

Study on the Modification of Epoxy Resin by a Phosphorus- and Silica-Containing Hybrid

Zhengfang Wang,^{1,2} Weiqu Liu,¹ Chaohui Hu,^{1,2} Songqi Ma^{1,2}

¹Key Laboratory of Polymer Materials for Electronics, Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, People's Republic of China

²College of Chemistry and Chemical Engineering, Graduate University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

Received 15 October 2010; accepted 23 November 2010

DOI 10.1002/app.33824

Published online 16 March 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: A novel phosphorus- and silica-containing hybrid (DPS) was synthesized by the reaction between diethyl phosphate (DEP) and polyhedral oligomeric siloxanes (POS) formed by hydrolysis condensation of 3-glycidoxypropyltrimethoxysilane (GPTMS). The novel phosphorus- and silica-containing hybrid was characterized by the Fourier transform infrared spectroscopy (FT-IR), silicon nuclear magnetic resonance, and gel permeation chromatography (GPC). Then, the determination of the activation of the reaction between epoxy resin and phosphorus-, and silica-containing hybrids was studied by differential scanning calorimeter (DSC). In the presence of catalyst, the activation energies of the curing reaction were 63.3 and 66.7 kJ/mol calculated by Kis-

singer model and Ozawa model respectively. The thermal and flame retardant properties of the cured epoxy modified by DPS were determined by differential scanning calorimeter (DSC), thermal gravimetric analysis (TGA), and limited oxygen index (LOI). The results revealed that those properties were improved in comparison with unmodified epoxy resin. In addition, scanning electron microscopy (SEM) was used to investigate the morphology of the cured epoxy resin modified by DPS. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 2213–2219, 2011

Key words: epoxy resin; fire-resistance; kinetics; thermal properties; hybrid of phosphorus and silica

INTRODUCTION

Epoxy resin was widely used as the adhesives, coatings and encapsulated materials, due to its good mechanical properties and attractive chemical and electronic properties. However, like other polymers, the flame retardant of epoxy resin was a main drawback, limiting its applications. Recently, many researches to improve flame retardant properties of epoxy resin were around halogen-containing flame retardant.^{1–5} However, the halogen-containing epoxy resin could produce the pernicious smoke and toxic gas, such as polychlorinated dibenzodioxin, polychlorinated dibenzofuran, which can induce cancer in the human body and is harmful to the earth for sustainable development. Regarding these issues, phosphorus, silicon and nitrogen are commonly considered as environmental friendly flame retardants.^{6–8}

The phosphorus-containing flame retardant was considered as the most effective halogen free flame

retardant.^{9,10} For example, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO)-containing epoxy resin has attracted much attention in the study on modification of epoxy resin due to its bulk group and aromatic group which can successfully improve the flame retardant properties. However, the phosphorus introduced by this method would decrease T_g , because of chemical structure design limited and a relatively lower crosslink density of the cured epoxy resin.

To compensate the disadvantage of phosphorus-containing epoxy resin, in our previous reports,^{11,12} the dendritic polymers formed by hydrolysis condensation of 3-glycidoxypropyltrimethoxysilane (GPTMS) was introduced to react with the P-H bond in 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) to obtain the dendritic polymers of phosphorus- and silica-containing hybrids (DPS). Epoxy resin modified by DPS displayed good flame retardant and high thermal properties. But there would be still absent in the understanding about the procedure of the reaction between epoxy resin and DPS.

So in this communication, to investigate the kinetics of the reaction between epoxy resin and DPS in the presence of dibutyltin dilaurate (DBTL), a novel phosphorus- and silica-containing hybrid was synthesized via the reaction between diethyl

Correspondence to: W. Liu (liuwq@gic.ac.cn).

Contract grant sponsor: Ministry of Science and Technology of the Peoples' Republic of China; contract grant number: 06c26214401627.

phosphate (DEP) and polyhedral oligomeric siloxanes (POS) formed by hydrolysis condensation of 3-glycidoxypropyltrimethoxysilane (GPTMS). GPC was adopted to determine the molecular weight of DPS, while FT-IR and ^{29}Si NMR were used to confirm the structure of DPS. DPS at 30% ratio with or without catalyst was exploited to study the behavior of curing procedure. In comparison, sample of unmodified epoxy resin was also cured at the same condition. The thermal and flame retardant properties of the cured products were characterized by DSC, TGA, LOI.

EXPERIMENTAL

Materials

Bisphenol-A epoxy resin (Ep 828 with an epoxide equivalent weights of 196 g/eq.) was purchased from Guangzhou Epons Trading development LTD. 4,4'-Diamino-diphenyl-methane (DDM), chemical grade, was bought from Shanghai SSS Regent CO., LTD. 3-Glycidyloxypropyltrimethoxysilane (GPTMS), industrial grade, was supplied by Xinghuo Chemical Co. of China. Diethyl phosphate (DEP), industrial grade, was purchased from Jitai chemical company in Shan Dong Province, China. Triphenyl phosphine (TPP), analytical pure, was purchased from Lingfeng chemical company in Shanghai of China. Dibutyltin dilaurate (DBTL), analytical pure, was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd., China.

Analysis

Fourier transform infrared spectroscopy (FT-IR) was recorded on a Perkin-Elmer Spectrum One FT-IR in the range from 400 cm^{-1} to 4000 cm^{-1} .

^{29}Si NMR was registered with a 400MHz Bruker NMR spectrometer, taking CDCl_3 as solvent and tetramethylsilane as the internal reference.

Gel permeation chromatography measurement was performed using a Waters 515 GPC with tetrahydrofuran as a solvent at the flow rate of 1.0 mL/min.

The glass transition temperature was characterized by the differential scanning calorimetry measurement, which was performed on the Perkin-Elmer DSC-7 differential scanning calorimetry at a heating rate of $20^\circ\text{C}/\text{min}$ from 50 to 200°C under nitrogen atmosphere. The middle of the capacity change was taken as the glass transition temperature. The exothermic heat curves were performed on the Perkin-Elmer DSC-7 differential scanning calorimetry at a heating rate of $20^\circ\text{C}/\text{min}$ from 50 to 200°C under nitrogen atmosphere.

The thermo gravimetric analysis—a common method to determine the thermal stability of polymers was performed on the Perkin-Elmer thermogra-

vimetric analyzer in the range from 50 to 800°C at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen or air. The gas flow rate was 100 mL/min.

Limited oxygen index (LOI) values were measured on a ZRY-type instrument (China) with a test specimen bar of $120 \times 6 \times 3\text{ mm}^3$ according to the standard "oxygen index" test ASTM D 2836.

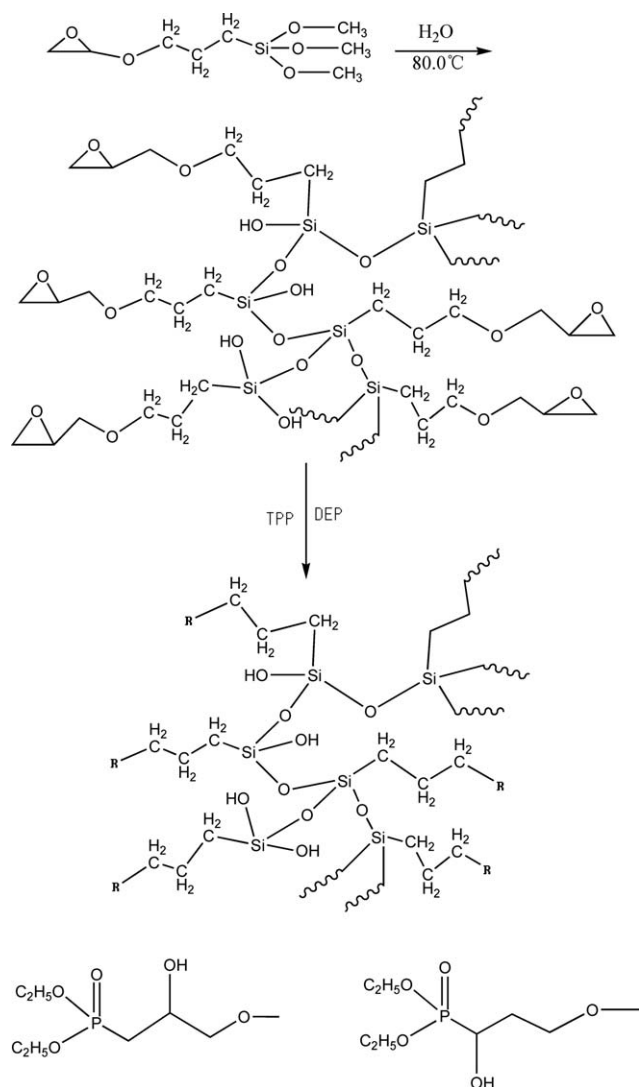
The morphology of the cross section of the cured epoxy resin modified by DPS was detected by scanning electron microscopy (Hitachi S-4300, Tokyo, Japan). The distribution of DPS in the matrix of epoxy resin was obtained from the photographs of cross section of the cured epoxy resin.

Synthesis of a hybrid containing phosphorus and silica

The hybrid containing phosphorus and silica (DPS) was synthesized by the reaction between diethyl phosphate (DEP) and branched oligomeric siloxanes (POS) formed by hydrolysis condensation of 3-glycidoxypropyltrimethoxysilane (GPTMS). The POS was synthesized by hydrolysis condensation of GPTMS in THF via the previous method.¹² The hydrolysis condensation of 236 g GPTMS kept in 110 g THF under 1% DBTL as catalyst, for 4.5 h at 80°C . Then, 138 g DEP was added to react with the epoxide group in POS under the catalyst (TPP) to gain the product (DPS). Finally the solvent and residual water and by-product methanol were removed by rotary evaporation from the reaction system. Molecular weight and molecular weight distribution were studied to confirm the dendritic polymers of the hybrid containing phosphorus and silica formed. The structure and synthesized procedure of DPS were shown in Scheme 1.

Estimation of the activation energy of epoxy resin modified by DPS

The estimation of the activation energy of epoxy resin modified by DPS was studied on differential scanning calorimetry (DSC). To a three necked flask equipped with temperature controlled and a stirrer, 100 g Diglycidylether of bisphenol-A (epoxy equivalent weight, $\text{EEW} = 196$) and 30 g DPS was added and heated to 60°C with stirring. Then different amounts of catalyst (dibutyltin dilaurate) were dropped into the mixture. The estimation of the activation energy of epoxy resin modified by DPS was conducted by DSC at four different heating rate (5, 10, 15, $20^\circ\text{C}/\text{min}$) in the temperature range from 50 to 200°C under nitrogen atmosphere. In comparison, the DPS was studied at the same condition. Tested data and calculated data were concluded in the Table I.



Scheme 1 The synthesis and structure of DPS.

The curing procedures of epoxy resin modified by DPS

100 g bisphenol A epoxy resin with EEW = 196 g/eq and 30 g DPS were mixed at 90°C and stirred to be clear. Bubbles and residual small molecules were removed under the vacuum condition. After the calculated DDM (the mole ratio of amine hydrogen atom to epoxide group was

TABLE I
The Kinetic Data Tested and Calculated

q (°C/min)	T _{epoxy+DPS} , °C	T _{DPS} , °C
5	132	160
10	148	172
15	156	178
20	160	182
E _a , kJ/mol		
Kissinger	63.3	94.9
Ozawa	66.7	97.1

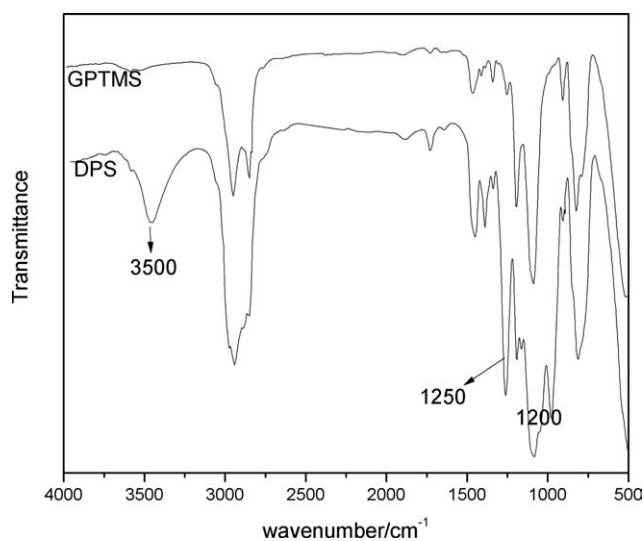


Figure 1 FT-IR spectra of DPS and GPTMS.

1 : 1. And the epoxide content in the mixture was EEW = 196 g/epuiv) was added to the mixture, the mixture was stirred to be clear again. Then the blend was placed in a mold and cured under the condition: 90°C/3 h, 150°C/2 h, and 180°C/4 h. The contrast sample based unmodified epoxy resin was prepared at the same experimental procedure.

RESULTS AND DISCUSSION

The characteristic of DPS structure

FT-IR

To confirm the DPS chemical structure, FT-IR spectrums of 3-Glycidyloxypropyltrimethoxysilane (GPTMS) and DPS were recorded on a Perkin-Elmer Spectrum One FT-IR. Moreover, ²⁹SiNMR and GPC of DPS were also introduced to confirm the structure further. The FT-IR spectrums of GPTMS and DPS were shown in Figure 1. Compared to 3-Glycidyloxypropyltrimethoxysilane (GPTMS), the FT-IR spectrum of DPS appeared the absorption of —OH at 3500 cm⁻¹ which was formed by hydrolysis condensation, and the peak at about 1200 cm⁻¹ broadened because of the forming of Si—O—Si bond. The absorption of P=O bond at 1250 cm⁻¹ was observed in the spectrum of DPS, indicating the DPS contained the structure of DEP. The disappearance of epoxy absorption at 930 cm⁻¹ and P—H bond absorption at about 2380 cm⁻¹ basically, could be explained that the functional group P—H bond reacted with epoxide group in 3-Glycidyloxypropyltrimethoxysilane (GPTMS) and the hydrolysis condensation had been taken out. Those implied that the structure of DPS formed.

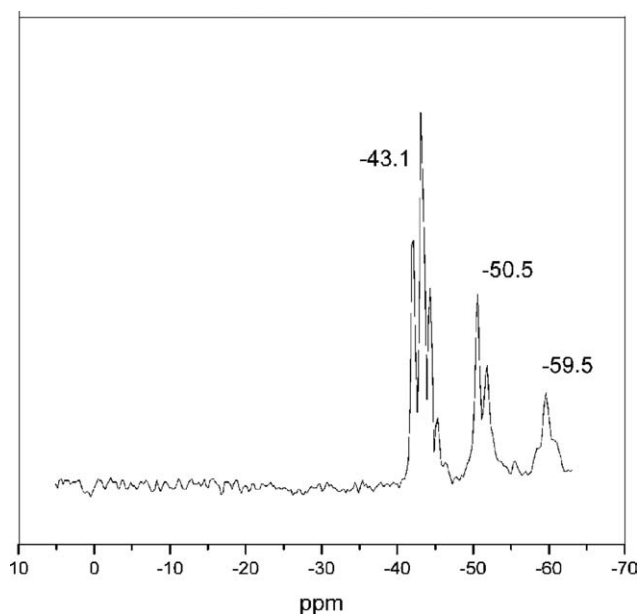


Figure 2 $T^{29}\text{SiNMR}$ spectrum of DPS.

$^{29}\text{SiNMR}$

The structure of DPS was determined with $^{29}\text{SiNMR}$ further. As shown in Figure 2, three major signals at -43.1 , -50.4 , and -59.5 ppm were absorptions of the, dihydroxy-substituted silica, monohydroxy-substituted silica and nonhydroxy-substituted silica respectively. The spectrum of $^{29}\text{SiNMR}$ indicated that nonhydroxy-substituted, monohydroxy-substituted and dihydroxy-substituted silica appeared in the branched structure of DPS.

GPC

GPC was used to determine the molecular weight and molecular weight distribution of DPS. As shown in

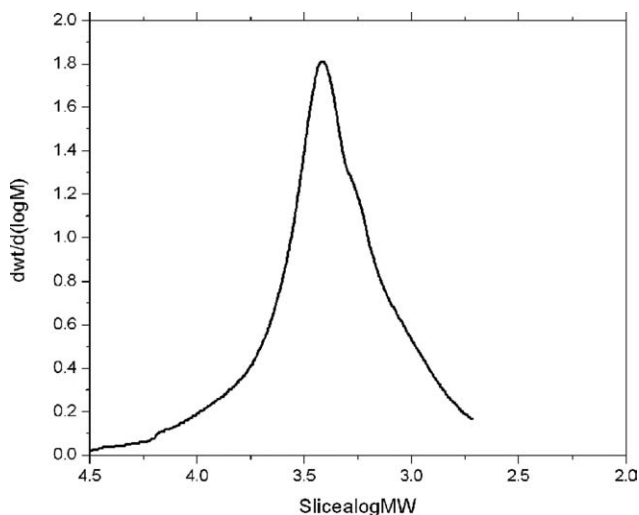


Figure 3 GPC diagram of DPS.

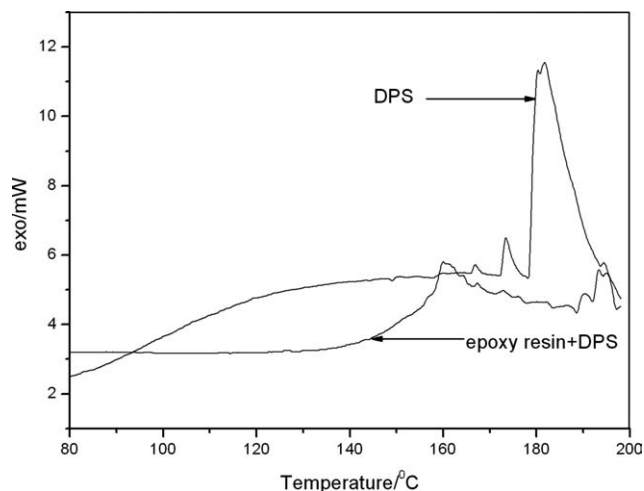


Figure 4 The curve about the effect of catalyst on the activation of the reaction between epoxy resin and DPS.

Figure 3, the mainly molecular weight distribution peak in the diagram of GPC was at 2793, indicating the branched structure of DPS contained about 8 monomers. The molecular weight distribution of DPS was 1.72.

The estimation of the activation energy of epoxy resin modified by DPS.

Comparisons of reactivity DPS with respect to itself and to epoxy resin.

The effect of the catalyst on the activation of the reaction between epoxy resin and DPS was determined by DSC in the presence of 1% dibutyltin dilaurate (DBTL).¹³ The promotion of catalyst (dibutyltin dilaurate) to the reactivity of DPS respect to itself or to epoxy resin was showed in Figure 4. In the presence of catalyst (DBTL), the max exothermic heat peak of the reaction between DPS and epoxy resin was at about 160°C , while the reaction of DPS itself was at about 182°C . The max exothermic heat peak of the reaction is lower, the reactivity of the reaction is higher. The max exothermic heat peak of the reaction between DPS and epoxy resin was lower than that of DPS itself, which indicated that the reactivity of the reaction between epoxy and DPS was higher. When DPS and epoxy resin were blended together, DPS would react with the epoxy first as demonstrated by the lower temperature of max exothermic peak.

The effect of catalyst concentration

The reaction of epoxy and DPS under different catalyst concentration (0.5%, 1% of total weight of the mixture) was depicted in Figure 5.

It can be seen clearly, in the presence of 1% catalyst, the max exothermic heat peak of the reaction between DPS and epoxy resin was at 160.4°C , while in the present of 0.5% catalyst, that was 172.7°C . In the presence of more catalyst, the max exothermic

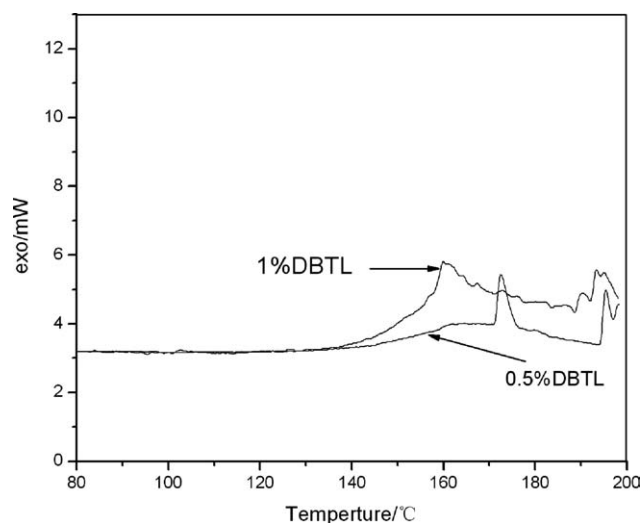


Figure 5 The curve about the effect of catalyst concentration on the reaction between DPS and epoxy resin.

heat peak of the reaction between DPS and epoxy resin was lower than that in the presence of less catalyst. That indicated the reactivity of the reaction between epoxy resin and DPS increased with the increment of amount of catalyst in the research scope. So the reaction between the DPS and epoxy resin could carry out at relatively lower temperature when more catalyst was added in the system in the research scope.

The activation energy of the reaction between DPS and epoxy resin

Kissinger method and Ozawa method were often used to calculate the activation energy, because those models could be used to calculate the reaction energy by different heating rates without knowing the mechanism of reaction previously.^{5,6,14-17} The estimation of the activation energy of the reaction between DPS and epoxy resin was conducted on DSC with the different heating rate by Kissinger method and Ozawa method respectively. The DPS mixed with epoxy resin and the pure DPS at present of the same catalyst concentration (1% weight ratio of materials) were carried out on DSC at four different heating rates (5, 10, 15, 20°C/min). The temperature of max endothermic peak was noted in the second column of the Table I. Ozawa method and Kissinger method were introduced to further compare the reactivity of the two systems.

The Ozawa equation was the eq. (1), this method offered a simple way to gain the activation energy.

$$E_a = \frac{-Rd \ln q}{1.052d(1/T_{\text{peak}})} \quad (1)$$

where q is the heating rate, T_{peak} is the peak exotherm temperature, E_a is the activation energy, and R is the universal gas constant.

The Kissinger method was described as the eq. (2), which was also introduced to calculate the activation energy.

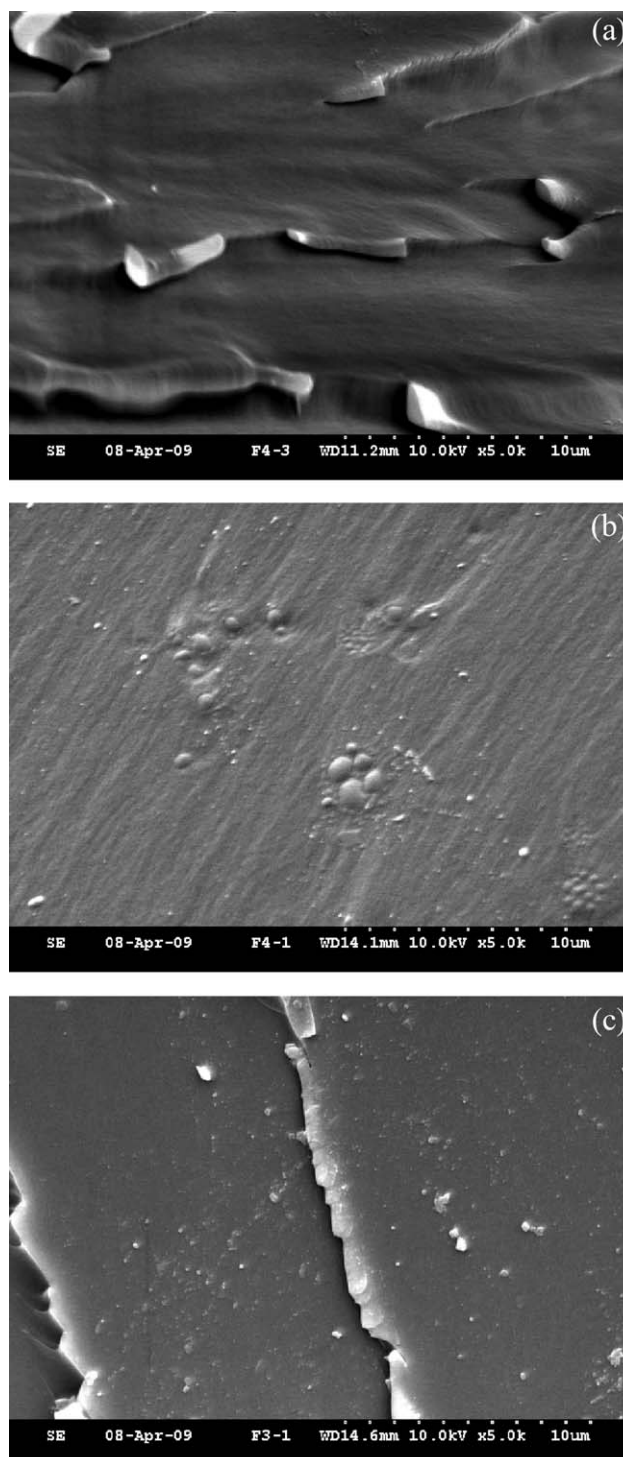


Figure 6 The morphology of the cross section of samples (a: E-51, b: E-51 + 30%DPS, c: E-51 + 30%DPS + 1% catalyst).

TABLE II
The Properties of the Cured Epoxy Resin

Sample code	T_{g_r} , °C	T_d 5%, °C		T_d 50%, °C		T_d 80%, °C		Char yield at 750°C, %		LOI, %
		N ₂	Air	N ₂	Air	N ₂	Air	N ₂	Air	
E51	161	386	396	439	440	770	673	20.5	9.20	21.8
E51/30DPS	163	324	317	418	429	A	789	31.0	23.3	29.6
E51/30DPS/1%DBTL	162	333	327	420	424	B	C	29.5	28.4	31.2

A, B, C couldn't be determined in the studied temperature range from 50–800°C, and the char yield at 800°C was 30.3, 28.2, 26.9 for A, B, C respectively.

$$\frac{d \ln\left(\frac{q}{T_{\text{peak}}^2}\right)}{d\left(\frac{1}{T_{\text{peak}}}\right)} = -\frac{E_a}{R} \quad (2)$$

where q is the heating rate, T_{peak} is the peak exotherm temperature, E_a is the activation energy, and R is the universal gas constant.

The peak exothermic temperature recorded with differential scanning calorimetry (DSC) and the data calculated by two methods concerned above were summarized in the Table I. The reaction activation energy was calculated by the slope of $\ln q - \frac{1}{T_{\text{peak}}}$ in Ozawa method, while it was gained by the slope of $\ln\left(\frac{q}{T_{\text{peak}}^2}\right) - \frac{1}{T}$ in the Kissinger method equation.

The activation energy of the reaction between epoxy resin and DPS was 63.3 kJ/mol by Kissinger method which was lower than 66.7 kJ/mol calculated by Ozawa method, respectively. This result was consistent with the previous reports.¹⁸ Comparison of the activation energies of the reaction of DPS with respect to epoxy resin and itself, it can be seen clearly that the activation energy of reaction between epoxy resin and DPS was lower, implying that the reactivity of reaction between epoxy resin and DPS was higher.

SEM

The morphology of the cross section of epoxy resin modified by DPS was examined on scanning electronic microscopy (Hitachi S-4300, Tokyo, Japan) and the cross section of all samples was amplified by 5000 times. SEM photographs of cross section's morphology of the cured epoxy resin were showed in Figure 6. Compared with the unmodified cured epoxy resin, the aggregation of DPS was determined by the SEM photographs whether the catalyst present or absent. It is possible that the reaction between epoxy resin and DPS did not occur in the presence and in the absence of catalyst. Under the present of catalyst, the aggregation of DPS in the matrix was less than that without catalyst, those may be explained that the transformation degree of DPS in epoxy resin was less in the presence of catalyst than in the absence of cata-

lyst, so there would be less DPS aggregation in the matrix in the presence of catalyst.

The thermal and flame retardant properties

The thermal properties of the epoxy resin modified by DPS were recorded on the DSC and TGA. The glass transition temperature and the temperature at 5, 50, and 80% weight loss in the nitrogen were summarized in the Table II. Compared with that of unmodified epoxy resin, the T_g s of epoxy resin modified with DPS wouldn't change practically in reality.

From the data in Table II, it is obviously seen that in the lower temperature range, the 5%, 50% weight loss temperature of the epoxy modified by the DPS were lower than their corresponding weight loss temperature of the pure epoxy resin, while in the higher temperature range, the 80% weight loss temperature of the epoxy resin modified by DPS was higher, compared with that of unmodified epoxy resin. The char yield at 750°C of the epoxy resin modified by DPS was higher than that of the unmodified epoxy resin both in the nitrogen and in the air. With 1% catalyst present, the char yield at 750°C in the air could increase to 28.4%, indicating that the thermal oxygen retardant was higher, comparing with cured unmodified epoxy resin. This phenomenon might result from that the degraded products of a hybrid containing phosphorus- and silica forming the protective layer which prevented degradation at the higher temperature.^{19,20} According to the condensation mechanism of the flame retardant, the higher char yields were, the higher flame retardant properties would be.²¹ The conclusion would be proved in the following discussion.

The limited oxygen index was a measuring method for the flame retardant, which was defined as the minimum oxygen content in oxygen and nitrogen mixture to sustain combustion.^{18,22,23} Compared with the unmodified epoxy resin, the LOI values of the epoxy resin modified by DPS with or without the catalyst were relatively higher, indicating more oxygen needed to support flammable after

the determined bar ignited. That is to say, the flame retardant of epoxy resin modified by DPS was higher than that of the pure epoxy resin. Table II also revealed that the limited oxygen index of the epoxy resin modified by DPS with the 1% catalyst was higher than that of the epoxy resin modified by DPS without catalyst. This could be explained that the DPS would be introduced to the network of the cured epoxy resin more easily with catalyst than without catalyst. According to the definition of limited oxygen index, the higher oxygen index is, the higher flame retardant property is. The flame retardant of epoxy resin was the highest in the present of 1% catalyst. This result was consistent with the conclusion aforementioned.

CONCLUSIONS

The hybrid containing phosphorus- and silica (DPS) was synthesized by the hydrolysis condensation. The structure and the molecular weight of DPS were confirmed by FT-IR, $^{29}\text{SiNMR}$ and GPC, respectively. The estimation of the activation energy of modification of epoxy resin by DPS was studied by Kissinger method and Ozawa method. The calculated results indicated that the activation energy of reaction between epoxy resin and DPS (63.3, 66.7 kJ/mol) was lower than that of DPS itself (94.9, 97.1 kJ/mol) in the presence of catalyst. The flame resistance of the cured epoxy resin modified by DPS was improved, while its thermal properties were not promoted in reality. The photographs of the cross section showed the DPS aggregated in the presence of catalyst in the epoxy resin matrix faster than that in the absence of catalyst. However, the mechanical properties of epoxy

resin is not studied in our paper, it will be further studied in the following research.

Reference

1. Weil, E. D.; Levchik, S. *J Fire Sci* 2004, 22, 25.
2. Levchik, S. V.; Weil, E. D. *J Fire Sci* 2006, 24, 345.
3. Levchik, S. V.; Weill, E. D. *Polym Int* 2004, 53, 1585.
4. Chiang, C. L.; Chang, R. C., *Adv Compos Mater Struct Part 1* 2007, 2, 334–335, 665.
5. Chiang, C. L.; Chang, R. C. *Compos Sci Technol* 2008, 68, 2849.
6. Zhang, X. H.; Liu, F.; Chen, S.; Qi, G. R. *J Appl Polym Sci* 2007, 106, 2391.
7. Ribera, G.; Mercado, L. A.; Galia, M.; Cadiz, V. *J Appl Polym Sci* 2006, 99, 1367.
8. Wang, Q. F.; Shi, W. F. *Polym Degrad Stab* 2006, 91, 1747.
9. Wang, C. S.; Shieh, J. Y. *Polymer* 1998, 39, 5819.
10. Wang, C. S.; Shieh, J. Y. *J Appl Polym Sci* 1999, 73, 353.
11. Yu, D.; Liu, W. Q.; Liu, Y. F. *Chem Lett* 2008, 37, 1118.
12. Dan Yu, W. L.; Yunfeng, L. *Polym Compos* 9999, NA 2009.
13. Han, S.; Kim, W. G.; Yoon, H. G.; Moon, T. J. *J Appl Polym Sci* 1998, 68, 1125.
14. Han, S.; Kim, W. G.; Yoon, H. G.; Moon, T. J. *J Polym Sci Part A-Polym Chem* 1998, 36, 773.
15. Wang, C. S.; Lin, C. H. *J Appl Polym Sci* 1999, 74, 1635.
16. Park, S. J.; Seo, M. K.; Lee, J. R. *J Polym Sci Part A-Polym Chem* 2000, 38, 2945.
17. Laza, J. M.; Vilas, J. L.; Mijangos, F.; Rodriguez, M.; Leon, L. M. *J Appl Polym Sci* 2005, 98, 818.
18. Gao, L. P.; Wang, D. Y.; Wang, Y. Z.; Wang, J. S.; Yang, B. *Polym Degrad Stab* 2008, 93, 1308.
19. Hoang, D.; Kim, J.; Jang, B. N. *Polym Degrad Stab* 2008, 93, 2042.
20. Chiu, Y. C.; Liu, F. Y.; Ma, C. C. M.; Chou, I. C.; Riang, L.; Chiang, C. L.; Yang, J. C. *Thermochimica Acta* 2008, 473, 7.
21. Shan, W. C.; Hsuan, L. C. *Polymer* 1999, 40, 4387.
22. Hou, M. H.; Liu, W. Q.; Su, Q. Q.; Liu, Y. F. *Polym J* 2007, 39, 696.
23. Toldy, A.; Anna, P.; Csontos, I.; Szabo, A.; Marosi, G. *Polym Degrad Stab* 2007, 92, 2223.