

# Study on Flame-retardant Mechanism of Epoxy Resin containing Polyvinylphenylsilsesquioxane

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## ABSTRACT

*In this study, a novel flame retardant polyvinylphenylsilsesquioxane (PVP) was added into epoxy resin (EP) to prepare EP/PVP (FREP) composites. The results of cone calorimeter measurement showed that in comparison with virgin EP, the peak heat release rate (PHRR) and total heat release (THR) of FREP were reduced by 27.3% and 10.4%, respectively. Moreover, the thermal degradation behavior of FREP was studied by the Kissinger and Ozawa-Flynn-Wall methods. The results suggested that the addition of PVP greatly enhanced the thermal stability of EP in the final stage, which could be attributed to that the branched silicone with vinyl and phenyl accelerated the formation of an insulating carbon layer and improved the flame retardancy of EP composites, because the char layer played an important role for the flame-retardant behavior of polymer system.*

**KEYWORDS:** *Flame retardancy, Epoxy resin, Polyvinylphenylsilsesquioxane, Cone calorimeter; Mechanism*

## 1. INTRODUCTION

Epoxy resins (EP) are the most important class of thermosetting resins and find applications in the fields of adhesive, coating, electronic/electrical insulation, and composite applications because of their low cost, good chemical and electrical resistance, superior mechanical properties, low shrinkage upon

curing and outstanding adhesion properties<sup>[1-4]</sup>. However, one of the main problems of these systems is their flammability. In order to fulfill the requirements of flammability tests for applications in electric/electronics, transportation, and construction industries, much work has been done to improve the flame retardancy of epoxy resins and a great progress has been achieved so far<sup>[5-8]</sup>.

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J. Polym. Mater. Vol. **36**, No. 4, 2019, 381-389

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DOI : <https://doi.org/10.32381/JPM.2019.36.04.7>

Traditionally, these include inorganic flame retardants, such as aluminum trioxide, ammonium polyphosphate, and red phosphorus; halogenated flame retardants, primarily based on chlorine and bromine; organophosphorus flame retardants, mainly being phosphate esters; and nitrogen based organic flame retardants. Halogenated flame retardants have been proven to be effective on epoxy resin in that they have high flame retardant efficiency, are low cost, and require only a low loading. However, it can produce large amounts of toxic smoke during combustion, which poses a great threat to human safety and significantly restricts their applications in many areas<sup>[9-12]</sup>.

Aluminum hydroxide (ATH), a very important halogen-free flame retardant, has received much attention because of its environmental friendliness, low toxicity, low cost, low smoke, and corrosive gas is not produced upon combustion. However, more than 50 wt% of aluminium hydroxide is generally required for compliance with various flame retardant standards for polymers. Moreover, the addition of fillers in such high amounts often leads to a processing problem and marked deterioration in mechanical properties of the composites<sup>[13-15]</sup>.

Phosphorus containing flame retardants act both in the vapor phase and the condensed phase, not only can capture free radical to suppress combustion but also promote char formation on polymer surface. Phosphorus-containing compounds are the most common halogen-free flame retardants, which produce less toxic gas and smoke than halogen-containing compounds. Although they can act in both gas and condensed phase which

results in better flame retardancy than other halogen-free flame retardants, the high loadings (over 30 wt%) are necessary for most phosphorus-containing flame retardants, such as ammonium polyphosphate, melamine polyphosphate and aluminium phosphinates, to achieve UL94 V-0 rating in PA6<sup>[16-18]</sup>. Moreover, most commercialized phosphorus-containing flame retardants, for example red phosphorus and ammonium polyphosphate, are hydrophilic and hygroscopic, which will lead to remarkable hydrolysis of moisture sensitive composites during processing<sup>[19-21]</sup>.

Because of high heat-resistance, nontoxicity, and nongeneration of toxic gases in the case of fire, silicone derivatives have been used as flame retardants in EP. Moreover, the addition of silicone derivatives did not cause an environment hazard during combustion, and thus, the research efforts on the silicone flame retardants are increasing<sup>[22-24]</sup>. As reported in the literature, various silicones, for example, aminosilicone, methylsilicone, epoxysilicone and phenylsilicone have been used in flame-retardation systems for epoxy resins<sup>[25-27]</sup>. However, the effect of vinylsilicone on the flame retardancy and thermal stability of epoxy resin was seldom reported. In combustion, the vinyl groups in flame retardant could react with the main polymer chains, and then promoted quickly the formation of char layer.

In the present work, the effectiveness of the vinylsilicone, as a flame retardant in epoxy resin, has been studied by cone calorimeter measurement. The thermal degradation kinetics was analyzed by the Kissinger and Ozawa-Flynn-Wall methods with the aid of TGA and compared with that of the standard formulation.

## 2. EXPERIMENTAL

### 2.1 Materials

Polyvinylphenylsilsequioxane (PVP)<sup>[28]</sup>, synthesized by hydrolysis and condensation reaction of vinyltrimethoxysilane (VTMS) and phenyltrimethoxysilane (PTMS), consisted of 75 mol% PTMS and 25 mol% VTMS units. The molecular weight of PVP was 2680 g/mol. EPON 826 with an epoxy equivalent weight of 178-186 grams was supplied by Hexion and used as received. The hardener, Jeffamine D230, with an amine equivalent weight of 60 grams, was supplied by Huntsman Corporation and also used as received.

### 2.2 Preparation of epoxy composites

Briefly, the EP/PVP (FREP) composite was prepared as follows: 5g PVP (different contents, such as 1, 3, 7, 9 wt% were also used) was added into EPON 826 (71.25 g), respectively, and dispersed by a mechanical stirrer for 30 min. Subsequently, D230 (23.75 g) was added into the mixture and stirring for 30 min. After degassed in vacuum for 10 min to remove any trapped air, the samples were cured at 80 °C for 2 h and post cured at 135 °C for 2 h. For comparison, virgin EP was also prepared at same processing condition.

### 2.3 Characterization and measurement

Cone calorimeter measurement was performed on an FTT cone calorimeter (Britain) according to ASTM

E1354 with heat flux of 50 kW/m<sup>2</sup>. The dimensions of each specimen was 100 × 100 × 3 mm<sup>3</sup>. The limiting oxygen index (LOI) was measured on an oxygen index instrument JF-3 produced by Jiangning Analysis Instrument Factory and performed according to GB2406-93. Dynamic mechanical thermal analysis (DMA) was determined using a Rheometric Scientific SR-5000 dynamic mechanical analyzer. Data were collected from 40 °C to 140 °C at a scanning rate of 5°C/min. Thermogravimetric analysis (TGA) was carried on a TA instrument Q5000 thermogravimetric analyzer. The sample (about 10 mg) was heated from 50 °C to 600 °C at a set heating ramp rate in nitrogen atmosphere.

## 3. RESULTS AND DISCUSSION

### 3.1 Flame retardancy

The flame retardancy of virgin EP and EP composite with 5 wt% PVP were studied by cone calorimeter tests. Cone calorimeter test provides a useful method for studying the flammability properties of epoxy materials. Heat release rate (HRR), especially the peak HRR (PHRR), has been found to be an important parameter to evaluate fire safety. In comparison with virgin EP, the PHRR of FREP with 5 wt% PVP loading was reduced by 27.3%, as shown

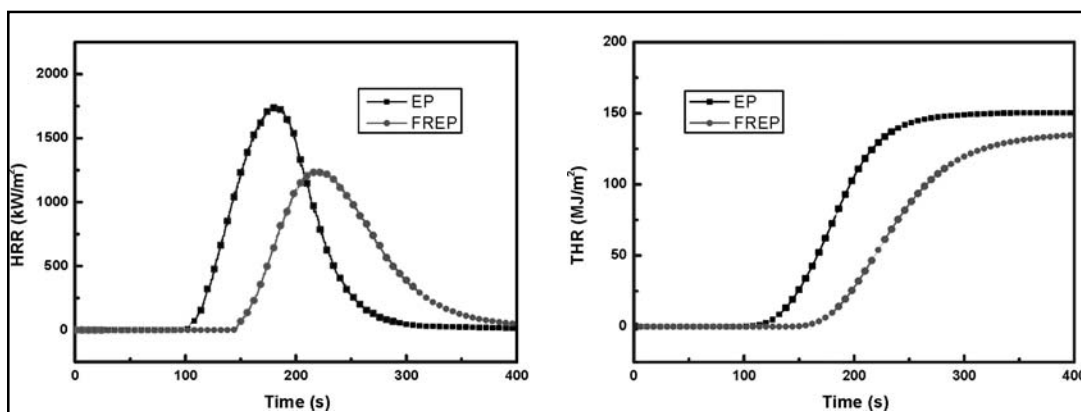


Fig. 1. HRR and THR curves of EP composites

in Fig. 1. And the time-to-PHRR was increased from 181s of virgin EP to 220s, which indicated that the addition of flame retardant PVP improved the thermal stability of EP and decreased the speed of combustion. Moreover, the total heat release (THR) of FREP was also decreased by 10.4% over that of virgin EP, which revealed that the flame retardancy of FREP was higher than that of the virgin EP.

As shown in Fig. 2, the LOI of virgin epoxy was 19.2. When adding the PVP in the virgin epoxy, the LOI value significantly increased. The LOI of

composites increased to 26.0 when the PVP in the composites reached 5 wt%. When the amount of PVP in the composites increased to 9 wt%, the LOI of composites was 27.2. It was suggested that flame retardant PVP could improve the flame retardancy of EP composites.

### 3.2 Methanical properties

The storage modulus and tan delta of virgin EP and EP/5 wt% PVP (FREP) composites were carried out through DMA measurement, as shown in Fig. 3. The storage modulus curve of FREP composite was closed to the virgin EP.

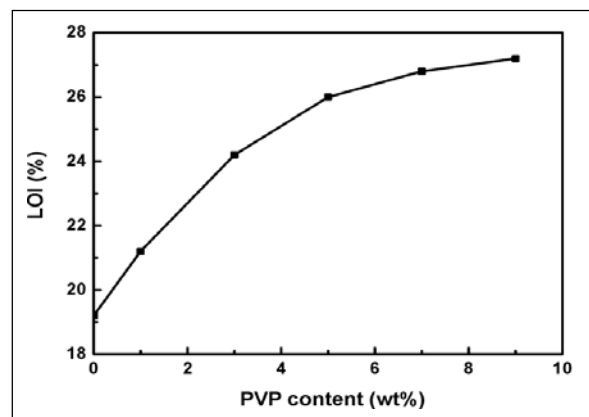


Fig. 2. The LOI of EP composites

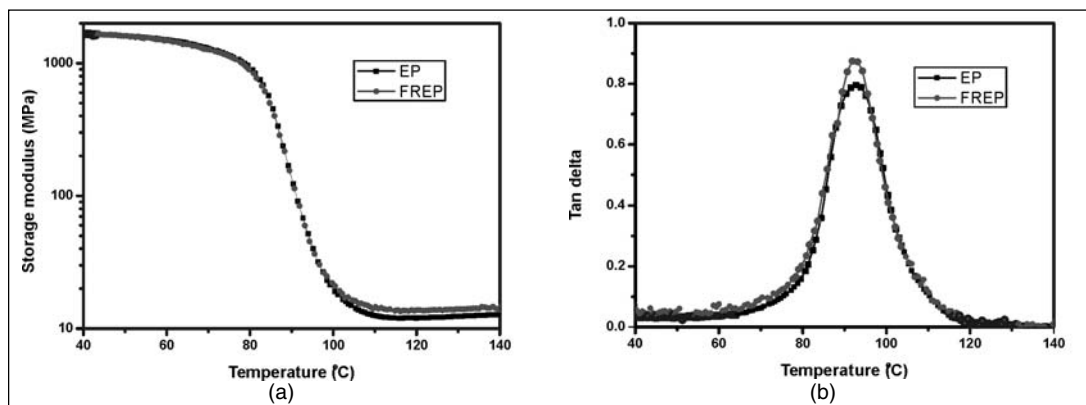


Fig. 3 Storage modulus (a) and tan delta (b) curves for EP and FREP in the DMA test

Moreover, the glass transition temperature ( $T_g$ ) was widely determined by the tan delta peak temperature in DMA. As shown in Fig. 3(b), there was a lightly decrease in  $T_g$  (ca.  $0.8^\circ\text{C}$ ) at 5 wt% of PVP than that of virgin EP, indicating the movements of polymer chain wasn't restricted by the incorporation of PVP.

### 3.3 Thermal stability

The onset degradation temperature ( $T_{5wt\%}$ ) can be defined as the temperature at which the

weight loss is 5%. The relative thermal stability of the samples can be evaluated by the  $T_{5wt\%}$ , the temperature of maximum rate of weight loss ( $T_{max}$ ) and the residual char yield at  $600^\circ\text{C}$ . The typical TGA and DTG curves for virgin EP and FREP (5 wt% PVP) composites under nitrogen atmosphere were presented in Fig. 4, and these data was listed in Table 1.

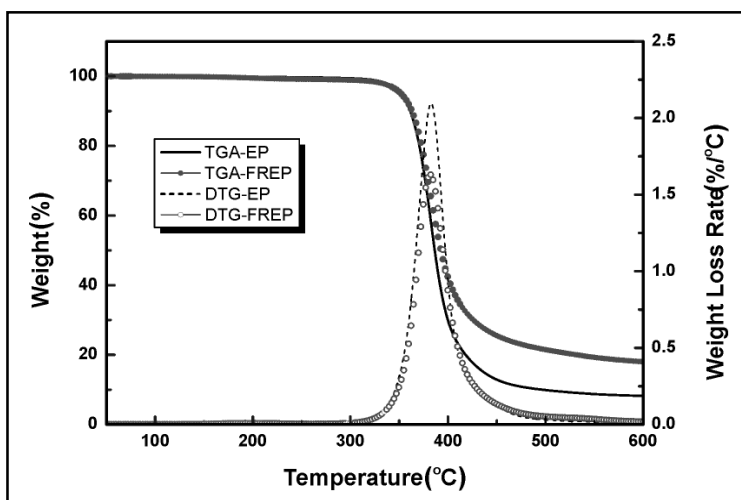


Fig. 4. Thermal stability of EP composites

TABLE 1 TGA data of EP composites

	Temperature ( $^\circ\text{C}$ )		Peak rate (wt%/°C)	Residual char (wt%)
	$T_{5wt\%}$	$T_{max}$		
EP	351.7	382.6	2.10	8.27
FREP	351.9	381.7	1.63	18.02

The  $T_{5wt\%}$  for virgin EP was  $351.7^\circ\text{C}$ , and its TGA curve showed only one weight-loss stage. The stage was in the temperature range of  $350\text{--}450^\circ\text{C}$  corresponding to a single DTG peak at

$382.6^\circ\text{C}$  ( $T_{max}$ ) and the residual char yield at  $600^\circ\text{C}$  was about 8.27%. For the FREP, the  $T_{5wt\%}$  was similar with virgin EP, indicating that the addition of PVP had little influence on the

initial thermal degradation process of virgin EP. Both of the  $T_{max}$  and peak rate of FREP were lower than those of virgin EP. Furthermore, it could be obtained that the amounts of residual char shifted from 8.27 wt% (for EP) to 18.02 wt% (for FREP) of the initial mass, which was about 10 wt% more than that of virgin EP. This result further confirmed that the branched PVP with vinyl and phenyl could induce the cross-linking reactions during the thermal degradation process and promoted the formation of the char layer, which played an important role for the increasing of EP flame retardancy.

### 3.4 Thermal degradation kinetics

The Kissinger expression is as follows [29]:

$$\ln\left(\frac{\beta}{T_{max}^2}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT_{max}} \quad (1)$$

Where,  $\beta$  is the heating rate,  $T_{max}$  is the temperature of the peak rate,  $A$  is the absorbance,  $R$  is a gas constant,  $E$  is the activation energy for the thermal degradation process.

The TGA and DTG curves for EP and FREP at different heating rates were shown in Fig. 5.

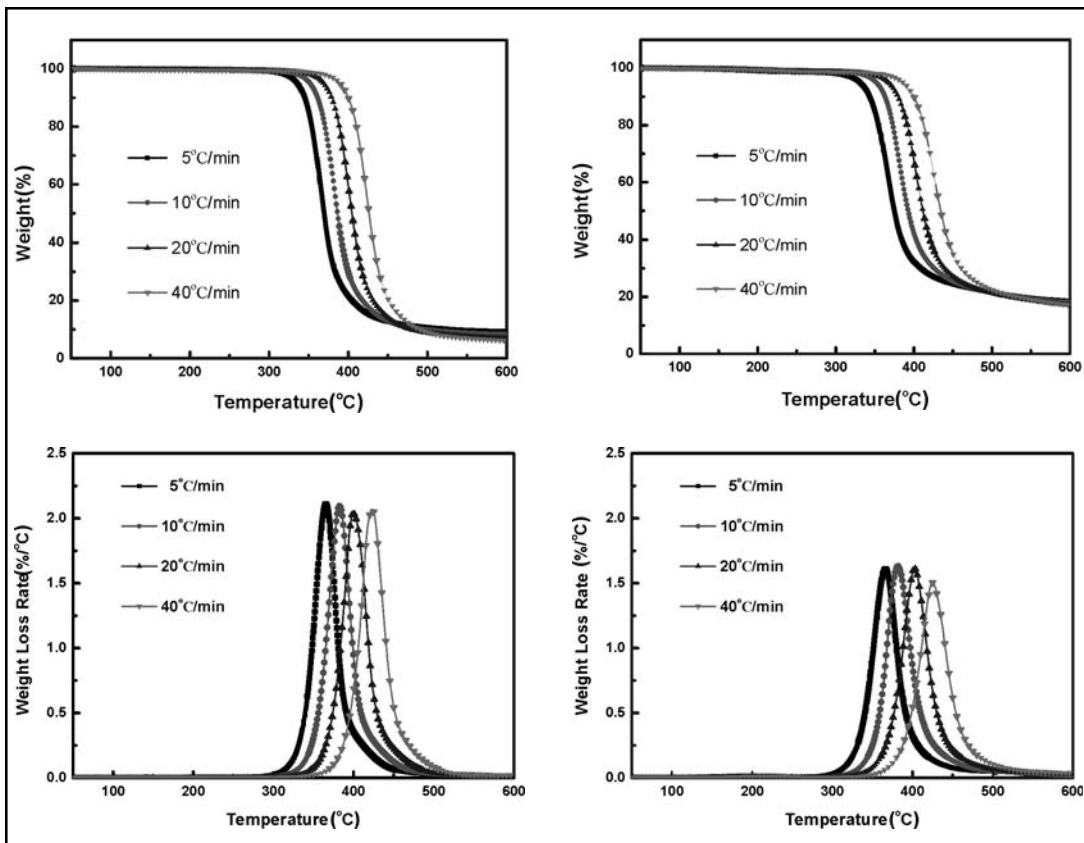


Fig. 5. TGA and DTG curves of EP (a) and FREP (b) composites

Using Kissinger's Equation (1), the degradation activation energies for EP and FREP were calculated by the plots of  $(\ln \beta/T^2_{max})$  vs  $1/T_{max}$  and the data was listed in Table 2. It was

clear that the activation energy of FREP was 119.4 kJ/mol, which was light lower than that of virgin EP (122.1 kJ/mol).

TABLE 2. Kinetic data for the degradation of EP and FREP by Kissinger method

	$T_{max}$ (°C)				$E$ (kJ/mol)	$\ln A$ (1/min)
	5°C/min	10°C/min	20°C/min	40°C/min		
EP	365.4	382.6	400.1	423.5	122.1	14.4
FREP	366.5	381.7	402.8	424.9	119.4	13.9

The Flynn-Wall-Ozawa method is an integral method also independent of the degradation mechanism. The equation can be expressed as follows [30-31]:

$$\lg(\beta) = \lg AE/g(\alpha) R - 2.315 - 0.457 \frac{E}{RT} \quad (2)$$

Where,  $\alpha$  is the degree of conversion,  $g(\alpha)$  is the integrated forms of mechanism.

According to equation (2), the conversion degrees ( $\alpha$ ) of 2%, 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 95% and 98% for the degradation of EP and FREP were selected. As shown in Fig. 6, the activation energy at various  $\alpha$  could, therefore, be obtained from a plot of  $\lg(\beta)$  against  $1/T$ .

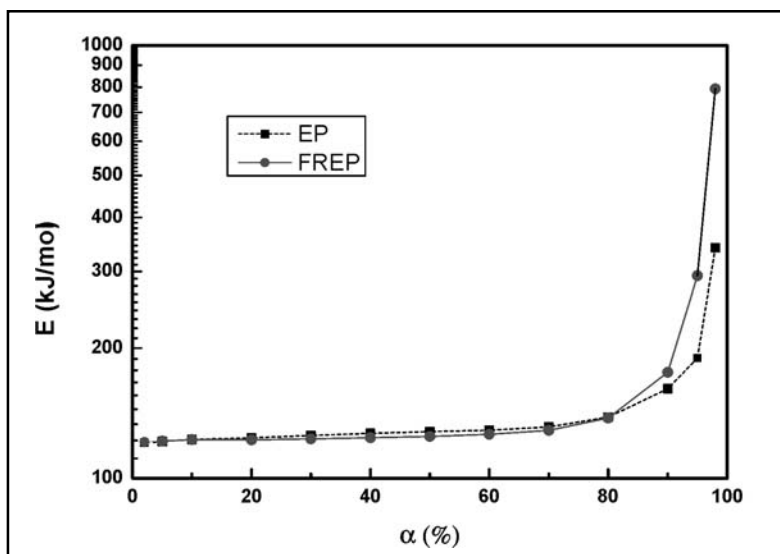


Fig. 6. Activation energy curves of EP and FREP by Flynn-Wall-Ozawa method

It could be noticed that the activation energies of thermal degradation increased with the increase of the conversion degree for EP and FREP. Two distinct regions could be observed from Fig. 6, the first for values of  $\alpha$  up to 80%, where E presented a slightly increase and the second ( $\alpha > 80\%$ ), where E presented a marked increase. Moreover, it could be seen that the activation energies of FREP were light lower than those of virgin EP in the first region, which was agreed well with the resulting data of Kissinger method. However, in the second region, the activation energies of FREP were great higher than those of virgin EP, indicated that the addition of PVP greatly enhanced the thermal stability of EP in the final stage. Thus, It might be concluded that the branched silicone with vinyl and phenyl accelerated the formation of an insulating char layer and improved the flame retardancy of EP composites, because the char layer played an important role for the flame-retardant behavior of polymer system.

#### 4. CONCLUSIONS

In summary, the flame retardant polyvinylphenylsilsesquioxane (PVP) was added into epoxy resin (EP) to prepare EP/PVP (FREP) composites. Cone calorimeter measurement showed that the peak heat release rate (PHRR) and total heat release (THR) of FREP were reduced by 27.3% and 10.4%, respectively, in comparison with virgin EP. Moreover, the thermal degradation kinetics of FREP system was studied by the Kissinger and Ozawa-Flynn-Wall methods. The results suggested that the addition of PVP greatly enhanced the thermal stability of EP in the final stage, which could be attributed to that the branched silicone with vinyl and phenyl

accelerated the formation of an insulating char layer and improved the flame retardancy of EP composites.

#### ACKNOWLEDGEMENTS

The authors wish to thank the Ningbo Natural Science Foundation(2019A610032), National Undergraduate Training Program for Innovation and Entrepreneurship(201911058006), Chongben Foundation(2019010) and Ningbo Municipal Program for Leading and Top-Notch Talents for financial support.

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Received: 10-09-2019

Accepted: 10-10-2019