Study on Heat Resistance and Flame Retardation of Polyfunctional Epoxy–Silica–Phosphorus Hybrid Resins

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A novel epoxy resin modifier, phosphorus-containing epoxide siloxane (OPS), was prepared from the sol–gel reaction of GPTMS-DOPO, which was synthesized by the reaction of 3-glycidoxypropyltrimethoxysilane (GPTMS) with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). OPS with superfluous epoxide groups were confirmed by ^{29}Si NMR, gel permeation chromatography (GPC), elemental analysis, and Fourier transform infrared (FTIR) spectroscopy. Compared with those with no epoxide group and unmodified resins, the hybrid epoxy resins exhibited high glass-transition temperature (T_g), good limited oxygen index (LOI) and tensile strength.

Epoxy-based resins are commonly used for applications including adhesives, insulating materials as well as electrical packing materials. The growing importance of modern epoxy resins for the modification of thermal and flame properties reflects the increasing requirements for heat resistance and flame retardation of conventional epoxy resins.[1,2]

With regard to flame retardation of epoxies, phosphorus-containing compounds such as the 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) have attracted much attention for successfully increasing the flame retardation of epoxy resins,[3–8] while avoiding many disadvantages such as poor compatibility and release of toxic gases upon burning as compared with other common compounds. However, the application of such compounds often negatively affects glass-transition temperature (T_g) owing to the limit of chemical structures in molecular design during the introduction of phosphorus and the low crosslink density of the cured epoxy resin.

To compensate for the disadvantages of DOPO on T_g decrease, in accordance with previous reports,[9,10] silane coupling agents (GPTMS (3-glycidoxypropyltrimethoxysilane)) were selected to modify epoxy–phosphorus composites for better thermal stability. The use of either nonreactive or reactive silica–phosphorus composites with tailored chemical structures especially leads to optimized overall performance at low phosphorus contents.[11] However, there still exists a lack of understanding concerning the use of such reactive additives for effects on the heat-resistance and flame-retardation performance.

In this connection, a novel modifier for epoxy resins, reactive phosphorus-containing epoxide siloxane (OPS) (Scheme 1), was synthesized by the sol–gel reaction of GPTMS-DOPO, which is traced by EEW titration (experimental details in Supporting Information[13]). To avoid the gel formation during the storage, the dry tetrahydrofuran was incorporated into OPS with being put in a cool place to prevent from the strong sunshine and high temperature.

Compared with OPS, nonreactive epoxy modifier (OPS′), having no epoxide group in the structure, was prepared with DOPO and GPTMS in the stoichiometic ratio in the same way. The structure of OPS was confirmed by Fourier transform infrared (FTIR) and ^{29}Si NMR measurements and elemental analysis. Bisphenol-A diglycidyl ether (E-54), modified with OPS, was then characterized by differential scanning calorimetry (DSC), limited oxygen index (LOI) testing and tensile testing.

Table 1 show the compositions used in this study. Mixtures of E-54 having varying additives were cured with 4,4′-diaminodiphenylmethane (DDM) (Scheme S1, in Supporting Information[13]) as curing agent in a stoichiometric ratio (epoxide group to amino group equivalent ≈ 1:1) at 90 °C (3 h), 150 °C (2 h), and 175 °C (1 h) (Scheme S1). The composite references based on the nonreactive epoxy systems (OPS′) were already with an identical experimental procedure, and epoxy resins containing DOPO only were obtained at 160 °C for 5 h according to ref 12.

The EEW was analyzed during the reaction to trace the reaction between DOPO and GPTMS. For the DOPO-GPTMS system the EEW at 0% conversion is 308 g/eq, and the EEW at 100% conversion is 462 g/eq theoretically. The EEW increases with time and reaches a theoretical value at 250 min, implying the reaction is near completion after 250 min.

The FTIR spectrum is shown in Figure 1. After the reaction, no absorption peak at 2384 cm^{-1} (P–H) was observed in OPS curve, indicating that the reaction is near completion, which is consistent with the EEW titration. In addition, the existence of the absorption peaks at 1587 (Ph), 1466 (P–Ph), and 1203 (P=O) implied that the resulting OPS contained the cyclic DOPO structure. The characteristic absorption peak at 915 cm^{-1} of the epoxide ring implied that reactive groups still were left in the system. The network formation of OPS was measured with ^{29}Si NMR analysis, as shown in Figure 2 and Scheme 1. Three major signals at about −59.4, −50.4, −41.8 ppm were assigned to nonhydroxy-substituted silica (T_3), monohydroxy-substituted silica (T_2), and dihydroxy-substituted silica (T_1), respectively. According to the spectrum, the absorbtion peak integration area is $T_3 > T_2 > T_1$ with small differences, indicating the conversion of the gel reaction of silanol groups is moderate and silica network is formed to some extent. The molecular

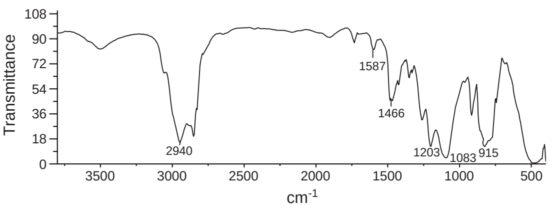


Figure 1. FTIR spectrum of OPS.

Table 1. Flammability, mechanical and thermal analysis of the cured epoxy resins

Code	E54/DOPO /OPS(OPS′) (g/g/g)	GPTMS:DOPO (molar ratio)[b]	P contents /wt %	Si contents /wt %	T_g/°C[e]	LOI	Tensile strength /MPa
1	100/0/0	0	0	0	152.9	22	45.1
2	98/2/0	0	0.3[c]	0	146.2	22	46.5
3	96/0/4[a]	1	0.3[d]	0.25	155.3	22	46.4
4	80/0/20	6	0.3[d]	2.0	163.9	28	46.8
5	96/4/0	0	0.6[c]	0	137.1	23	46.8
6	92/0/8[a]	1	0.6[d]	0.5	159.97	24	57.5
7	80/0/20	3	0.6[d]	1.8	175.9	28	58.3
8	94/6/0	0	0.9[c]	0	125.5	24	47.1
9	88/0/12[a]	1	0.9[d]	0.75	165.13	26	61.8
10	80/0/20	2	0.9[d]	1.4	183.6	29	62.1

[a]The weight of OPS′. [b]The molar ratio of GPTMS and DOPO in the preparation of OPS. [c]Calculated by the formula: (weight of DOPO/total weight of the system) × 14.34 wt % × 100%. [d]Measured by the elemental analysis. [e]Mesured with DSC at a heating rate of 10 °C/min in nitrogen.

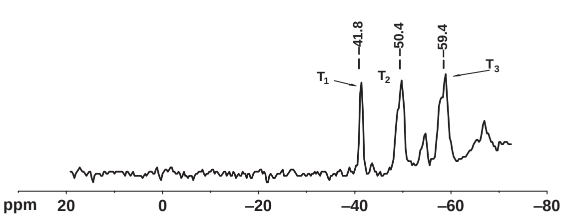
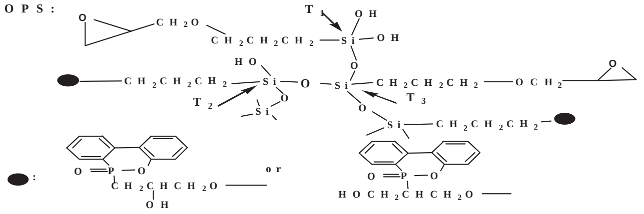


Figure 2. ^{29}Si NMR spectrum of OPS.



Scheme 1. Structure of OPS.

weight was also determined by GPC. The main distribution peaks at molecular weight of 5898 and 189 appeared in diagram of OPS and the oligomer, respectively. (Figure S1, in Supporting Information).

The analysis results of values of T_g and LOI of the cured resins are given in Table 1. As shown, both the nonreactive OPS′ and reactive OPS could enhance T_g as compared to the neat E-54 especially to the epoxy resins containing DOPO only. Obviously, the T_g increase of OPS-containing samples is more marked than those of OPS′.

For the OPS-containing systems, three possible factors significantly contributed to T_g increase are the restriction of chain motion of the resins from the formed silica network, the greater number of crosslink sites from the reaction of superfluous epoxide groups of OPS with the stoichiometric DDM and the rigid DOPO structure, respectively. The second factor is also the reason why OPS led to higher T_g of based resins than nonreactive OPS′. The greater the proportion of GPTMS added, the greater the number of epoxide groups left, and a great opportunity for crosslinking and hence, a higher T_g. The further confirmation made by the sequence on T_gs of samples: code 4 < 7 < 10.

The LOI and tensile strength results were shown in Table 1. With OPS charged into the epoxy resins, the LOI value was raised from 22 to 29, demonstrating a significant improvement in the flame retardation of epoxy resins. The tensile strength shows that the OPS-modified epoxy also possess desirable mechanical properties.

A novel epoxy resin modifier, phosphorus-containing epoxide siloxane (OPS), was used to improve the thermal stability and flame retardation of epoxy resins. The chemical structure of OPS was confirmed by FTIR, GPC, and ^{29}Si NMR. Compared with nonreactive silica-phosphorus composites (OPS′), the reactive type OPS exhibited more optimized effects on T_g enhancement. This work was provided a novel approach to the easy preparation of epoxy resins with superior properties suitable for use as electronic materials.

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References and Notes

1 C.-S. Wang, Z.-K. Liao, *Polym. Bull.* **1991**, *25*, 559.
2 C.-S. Wang, J.-Y. Shieh, *J. Appl. Polym. Sci.* **1999**, *73*, 353.
3 J.-Y. Shieh, C.-S. Wang, *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 369.
4 C. H. Lin, C. S. Wang, *Polymer* **2001**, *42*, 1869.
5 M. Hussain, R. J. Varley, M. Mathus, P. Burchill, G. P. Simon, *J. Mater. Sci. Lett.* **2003**, *22*, 455.
6 J.-Y. Shieh, C.-S. Wang, *Polymer* **2001**, *42*, 7617.
7 C. S. Wang, C. H. Lin, *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 3903.
8 R. M. Perez, J. K. W. Sandler, V. Altstädt, T. Hoffmann, D. Pospiech, M. Ciesielski, M. Döring, *J. Mater. Sci.* **2006**, *41*, 341.
9 Y.-L. Liu, C.-S. Wu, Y.-S. Chiu, W.-H. Ho, *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2354.
10 M. Ochi, T. Matsumura, *J. Polym. Sci., Part B: Polym. Phys.* **2005**, *43*, 1631.
11 R. M. Perez, J. K. W. Sandler, V. Altstädt, T. Hoffmann, D. Pospiech, M. Ciesielski, M. Döring, *J. Mater. Sci.* **2006**, *41*, 341.
12 M. Hou, W. Liu, Q. Su, Y. Liu, *Polym. J.* **2007**, *39*, 696.
13 Supporting Information is also available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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