

# Nonisothermal Degradation Kinetics for Epoxy Resin Systems Containing Polymethylphenylsilsesquioxane

Jiangbo Wang, Yeyong Zhan, Jianghua Fang, Haoqi Gao

Department of Chemical Engineering, Ningbo University of Technology, Ningbo 315016, China

Received 31 January 2011; accepted 24 March 2011

DOI 10.1002/app.34550

Published online 9 August 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** The thermal degradation behaviors of polymethylphenylsilsesquioxane/epoxy resin (PMPSQ/EP) systems were investigated by thermogravimetric analysis (TGA) under nonisothermal conditions in nitrogen atmosphere. During nonisothermal degradation, Kissinger's and Flynn-Wall-Ozawa's methods were both used to analyze the thermal degradation process. The results showed that a remarkable increase of activation energy was observed in the presence of PMPSQ, which indicated that the addition of PMPSQ retarded the thermal degradation of EP.

Flynn-Wall-Ozawa's method further revealed that PMPSQ significantly increased the activation energy of EP thermal degradation especially in the early and final stage of thermal degradation process, which illustrated that the PMPSQ stabilized the char layer and improved the flame retardancy of EP. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1024–1031, 2012

**Key words:** epoxy resin; polymethylphenylsilsesquioxane; thermal degradation; kinetics; activation energy

## INTRODUCTION

Commonly used epoxy resins (EPs) are obtained by mixing oligomers based on diglycidyl ether of bisphenol A (DGEBA), and using aromatic or aliphatic amines as curing agent. These formulations exhibit a broad range of thermal and mechanical properties depending on the molecular weights of the epoxy oligomers in the backbone, the functionality of the hardener, and on curing conditions.<sup>1–3</sup> However, one of the main problems of these systems is their flammability.

To fulfill the requirements of flammability tests for applications in some fields, such as electrotechnics/electronics, transportation, and construction industries, flame retardants have to be used. It is reported that EPs can be modified with boron, phosphorus, silicone, polyurethanes, melamine, and montmorillonite, etc.<sup>4–7</sup> Among them, the incorporation of silicone is considered as a promising method owing to its enhanced properties over the base polymer and its environmental friendliness. Recently, silicone derivatives especially polysilsesquioxane have been used as flame retardants in EP because of high heat-resistance, nontoxicity, and nongeneration of toxic gases in case of fire.<sup>8–11</sup> Various methoxy-phenyl or ethoxy-phenyl polysiloxanes at 10 wt % loadings showed V-0 ratings in EP cured with phenol-

formaldehyde novolac, and methyl-phenyl silicone copolymerized with some siloxane units showed V-0 ratings in a similar resin at 9 wt %.<sup>12,13</sup> Ni and Zheng<sup>14</sup> prepared polyphenylsilsesquioxane/EP composites by two strategies. The results showed that the organic-inorganic composites displayed improved thermal stability and flame retardancy in terms of thermogravimetric analysis (TGA).

Based on above literatures, it can be anticipated that the present researches concentrate on the flame-retardant behaviors of EP system containing silicone derivative.<sup>15–17</sup> There is no systematical study on the flame-retardant mechanism and pay little attention on the thermal degradation behaviors of flame-retardant EP. In practice, the flame-retardant property and processing of polymer materials strongly depend on their degradation behavior and thermal stability. So, it is important to study the thermal degradation processing.

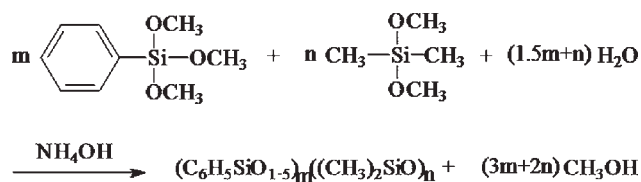
In this work, we present results of our studies on the thermal degradation behaviors of polymethylphenylsilsesquioxane/EP systems to understand the combustion process, and try to reveal the flame-retardant mechanism of polymethylphenylsilsesquioxane/EP system through the TGA measurement under nonisothermal conditions in nitrogen atmosphere.

## EXPERIMENTAL

### Materials

The EP used was the DGEBA from Shanghai Resin, China, with a mass per epoxy equivalent of 0.51 eq/

Correspondence to: J. Wang (jiangbowang@163.com).



Scheme 1 Synthesis of PMPSQ.

100 g. Epoxy curing agent was 4,4'-diamino-diphenyl methane (DDM) from Shanghai Resin, China. All components were used as received without further purification.

The synthesis of polymethylphenylsilsesquioxane (PMPSQ) consisting of 81.5 mol % phenyltrimethoxysilane (PTMS) and 18.5 mol % dimethyldimethoxysilane (DMDS) units, prepared by hydrolysis and condensation reaction in the presence of  $\text{NH}_4\text{OH}$  was accomplished according to the following procedure.<sup>18</sup> The reaction was carried out in a 250-mL four-neck glass reactor equipped with a mechanical stirrer and a refluxing condenser at atmospheric pressure and 20°C. The monomers (DMDS and PTMS) and deionized water were introduced into the reactor, and then an ammonia solution was added into the mixture quickly. After the mixture was slowly stirred for 4 h, the stirrer was stopped. Then, the condensation reaction was kept for 4 h, and the products were generated. The reaction condition in feed as following: monomers/water ratio (vol) is 1/5, PTMS/DMDS ratio (mol) is 80/20 and  $\text{NH}_4\text{OH}$  concentration in reaction system is 0.04 wt %. The copolymerization reaction is described by the following formula:

The above reaction product was coagulated in a 3 wt % aqueous calcium chloride solution, via slow addition of 1 part product to 1.5 part of aqueous calcium chloride solution. The resulting product was filtrated and the filter was repeatedly washed with deionized water. Then the sample was dried under a vacuum for 24 h.

Values of molecular weights of PMPSQ:  $M_w$  is  $4.968e + 4$  g/mol and  $M_n$  is  $7.597e + 3$  g/mol. It has been confirmed that the end groups of PMPSQ were mainly methyls and phenyls with a few hydroxyls by the NMR spectrum and Fourier transform infrared spectroscopy methods. The ratio of organic groups to silicon atoms (R/Si), which was used to indicate the branched extent of a polysilsesquioxane structure was 1.18.

### Preparation

PMPSQ was dispersed in DGEBA, followed by the addition of the curing agent DDM. The mixtures were cured at 100°C for 2 h and postcured at 150°C for 2 h in an oven. The typical weight percentage of PMPSQ in epoxy composite was 10 wt %. Then the

TABLE I  
Flame Retardancy of EP Systems with Different Contents of PMPSQ

Systems	S <sub>0</sub>	S <sub>3</sub>	S <sub>7</sub>	S <sub>10</sub>	S <sub>15</sub>	S <sub>20</sub>
LOI	20.2	22.8	25.6	28.2	29.4	29.8
UL-94(rating)	-	V-2	V-2	V-1	V-1	V-1

S<sub>n</sub>, The subscript numbers are the content of PMPSQ added to the EP.

cured specimens of flame retardant EP were obtained. The compositions and flame retardancy of the investigated materials are shown in Table I.

### Characterization

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 of "Plastics-Determination of flammability by oxygen index." Flame retardancy of test specimens was examined in accordance with UL94 method. TGA was carried out using a TA Q600 thermal analyzer and around 4 mg samples were placed into an aluminium pan. The sample was heated from 50 to 700°C at a set heating rate of 5, 10, 20, or 40°C/min. All the tests were performed in a nitrogen or air flow with a flow rate of 20 mL/min. Scanning electron microscopy (SEM) experiments were performed with a Hitachi S-4800 scanning electron microscope. Samples for SEM were the residue after the LOI test and sputtering the surface with gold.

### Thermal degradation theory

The kinetics of thermal transformation of a solid state chemical reaction is generally based on the assumption that the reaction rate is:

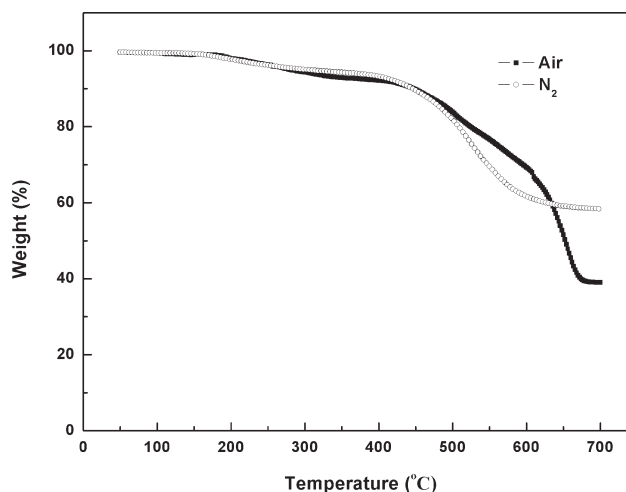


Figure 1 TGA curves of PMPSQ samples in different atmospheres.

TABLE II  
TGA Data of PMPSQ Samples in Different Atmosphere

Atmosphere	Temperature (°C)				Peak rate (%/min)	Residues (wt %)
	$T_{1\%}$	$T_{5\%}$	$T_{10\%}$	$T_{\max}$		
Air	144	281	448	653	6.2	39.0
N <sub>2</sub>	160	303	445	519	2.8	58.3

$$r = \frac{da}{dt} = kf(a) \quad (1)$$

where  $f(a)$  is the reaction model,  $a$  the degree of conversion,  $k$  the temperature dependent rate constant,  $t$  the time and  $r$  the rate of degradation.  $k$  is normally assumed to obey the Arrhenius equation:

$$k = A \exp(-E/RT) \quad (2)$$

where  $E$  is the activation energy of the kinetic process,  $A$  the pre-exponential factor,  $T$  the temperature, and  $R$  the universal gas constant.

Then, the rate of degradation, which is dependent on the temperature and the weight change of the sample, can be expressed as:

$$\frac{da}{dt} = Af(a) \exp(-E/RT) \quad (3)$$

Equation (3) is also used in its integral form, which for isothermal conditions becomes

$$\ln t = E/RT - \ln[A/g(x)] \quad (4)$$

For nonisothermal degradation, eq. (3) becomes

$$\frac{da}{dT} = (A/\beta)f(a) \exp(-E/RT) \quad (5)$$

where  $\beta$  is the heating rate ( $\beta = \frac{dT}{dt}$ ),  $g(x)$  is the integrated forms of mechanism ( $g(x) = \int_0^x \frac{da}{f(a)}$ ).

1. Kissinger's method<sup>19</sup>: The Kissinger's expression is as follows:

$$\ln\left(\frac{\beta}{T_{\max}^2}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT_{\max}} \quad (6)$$

where  $T_{\max}$  is the temperature of the peak rate. The peak rate temperatures determined at different heating rates allow the activation energy to be calculated by the Kissinger's method. Plotting the natural logarithm of  $\ln(\beta/T_{\max}^2)$  against the reciprocal of the absolute temperature ( $1/T_{\max}$ ), the slope of the resulting line is given by  $-E/R$ , which allows the value of  $E$  to be obtained.

2. Flynn-Wall-Ozawa's method<sup>20,21</sup>: The equation of Flynn-Wall-Ozawa's method can be expressed as follows:

$$\lg(\beta) = \lg AE/g(a)R - 2.315 - 0.457 \frac{E}{RT} \quad (7)$$

The above equation shows that  $\lg(\beta)$  is linearly proportional to  $1/T$ . The activation energy for any particular degree of degradation can then be determined by a calculation of the slope from the  $\lg(\beta)-1/T$  plots.

## RESULTS AND DISCUSSION

### Thermal stability of PMPSQ

TGA curves in different atmospheres of PMPSQ sample at a heating rate of 10°C/min are shown in Figure 1 and the characteristic weight loss data are listed in Table II. It can be seen that the temperature of 1 wt % weight loss for PMPSQ in air is 144 and 160°C for the PMPSQ in nitrogen atmosphere, which indicates that the weight loss onset temperatures of PMPSQ thermal degradation is affected by the atmosphere.

The weight loss prior to 180°C in air atmosphere is 1.3 wt %, this being mainly associated with volatilization of low-molecular-weight products. A weight loss of 6.7 wt % is observed at 180–400°C in air due to condensation reaction of residual silanol groups, followed by a large weight loss of 52.9 wt % from 400 to 680°C assigned to degradation of methyl and phenyl groups.<sup>22</sup> The PMPSQ in nitrogen

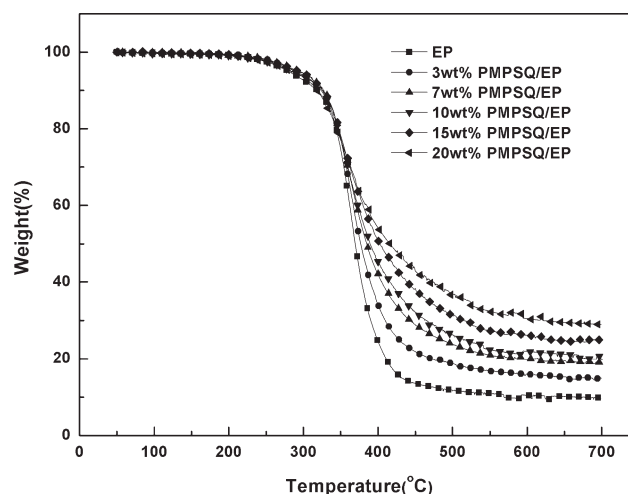


Figure 2 TGA curves of EP systems with various PMPSQ in N<sub>2</sub>.

**TABLE III**  
TGA Data of Epoxy Resin Systems with Various PMPSQ in N<sub>2</sub>

PMPSQ content (wt %)	Temperature (°C)				Peak rate (%/min)	Residue (wt%)
	T <sub>1%</sub>	T <sub>5%</sub>	T <sub>50%</sub>	T <sub>max</sub>		
0	212.4	280.4	369.6	366.4	14.2	9.8
3	217.8	290.6	376.8	365.5	11.7	14.9
10	223.6	293.7	402.7	360.9	7.3	24.8

atmosphere exhibits a weight loss of 6.7 wt % at a temperature below 400°C attributable to residuals silanol groups and low-molecular-weight products. A rapid weight loss of 34.7 wt % occurs from 400 to 680°C. Total weight loss in air atmosphere is 61.0 wt %, which is increased by 19.3 wt % than that in nitrogen atmosphere.

### Thermal analysis of EP/PMPSQ systems

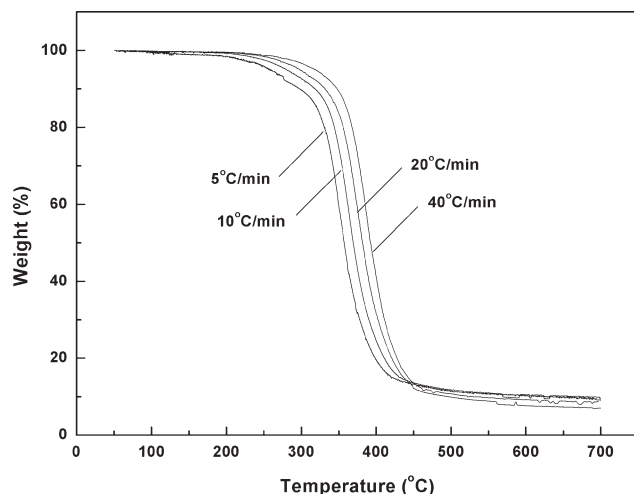
The importance of studying thermal degradation, understanding the processes occurring during thermal stress as well as the parameters affecting the thermal stability of EP are essential to effectively design EP having tailor-made properties suitable for the particular environment where they are to be used.

The TGA curves of EP and PMPSQ/EP systems observed in a nitrogen atmosphere are given in Figure 2, and the characteristic weight loss data are listed in Table III. It can be seen that the temperature of 1 wt % weight loss for EP is 212 and 224°C for the 10 wt % PMPSQ/EP system, which indicates that the weight loss onset temperatures of EP thermal degradation tend to increase with the increment of PMPSQ content. As the end groups of PMPSQ to be used contain residual silanol groups, these residual end groups in polymer chain could induce con-

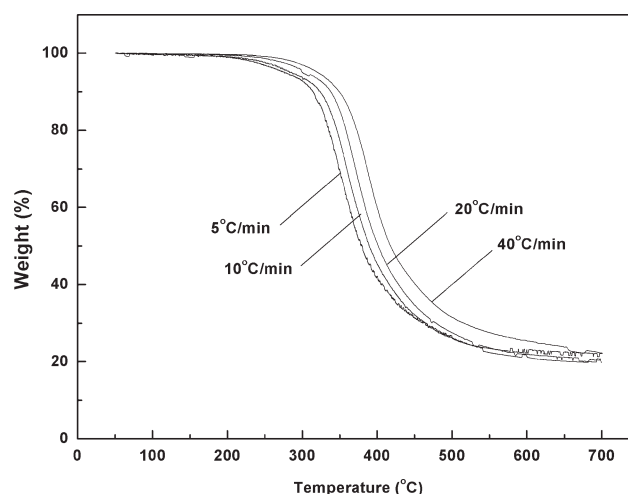
densation reaction with EP chain, which is a low activation energy process.

The TGA curves of EP and PMPSQ/EP systems all exhibit one step thermal degradation process, and the major degradation process occurs between 320 and 420°C. As evidenced from the curves and data, it can be obtained that the temperature of 50 wt % weight loss for 10 wt % PMPSQ/EP system is 402.7 and 369.6°C for the EP in nitrogen atmosphere, which indicates that the thermal stability of EP was enhanced by the PMPSQ. Meanwhile, PMPSQ widens the temperature range of EP thermal degradation process and the peak rate of weight loss curves decreases with the rising of PMPSQ content. It has been confirmed that in the major degradation step, Si—O bond and Si—Ph or Si—CH<sub>3</sub> bond of PMPSQ tend to form some silyl radicals or siloxane derivatives, which can react with EP or the evolved products of EP, and correspondently promote cross-linking reactions in the PMPSQ/EP systems and retard further pyrolysis during the thermal degradation process.

After the major thermal degradation of the PMPSQ/EP system, a much slower degradation process is followed, and the degradation residues of the PMPSQ/EP system at 700°C in nitrogen atmosphere are higher than that of EP. With the content of PMPSQ increasing, the amount of solid residues shifts from 9.8 wt % (for EP) to 24.8 wt % (for 10 wt

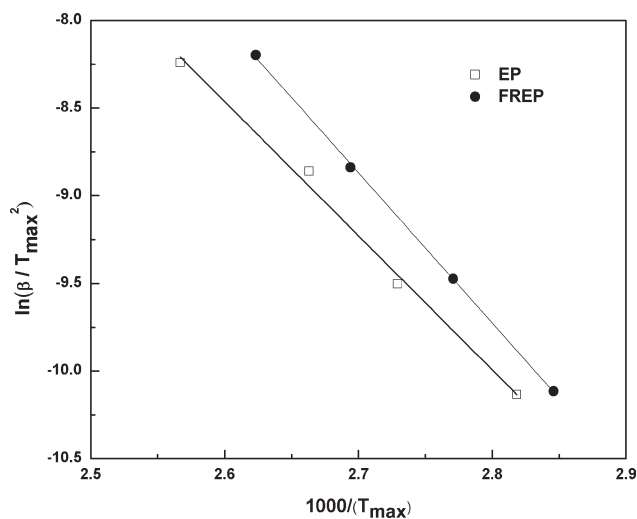


**Figure 3** TGA curves of EP at different heating rates in N<sub>2</sub>.



**Figure 4** TGA curves of FREP at different heating rates in N<sub>2</sub>.





**Figure 5** The curves of  $a = \frac{w_0 - w_t}{w_0 - w_\infty}$  vs.  $\left(\frac{\beta}{T_{\max}^2}\right)$  of EP and FREP.

% PMPSQ/EP) of the initial weight. This result further confirms that the branched PMPSQ containing methyl and phenyl groups can induce crosslinking reactions and promote the formation of the char during the thermal degradation process, which may play an important role for the flame retardancy of PMPSQ/EP systems.

### Nonisothermal degradation kinetics

The flame retardancy of a polymer is closely related to its thermal degradation behavior. So, to clarify the mechanism of the flame retardant, understanding the degradation behavior of a polymer is necessary.<sup>23</sup> The TGA curves of EP and 10 wt % PMPSQ/EP (FREP) systems at different heating rates in a nitrogen atmosphere are shown in Figures 3 and 4. All curves indicate that systems exhibit only single weight loss stage in the temperature range of 200–600°C.

With increasing the heating rate from 5 to 40°C/min, the TGA curves of EP shift to higher temperatures and then the onset degradation temperature enhances. The same trend is observed for FREP. Furthermore, it can be obtained from the figures that the maximum weight loss rate of FREP is lower than that of EP and the FREP is more stable than the EP,

which is in accord with the change of onset degradation temperature between EP and FREP.

Kinetic parameters of thermal degradation processes can be used to characterize the thermal stability of polymer and the activation energy ( $E$ ) can be considered as a semiquantitative factor.<sup>24</sup> According to the TGA curves in Figures 3 and 4, the thermal degradation processes of EP and FREP systems can be studied by the Kissinger's and Flynn-Wall-Ozawa's methods, respectively.

First, according to the eq. (6), the plots of  $\ln(\beta/T_{\max}^2)$  versus  $1/T_{\max}$  are drawn and shown in Figure 5, which indicates that there is a good linear relationship between  $\ln(\beta/T_{\max}^2)$  and  $1/T_{\max}$ . Then, the thermal degradation activation energy for EP and FREP systems can be obtained from the slope of corresponding straight line, and the pre-exponential factors are calculated from intercepts of the straight lines for samples. The calculation results for EP and FREP predicted by the Kissinger's method are shown in Table IV.

It can be found that the activation energy for the thermal degradation process of FREP (71.33 kJ/mol) is higher than that of EP (63.66 kJ/mol), and their fitting consistencies are both more than 99%. This means that the flame retardant PMPSQ is effective to increase the thermal degradation activation energy and retards the thermal degradation process of EP. It may be concluded that the branched silicone with methyl and phenyl accelerate the formation of an insulating char layer and improve the flame-retardant behaviors of FREP system, as the char layer plays an important role for the flame retardancy of FREP system.

Because of the relative limitation of the Kissinger's method, its data can only provide information at the peak temperatures. To make this possible, the TGA data is further studied by Flynn-Wall-Ozawa's kinetic analysis method. Flynn-Wall-Ozawa's method is one of the integral methods that can determine the activation energy without knowledge of reaction order and differential data of TGA. With the application of that method, more informative kinetic parameters are obtained.

Based on the datum of Figures 3 and 4 and the equation of  $a = \frac{w_0 - w_t}{w_0 - w_\infty}$  ( $w_0$  the initial weight of the sample,  $w_t$  the sample weight at any temperature  $t$ ,  $w_\infty$  the final sample weight), the degree of conversion as a function of temperature relative to the

**TABLE IV**  
Kinetic Data for Thermal Degradation of EP and FREP by Kissinger's Method

Systems	$T_{\max}$ (°C)				E (kJ/mol)	lgA (1/min)	$\gamma$ (%)
	5°C/min	10°C/min	20°C/min	40°C/min			
EP	346.5	366.4	375.5	389.6	63.66	20.39	99.17
FREP	341.1	360.9	371.2	381.2	71.33	23.35	99.95

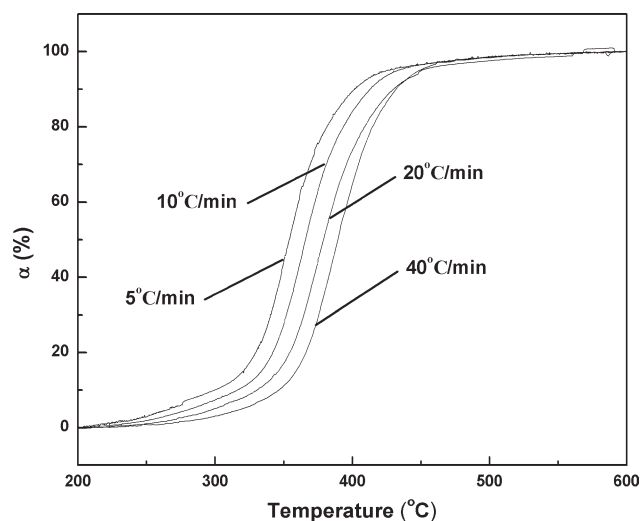


Figure 6 Conversion of EP in function of temperature.

degradation of both EP and FREP systems can be obtained, as shown in Figures 6 and 7.

According to eq. (7), the plots of  $\lg(\beta)$  versus  $1/T$  can be obtained and the typical  $\lg(\beta)$  versus  $1/T$  plots from 0.1 to 0.9 conversion for the thermal degradation of EP and FREP systems are shown in Figure 8 and 9. It can be seen that  $\lg(\beta)$  is linearly proportional to  $1/T$ . The activation energy for any particular degree of conversion can then be determined by a calculation of the slope from the plots. The activation energies of degradation calculated from these plots by Flynn-Wall-Ozawa's method are shown in Figure 10.

It can be observed that the activation energy of EP enhances with the increasing of the degree of conversion. The trend of FREP systems is rather similar and their values both increase from 36.65 to 93.50 kJ/mol. Moreover, the curves of EP and FREP systems both tend to exhibit three stages of activation

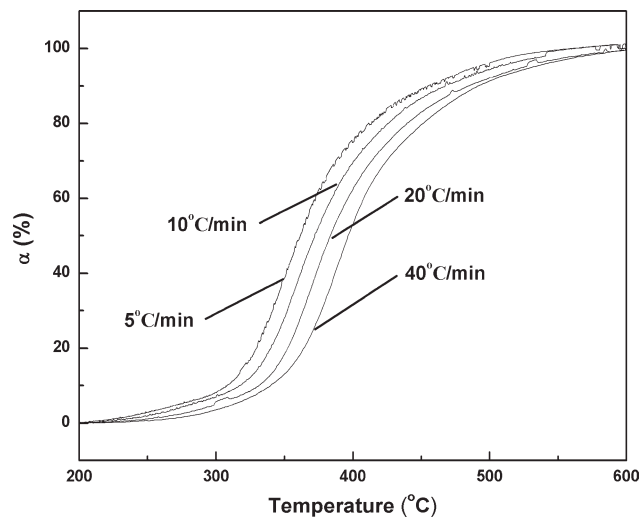


Figure 7 Conversion of FREP in function of temperature.

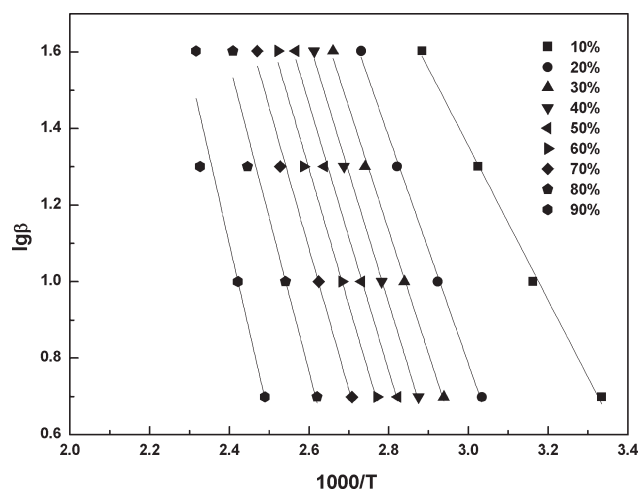


Figure 8 The curves of  $\lg(\beta)$  vs.  $1/T$  of EP.

energies in degradation. In the early stage, the weight loss of the light degradation compounds occurs such as carbon dioxide and the EP completes this stage before 20% weight loss generally. Then, the activation energies of FREP are higher than that of EP at lower degree of conversion. The resulting data, together with the analysis of the activation energies in this stage, indicates that the FREP system has better thermal stability than EP when the temperature is rising.

After the early stage, the activation energy of FREP rises as thermal degradation process and slowly increases until the degree of conversion is 50%. It can be obtained through the comparing of EP and FREP systems that their activation energy curves are closed each other, which means the thermal stability of above systems are rather similar in the middle stage. In the final stage, EP and FREP systems are different in the final stage (>50%) of the thermal degradation process. the addition of PMPSQ further increases the activation energy in EP thermal

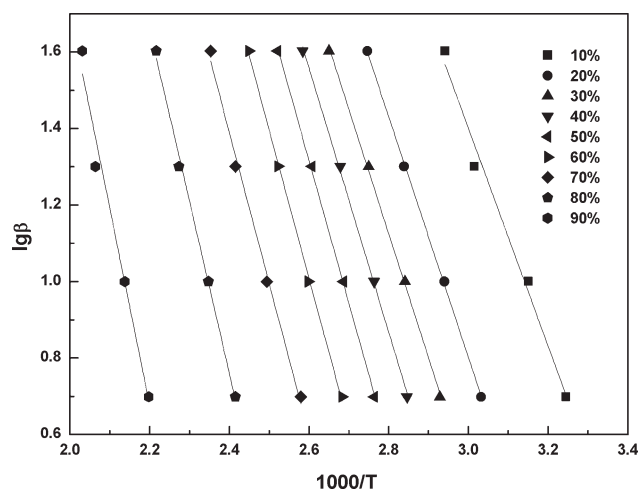
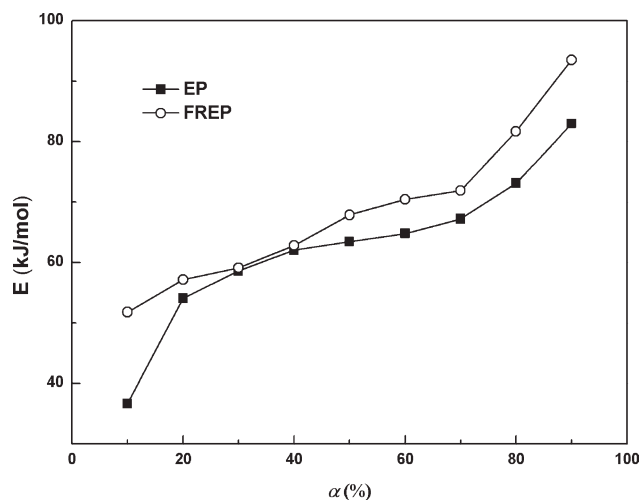


Figure 9 The curves of  $\lg(\beta)$  vs.  $1/T$  of FREP.



**Figure 10** Activation energy curves of EP and FREP systems by Flynn-Wall-Ozawa's method.

degradation, indicating that the flame retardant retards the degradation behaviors of EP. It reveals that the PMPSQ has the function of stabilizing the char layer and improving the flame retardancy of EP in the final period of thermal degradation process. In other words, the addition of PMPSQ causes less degradation rate of the EP system in the early and final stages. Furthermore, the kinetic parameters for EP and FREP progressively increase with increasing the degree of conversion, indicating that the thermal degradation mechanism varies with the weight loss.

Through the above resulting data, it can be found that the activation energy of EP and FREP systems in the thermal degradation calculated by the Kissinger's and Flynn-Wall-Ozawa's methods respectively are very close to each other. Therefore, the above two methods can be used to study the thermal stability behaviors and flame-retardant mechanism of EP and FREP systems.

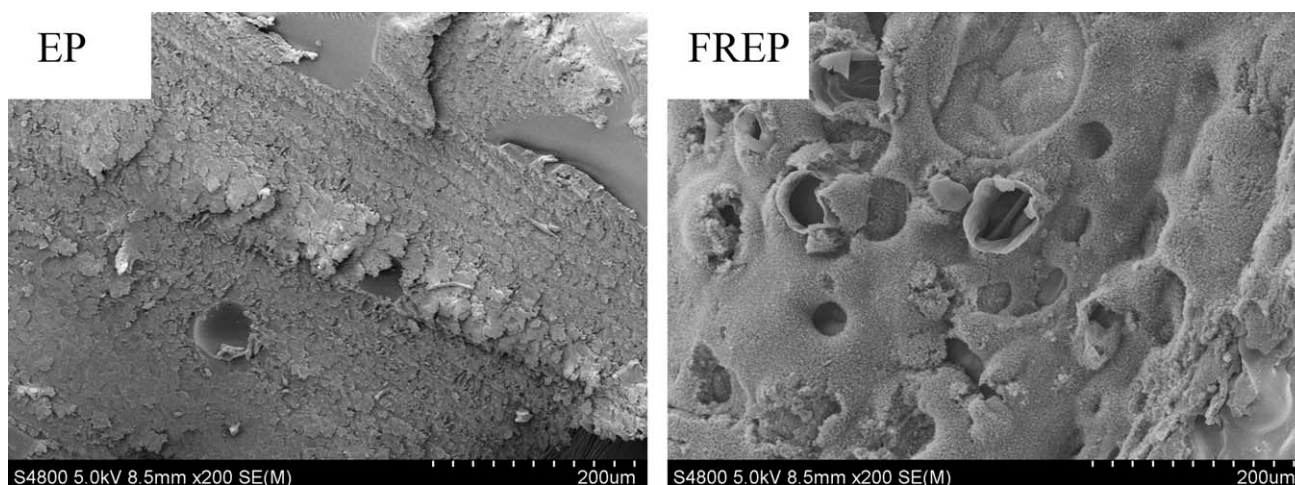
## SEM analysis

It is important to study the relationship of the combustion appearance, the structure of the residual char and the thermal stability of polymer. In burning, an instantaneous char formed on the surface of the material acts as thermal insulation facilitating the extinguishing of the flame. It prevents combustible gases from feeding the flame and also separates oxygen from the burning material. The carbonaceous char can be formed and destroyed repetitively in burning. Therefore, the residue is the final char.<sup>25</sup>

The morphology of the char on FREP differs from that of the EP system. Figure 11 shows the photographs of the residues char of the EP and FREP systems from LOI tests by SEM. The char of FREP during the combustion process becomes rapid swelling and forms spherical closed cells that seem to cut off the gases efficiently, but the char of the EP compound is an uncontinuous char layer, which has a lot of hole and sealing of the gases is not sufficient. The thermal stability of the char on FREP system is high in flame retardancy and even the thin char layer could cut off the gases, as the PMPSQ on the surface limit the heat transfer to the inside and prevent the temperature of system from rising.

## CONCLUSIONS

The thermal degradation behaviors of EP system containing PMPSQ have been investigated by TGA under nonisothermal conditions. Kissinger's and Flynn-Wall-Ozawa's methods were successfully used to deal with the thermal degradation process. The results showed that a remarkable increase of activation energy in the thermal degradation process was observed in the presence of PMPSQ, which indicated that the addition of PMPSQ retarded the thermal



**Figure 11** Residue chars morphologies of EP and FREP systems.

degradation of EP. Flynn-Wall-Ozawa's method further revealed that PMPSQ increased the activation energy of EP thermal degradation in the early and final stage, which illustrated that the PMPSQ stabilized the char layer and improved the flame retardancy of EP in the early and final period of thermal degradation process.

## References

1. Levchik, S. V.; Weil, E. D. *Polym Int* 2004, 53, 1901.
2. Marc, A. H.; Paul, M. L.; Damian A. *J Am Chem Soc* 1997, 119, 2749.
3. Omrani, A.; Rostami, A. A.; Ghaemy M. Kinetics and thermal properties of epoxy resin cured with Ni(II)-tris-(O-phenylenediamine) bromide. *J Appl Polym Sci* 2006, 101, 1257.
4. Park, C.; Choi, J.; Choi, B. US Pat.6,534,601, (2003).
5. Liu, Y. L.; Wu, C. S.; Chiu, Y. S.; Ho, W. H. *J Polym Sci, Part A: Polym Chem* 2003, 41, 2354.
6. Wu, K.; Song, L.; Hu, Y.; Lu, H. D.; Kandola, B. K.; Kandare, E. *Prog Org Coat* 2009, 65, 490.
7. Wu, C. S.; Liu, Y. L.; Chiu Y. S. *Polymer* 2002, 43, 4277.
8. Zhou, W. J.; Yang, H.; Guo, X. Z.; Lu, J. *Polym Degrad Stab* 2006, 91, 1471.
9. Iji, M.; Serizawa S. *Polym Adv Technol* 1998, 9, 593.
10. Wang, J. B.; Xin, Z. *e-Polymers* 2010, No. 1, 1.
11. Wang, W. J.; Perng, L. H.; Hsiue G. H. *Polymer* 2000, 41, 6113.
12. Yamamoto, K.; Yamaya, M.; Yamamoto, A.; Kobayashi, Y. US Pat. 6,184,312, (2001).
13. Itagaki, A.; Yamaya, M.; Kobayashi Y. US Pat. 6,326,425, (2001).
14. Ni, Y.; Zheng S. X. *J Polym Sci: Part A: Polym Chem* 2006, 44, 1093.
15. Ramírez, C.; Abad, M. J.; Barral, L. *J Therm Anal Calorim* 2003, 72, 421.
16. Hsiue, G. H.; Wang, W. J.; Chang F. C. *J Appl Polym Sci* 1999, 73, 1231.
17. Cao, Y. M.; Sun, J.; Wu J. S. *Polym-Plast Technol Eng* 2002, 41, 247.
18. Wang, J. B.; Xin, Z. *J East China Univ Sci Technol* 2008, 34, 694.
19. Kissinger, H. E. *Anal Chem* 1957, 29, 1702.
20. Flynn, J. H. *Polym Lett* 1966, 4, 323.
21. Flynn, J. H. *Polym Lett* 1967, 5, 191
22. Wang, J. B.; Xin Z. *J Appl Polym Sci* 2010, 115, 330.
23. Zhou, W.; Yang H. *Thermochimica Acta* 2007, 452, 43.
24. Vyazovkin, S.; Sbirrazzuoli N. *Macromol Rapid Commun* 2006, 27, 1515.
25. Jia, S. J.; Zhang, Z. C.; Du, Z. W.; Teng, R. R.; Wang, Z. Z. *Radiat Phys Chem* 2003, 66, 349.