Si protective layer when the nanocomposites thermal decomposed.^{31–33} The activation energy of thermal degradation of the IPTS-modified epoxy system was higher than DGEBA epoxy system, since the IPTS-

modified epoxy system contain alkyl silica type side chains. Furthermore, the ME system contained more Si protective layer during the thermal degradation. It is notably, the thermal degradation activation energy of ME-6L was higher than other nanocomposites of the ME ladder-like polysilsesquioxan system. These phenomena indicated that the ladder-like polysilsesquioxan content is higher in the epoxy/amine curing system, meanwhile, more oligomers might be generated and the thermal degradation is easier. Consequently, the thermal stability will be decreased.

Table II was the average activation energies of thermal degradation of various nanocomposites by Ozawa's method. Results of the thermal degradation activation energies of all nanocomposites increased with DPPETES monomer or DPPETES ladder-like polysilsesquioxan content. The DPPETES moiety possessed phosphorus group, which could form char. Meanwhile, the silica might migrate to the material surface serving as a protective layer during the

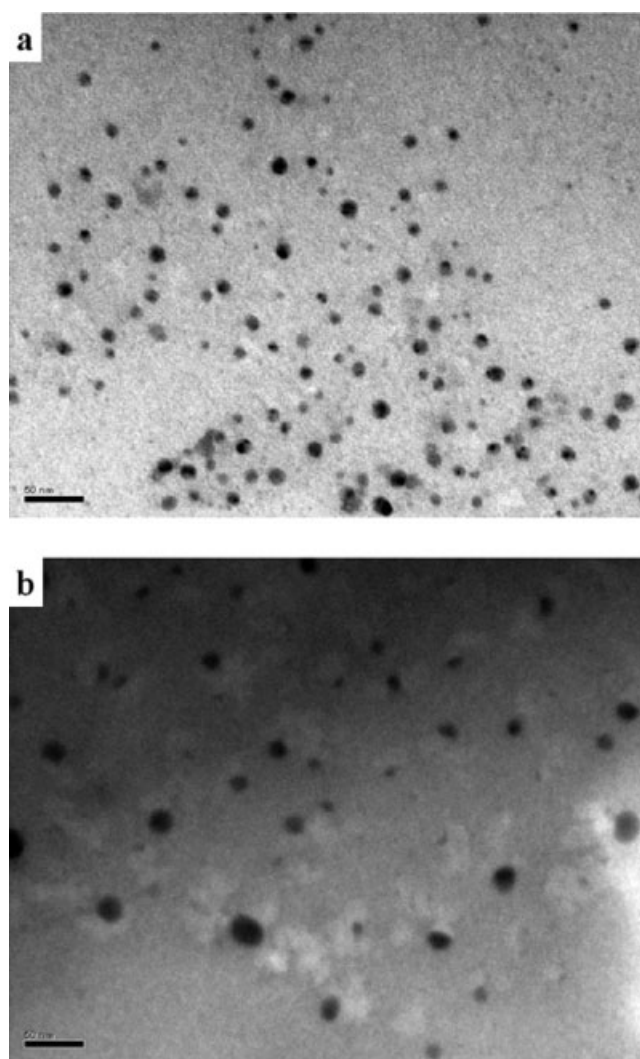


Figure 4 The TEM microphotographs of (a) EP-9L, (b) ME-9M ($\times 250K$, scale bar: 50 nm).

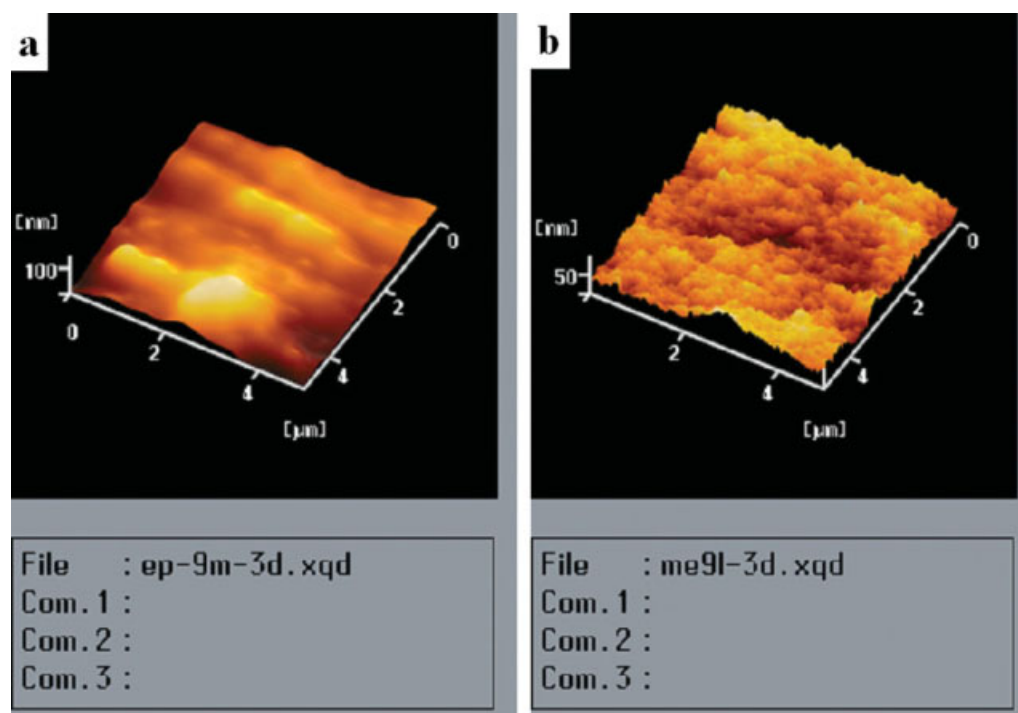


Figure 5 The AFM 3D-top photographs (a) EP-9M, (b) ME-9L. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

thermal degradation process. The enhancing effect of thermal stability attributed to the P/Si synergistic effect.^{34–37} The average activation energy of thermal degradation of ME-6L was higher than other nanocomposites when the polysilsesquioxan introduced into the ME system. Because the molecular architecture of polysilsesquioxan might interfere the epoxy/amine curing reaction, hence, increasing the production of oligomer.

The different between the Ozawa's method and Kissinger's method calculation might associate with the curing and sol-gel reactivity. The bulky ladder-like DPPETES inorganic particles and the siloxane

side chain of the modified epoxy could make the curing and sol-gel reactions are complex. Additionally, there were confused side reactions of this work. And which phenomenon influenced the maximum temperature of the first derivative weight loss curves. Additionally, the Ozawa's method and Kissinger's method calculation were obtained from the plot of $\log \beta$ vs. $1/T$ and the plot of $\ln(\beta/T_m^2)$ vs. $1/T_m$, respectively. Consequently, the investigation of the Ozawa's model and Kissinger's model were dissimilar.

The activation energies of various thermal degradation conversions (α) were calculated by Ozawa's method are shown in Figures 6–9. For the DGEBA

TABLE I
 The Activation Energies of Thermal Degradation of Nanocomposites by Kissinger's Method (in Nitrogen Atmosphere)

DGEBA epoxy system		Modified epoxy system	
Sample	Activation energy (kJ/mol)	Sample	Activation energy (kJ/mol)
EP-DDM	165.5	ME-DDM	193.7
EP-3M	154.2	ME-3M	176.7
EP-6M	141.9	ME-6M	189.7
EP-9M	191.8	ME-9M	222.1
EP-12M	209.7	ME-12M	305.5
EP-3L	152.1	ME-3L	171.5
EP-6L	150.4	ME-6L	208.5
EP-9L	186.1	ME-9L	174.5
EP-12L	204.0	ME-12L	169.8

TABLE II
 The Average Activation Energies of Thermal Degradation of Nanocomposites by Ozawa's Method (in Nitrogen Atmosphere)

DGEBA epoxy system		Modified epoxy system	
Sample	Activation energy (kJ/mol)	Sample	activation energy (kJ/mol)
EP-DDM	159.7	ME-DDM	200.0
EP-3M	163.2	ME-3M	180.0
EP-6M	161.1	ME-6M	197.8
EP-9M	209.7	ME-9M	242.5
EP-12M	201.5	ME-12M	402.1
EP-3L	161.7	ME-3L	175.2
EP-6L	159.3	ME-6L	207.9
EP-9L	197.8	ME-9L	190.4
EP-12L	197.7	ME-12L	194.7

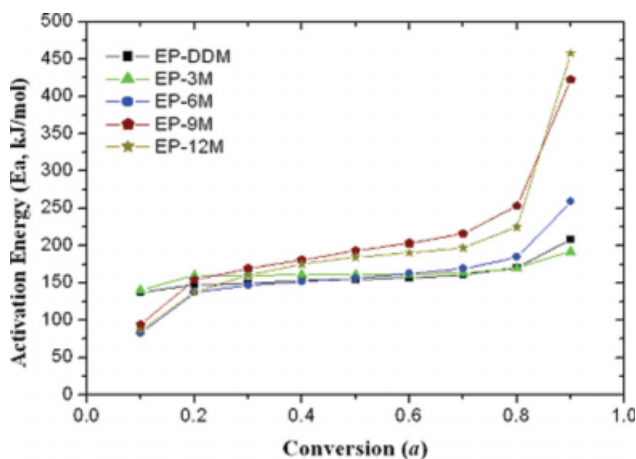


Figure 6 The activation energies of thermal degradation versus various thermal decomposition conversion (α) of EP DPPETES monomer system by Ozawa's method. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

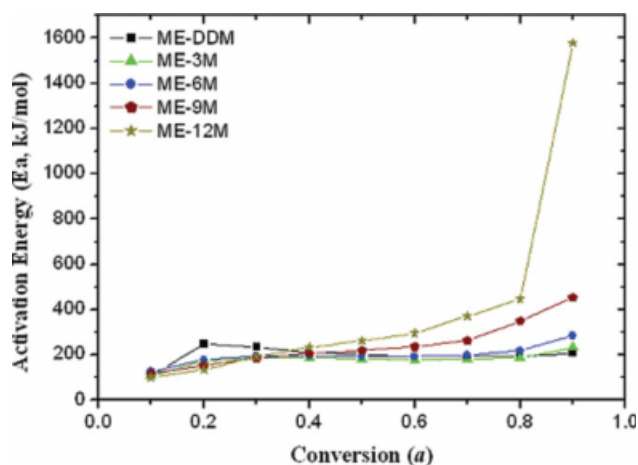


Figure 8 The activation energies versus of thermal degradation various thermal decomposition conversion (α) of ME DPPETES monomer system by Ozawa's method. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

epoxy system (Figures 6 and 7), the EP-9L and EP-9M possessed higher thermal degradation activation energies than other nanocomposites of EP system. Higher siloxane content could generate more oligomers, and lower siloxane content not sufficient to increase the P/Si protective layer of thermal degradation. Consequently, the 9 wt % of DPPETES monomer or DPPETES ladder-like polysilsesquioxan is the optimum concentration to enhance the EP system thermal stability. Between the conversions 0.3 and 0.6, the P element of the DPPETES and the ladder-like inorganic DPPETES particles caused the activation energies of thermal degradation increased slightly. The phosphorus architecture of DPPETES decreased at lower temperature and the ladder-like inorganic particle might generate the oligomer of the

curing reaction. Consequently, the P/Si synergistic effect could not improve the activation energies of thermal degradation dramatically. And the curve of the activation energies of thermal degradation plot displayed plateau phenomenon. For the ME/DPPETES monomer system (Fig. 8), the thermal degradation activation energy of ME-12M increased dramatically, since the DPPETES monomer reacted with the modified epoxy siloxane side chain by sol-gel method which possessed higher reactivity. For ME/DPPETES ladder-like polysilsesquioxan system (Fig. 9), all of the activation energies of thermal degradation were increased slightly, the range of thermal degradation activation energies between 150 and 250 kJ/mol, which lower than other three

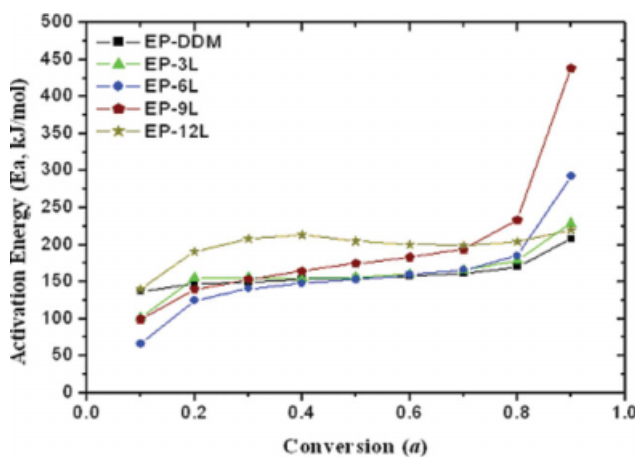


Figure 7 The activation energies of thermal degradation versus various thermal decomposition conversion (α) of EP DPPETES ladder-like polysilsesquioxan system by Ozawa's method. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

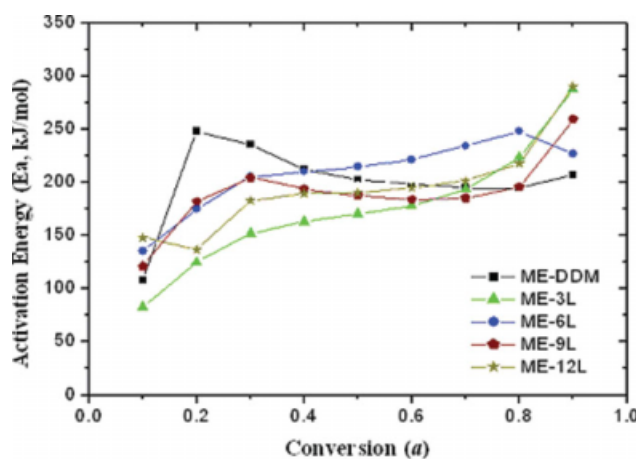


Figure 9 The activation energies versus of thermal degradation various thermal decomposition conversion (α) of ME DPPETES ladder-like polysilsesquioxan system by Ozawa's method. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

nanocomposites system. This phenomenon indicated that the triethyloxysilane side chains of modified epoxy reacted with DPPETES ladder-like PSSQ and caused more steric hindrance. Consequently, the ME DPPETES ladder-like polysilsesquioxan nanocomposite might generate more free volume and more oligomer in epoxy/amine curing reaction, which resulted in the thermal degradation activation energies increased slightly. Additionally, which system (Fig. 9) illustrated that the more abnormally than other systems. Because the modified epoxy possessed the siloxane side chain which further to reacted with the ladder-like inorganic DPPETES particle by sol-gel, and the bulky DPPETES architecture could influence the sol-gel and epoxy/amine curing reactivity. Hence, the ME-DPPETES ladder-like PSSQ system might possess more complex sol-gel and curing side reactions. Meanwhile, Figure 9 exhibited more random than other system (Figures 6–8). However, the activation energies of thermal degradation confirm that using DPPETES monomer or DPPETES ladder-like polysilsesquioxan as a thermal stable modifier could enhance the thermal stability of any epoxy material effectively.

The flammability of nanocomposites

Figure 10 illustrated the flammability of various nanocomposites, which investigated by LOI. In general, when the LOI value of material is higher than 26, it could exhibit self-extinguishing behavior and be considered low flammability material. The LOI values of EP system were higher than the ME system, since the ME system containing urethane-like side group might increase the flammability. It is notably, the LOI values of the nanocomposite containing 12 wt % DPPETES monomer or DPPETES ladder-like PSSQ were not increased significantly.

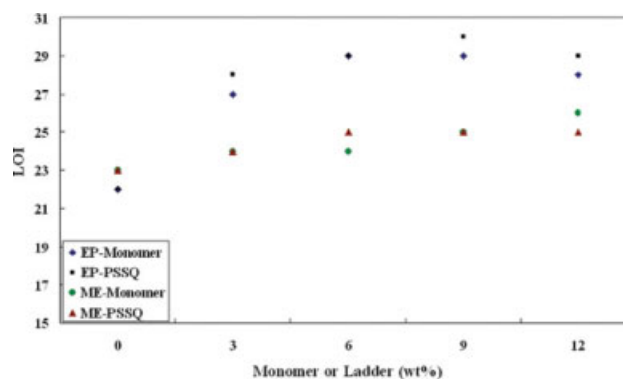


Figure 10 The LOI values of various nanocomposites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Which resulted from the higher silsesquioxane content could not increase the curing reactivity and exhibits lower crosslinking behavior from sol-gel reaction.^{38–40} Meanwhile, the increased oligomer of the epoxy/amine curing reaction might reduce the flame retardance.

The IPDTs of the nanocomposites were summarized in Figure 11. IPDT exhibited the inherent thermal stability of the resin, i.e., the decomposition characteristics of the silicon groups in the epoxy resins.¹⁴ Figure 11 illustrated that the IPDT of the nanocomposites increased with the DPPETES monomer or DPPETES ladder-like PSSQ content. Which phenomenon associated with the introduction of the inorganic DPPETES monomer or DPPETES ladder-like polysilsesquioxan segments could reduce the fraction of the volatile organic polymer. The superior flame retardance at high temperatures might enhance the IPDT of the resins.^{14,21,41} As can be seen from Figure 11, the IPDT value of ME system was higher than that of the EP system, since the ME system possessed silicon type side chain, consequently,

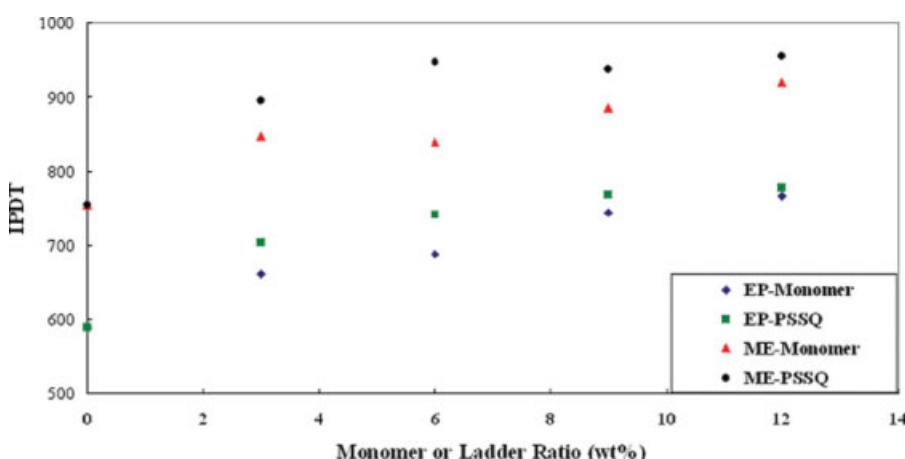


Figure 11 The IPDT values of various nanocomposites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

decreased the fraction of volatile organic polymer in the ME system and improved the IPDT.

CONCLUSIONS

A series of thermal stable epoxy nanocomposites have been fabricated with the introduction of nano-scale DPPETES monomer or DPPETES ladder-like poly-silsesquioxan. From morphological investigation (SEM, TEM, and AFM), the nanocomposites exhibit good miscibility between organic and inorganic phases, and the PSSQ particles are well distributed with sizes below 50 nm. In EP system, the activation energies of thermal degradation calculated by Kissinger's method and by Ozawa's method were 150–209 kJ/mol and 159–209 kJ/mol, respectively. In ME system, the activation energies of thermal degradation calculated by Kissinger's method and by Ozawa's method were 170–305 kJ/mol and 180–402 kJ/mol. The activation energies of thermal degradation increased with DPPETES monomer or DPPETES ladder-like polysilsesquioxan content. However, higher DPPETES ladder-like polysilsesquioxan content could interfere the epoxy/amine curing and decrease the thermal stability. The optimum content of DPPETES moiety was 9 wt %. Moreover, the T-formation side chain of IPTS modified epoxy might increase the steric hindrance and decrease the thermal stability. The nanocomposites show high IPDT value (968) and LOI value (30). The excellent thermal stability and flammability can be attributed to the P/Si synergistic effect of the DPPETES type ladder-like polysilsesquioxan or DPPETES monomer.

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