

The Effect of Polyepoxyphenylsilsesquioxane and Diethyl Bis(2-hydroxyethyl)aminomethylphosphonate on the Thermal Stability of Epoxy Resin

Rongfan Zhou, Xintong Wu, Xiaohui Bao, Fangyi Wu, Xiaoshuai Han, and Jiangbo Wang*

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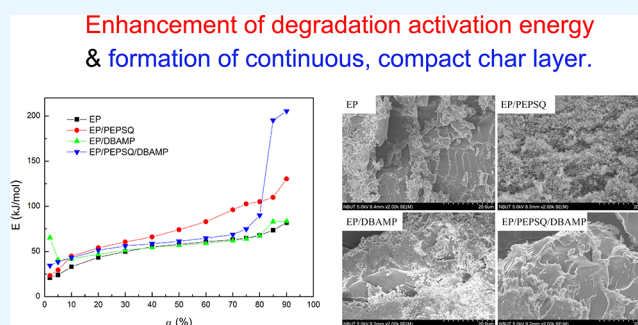
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ABSTRACT: Polyepoxyphenylsilsesquioxane (PEPSQ) and diethyl bis(2-hydroxyethyl) aminomethylphosphonate (DBAMP) can improve the flame retardancy of epoxy resin (EP). In this paper, the results of the limiting oxygen index (LOI) and UL94 tests exhibited that PEPSQ and DBAMP had good synergistic flame retardancy. The non-isothermal degradation kinetics of EP containing PEPSQ and DBAMP was investigated by the Kissinger and Flynn–Wall–Ozawa methods. The results of the Kissinger method displayed that the addition of two flame retardants, PEPSQ and DBAMP, can slightly enhance the activation energy of EP, indicating that the additives delayed the thermal degradation of EP. The Flynn–Wall–Ozawa method further confirmed that the activation energy of EP during the whole thermal degradation process can be significantly increased by addition of the two flame retardants PEPSQ and DBAMP. When the degree of conversion exceeded 80%, the increase was more significant. This illustrated that the flame retardants finally achieved the purpose of improving the flame retardancy of EP by stabilizing the char layer.



1. INTRODUCTION

Epoxy resin (EP) has been widely used in various fields such as chemical industry, electronics industry, transportation, and national defense construction due to its excellent chemical resistance, bonding properties, mechanical properties, and dimensional stability.^{1–7} However, the limiting oxygen index (LOI) of EP is 19.8, which is a highly flammable material. In fire, the EP material is the most flammable and produces a lot of smoke and toxic gas, thus limiting its application. Therefore, there is a need to modify EP by adding flame retardants.^{8–13}

Among various flame retardants, phosphorus-containing organic compounds are one of the most efficient and considered as the most promising alternatives to halogenated flame retardants. This is mainly because the products of phosphorous compounds decomposed by heat have a very strong dehydrating effect, which can make the surface of the covered polymer carbonized, form the char layer to isolate the air, and thus play the role as a condensation phase flame retardant. At present, phosphorus-containing organic compounds of various structures have been reported as flame retardants for EP.^{14–22} A phosphorus-containing organic compound, diethyl bis(2-hydroxyethyl) aminomethylphosphonate (DBAMP), has attracted intensive attention due to its high rate of performance and price.²³ Silicone flame retardants not only endow EP with excellent flame retardancy but also improve the processing properties, heat resistance, and so on. In addition, they do not release toxic gas during combus-

tion.^{24–27} For the purpose of better flame retardancy of EP, the synergistic effects on the flame retardancy of phosphorus and silicone have been investigated.²⁸

In previous studies, the flame retardancy of the EP system containing phosphorous and silicone flame retardants was studied more, but the thermal stability of composites was hardly studied. In fact, it is very necessary to investigate the thermal degradation process of composites, because the flame retardancy and processability of polymers in practice are closely related to their thermal stability. Because their products have good physical and mechanical properties, chemical resistance, and electrical insulation, 4,4'-diamino-diphenyl methane (DDM) and diglycidyl ether of bisphenol A (DGEBA) have become two important monomers in EP industrial production.^{29–32} In this study, they were used as raw materials to prepare bisphenol A-type EP. Polyepoxyphenylsilsesquioxane (PEPSQ) is a reactive flame retardant, which can be chemically bonded with the main chain of EP. Moreover, PEPSQ has excellent char formation performance in the combustion.^{33,34} Therefore, PEPSQ was used as a typical

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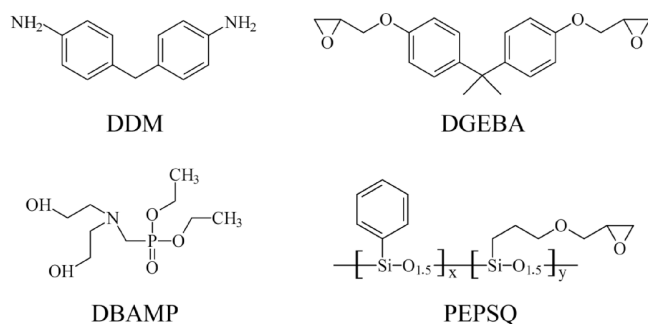


silicone-containing flame retardant and phosphorus-containing flame retardant DBAMP to improve the flame retardancy of EP. Subsequently, the non-isothermal degradation kinetics of EP containing PEPSQ and DBAMP was investigated by thermogravimetric analysis (TGA).

2. EXPERIMENTAL SECTION

2.1. Materials. DDM and DGEBA with a mass per epoxy equivalent of 0.51 eq/100 g were purchased from Shanghai Resin Co., Ltd. (Shanghai, China). The DBAMP flame retardant was supplied by Zhejiang Wansheng Chemical Co., Ltd. (Taizhou, China). PEPSQ was synthesized by hydrolysis and condensation reaction with alkali as catalyst.³⁵ The molecular weight and content of the epoxy group were 2.8916×10^4 g/mol and 0.0105 eq/100 g, respectively. The chemical structures of DDM, DGEBA, DBAMP, and PEPSQ are shown in Scheme 1.

Scheme 1. Chemical Structures of Raw Materials



2.2. Preparation. The flame retardants (PEPSQ and DBAMP, the total weight percentage was 10 wt %) were added in DGEBA, and then the curing agent DDM was added and stirred. The mixtures were cured at 100 and 150 °C for 2 h in an oven, respectively. The flame-retardant EP specimens are listed in Table 1.

2.3. Characterization and Measurement. The LOI was measured on an oxygen index instrument JF-3 (Nanjing Jiangning Analytical Instrument Co., Ltd., Nanjing, China) and performed according to GB2406-93. The flame retardancy of the test specimens was examined in accordance with the UL94 method, and the dimension of the test specimens was $125 \times 13 \times 3$ mm³. TGA was carried out using a Mettler Toledo TGA/DSC Simultaneous Thermal Analyzer (International Inc., Zurich, Switzerland), and around 4 mg of samples was placed on an aluminum pan. The sample was heated from 50 °C up to 700 °C at a set heating rate of 5, 10, 20, or 40 °C/min. All the tests were performed in a nitrogen flow with a flow rate of 80 mL/min. Differential scanning calorimetry (DSC) was carried

out with a Netzsch STA 449 F5 Thermal Analyzer (NETZSCH-Gerätebau GmbH, Selb, Germany) under a nitrogen atmosphere. Samples weighing approximately 10 mg were placed in the aluminum pan and heated from 50 to 250 °C with a heating rate of 5 °C/min. Scanning electron microscopy (SEM) experiments were performed with a Hitachi S-4800 scanning electron microscope (Hitachi, Ltd., Tokyo, Japan). Samples for SEM were obtained from the surface of the residue after the LOI test; the surface was sputtered with gold.

3. RESULTS AND DISCUSSION

3.1. Flame Retardancy. The LOI and UL94 methods were used to evaluate the flame retardancy of EP systems, as shown in Table 1. The experimental results indicated that the blank EP was easily flammable with a low LOI of 20.2, and the UL94 test was V-2 due to the melt drop phenomenon. Compared with the blank EP, the LOI of the EP-PEPSQ10 system increased to 28.6 and the UL94 V-1 rating was reached. Moreover, the EP-DBAMP10 system reached UL94 V-0 and the sample's LOI was better (29.6). Obviously, the flame retardancy of EP-PEPSQ systems can be improved effectively with a loading of DBAMP as the synergistic additive. With the introduction of DBAMP, the LOI of systems first increased until a maximum value was reached. Then, these values gradually decreased with the increase in DBAMP content. The peak value of the LOI in the EP-PEPSQ5-DBAMP5 system was 30.8 when the flame retardants PEPSQ and DBAMP were both added at 5%. Meanwhile, the UL94 test of systems can reach a V-0 rating. Therefore, although the effect of PEPSQ and DBAMP on the glass transition temperature (T_g) of EP was not clear (as shown in DSC curves in Figure S1), they did show a synergistic effect on the flame retardation of EP.

3.2. Thermal Degradation Kinetics. In order to obtain kinetic parameters such as activation energy and pre-exponential factor, it is necessary to obtain the test data of TGA at different heating rates. Figures 1–4 exhibited the TGA curves of blank EP, EP-PEPSQ10 (EP/PEPSQ), EP-DBAMP10 (EP/DBAMP), and EP-PEPSQ5-DBAMP5 (EP/PEPSQ/DBAMP) systems. The heating rates were 5, 10, 20, and 40 °C/min.

It can be seen from the above TGA curves that the curve moved toward a higher temperature as the heating rate increased. However, the main weight loss range of EP occurred between 300 and 500 °C.

The Kissinger expression is as follows:³⁶

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

T_{\max} is the temperature of the peak rate, which was determined at different heating rates and allows the activation energy to be

Table 1. Formulation and Flame Retardancy of the EP Systems

systems	formulation			LOI	UL94			
	EP/wt %	PEPSQ/wt %	DBAMP/wt %		grade	t1/s	t2/s	dripping
EP	100	0	0	20.2	V-2	24.7	12.5	yes
EP-PEPSQ10	90	10	0	28.6	V-1	15.8	3.3	no
EP-PEPSQ7.5-DBAMP2.5	90	7.5	2.5	30.0	V-0	5.4	3.2	no
EP-PEPSQ5-DBAMP5	90	5	5	30.8	V-0	2.3	3.6	no
EP-PEPSQ2.5-DBAMP7.5	90	2.5	7.5	30.4	V-0	3.1	2.7	no
EP-DBAMP10	90	0	10	29.6	V-0	5.9	4.5	no

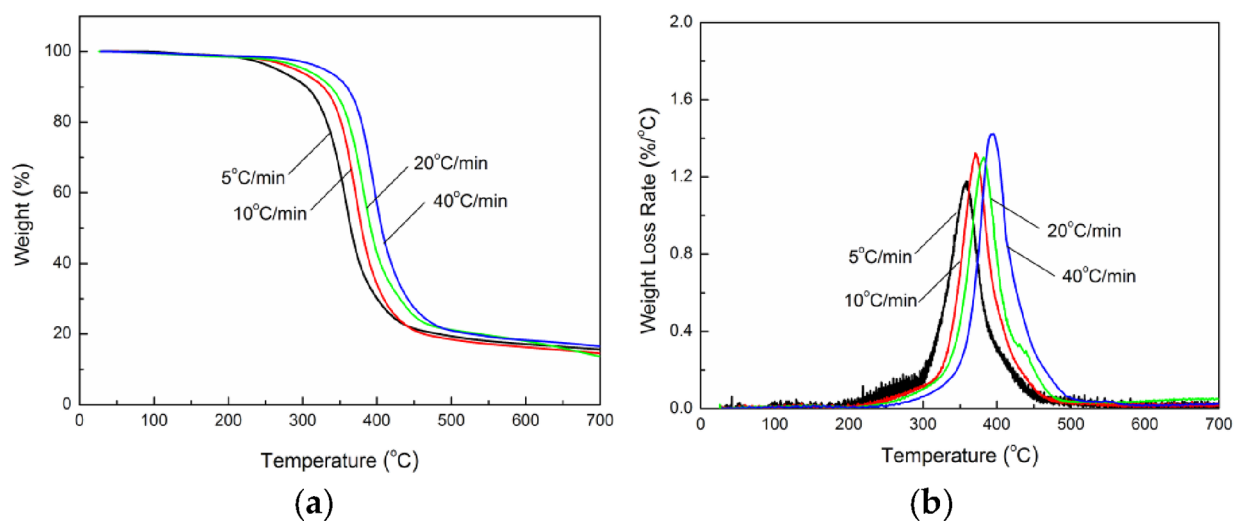


Figure 1. TGA (a) and DTG (b) curves of EP.

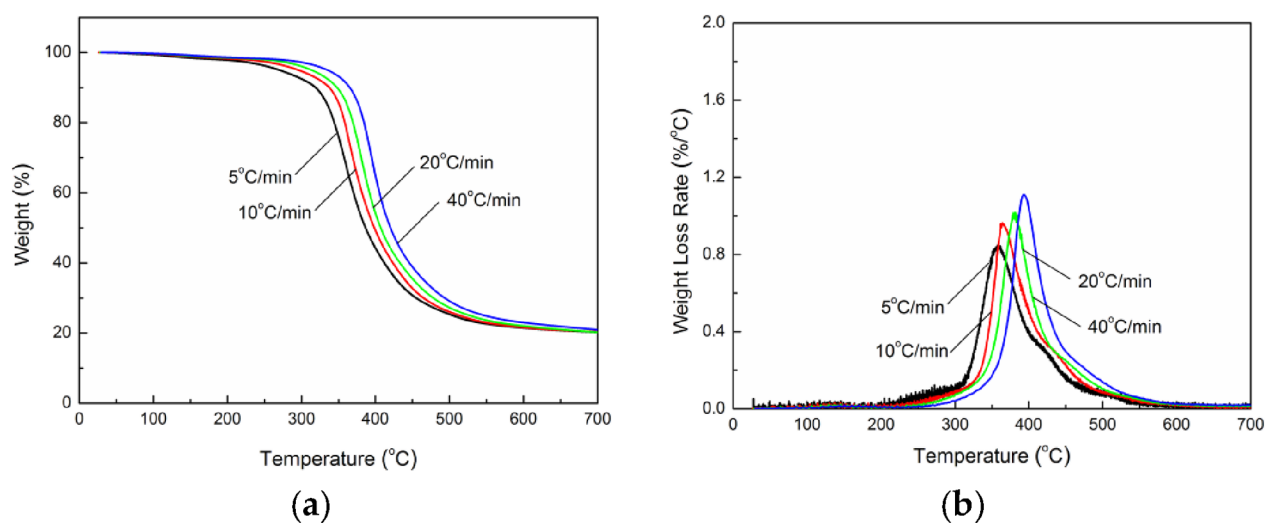


Figure 2. TGA (a) and DTG (b) curves of EP/PEPSQ.

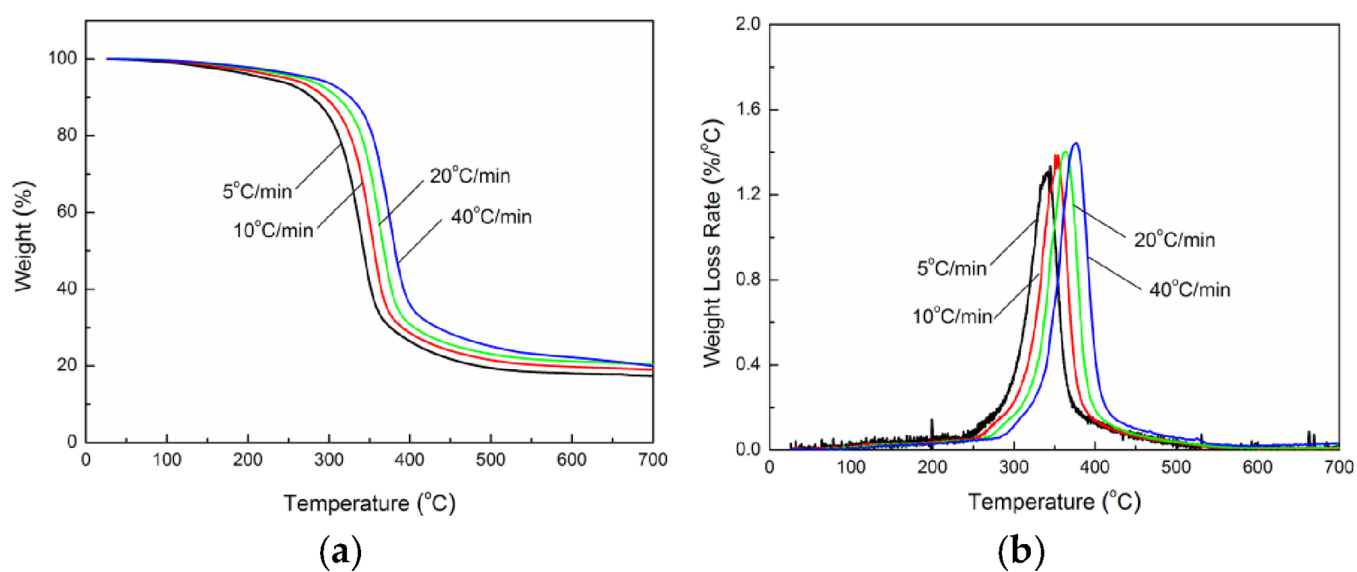


Figure 3. TGA (a) and DTG (b) curves of EP/DBAMP.

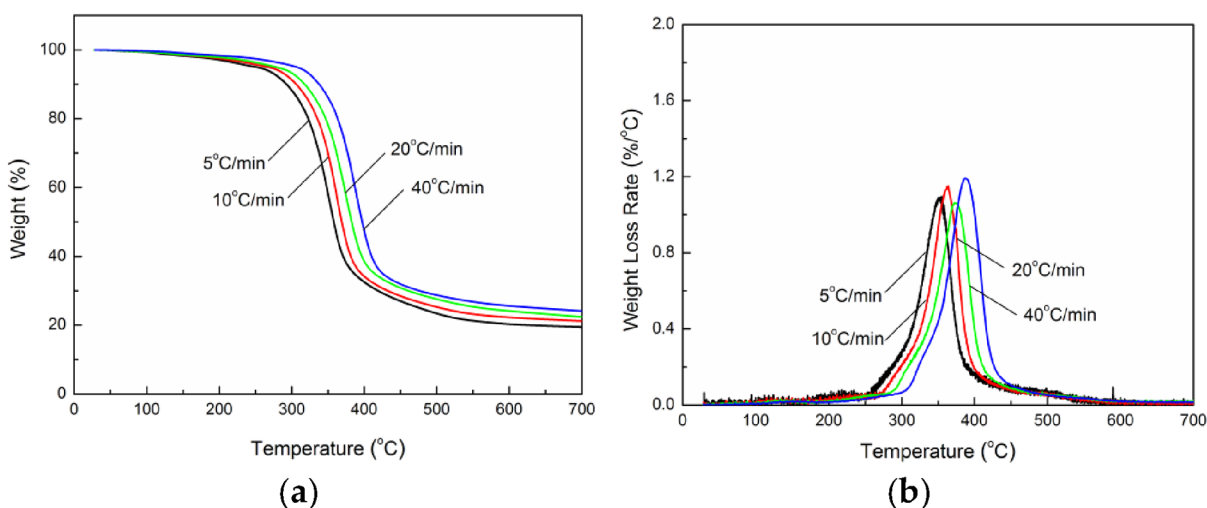


Figure 4. TGA (a) and DTG (b) curves of EP/PEPSQ/DBAMP.

Table 2. Kinetic Data for Thermal Degradation of EP Systems by the Kissinger Method

systems	temperature (°C)				<i>E</i> (kJ/mol)	lg <i>A</i> (1/min)	γ (%)
	5 °C/min	10 °C/min	20 °C/min	40 °C/min			
EP	358.5	371.3	382.3	395.9	60.00	18.83	99.71
EP/PEPSQ	357.8	370.3	381.9	393.3	62.28	19.67	99.60
EP/DBAMP	344.8	354.2	364.2	376.0	65.90	21.91	99.86
EP/PEPSQ/DBAMP	354.4	363.8	372.6	384.1	73.84	24.03	99.71

calculated by the Kissinger 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.

Thus, as shown in Figure S2, the Kissinger plots of $\ln(\beta/T_{\max}^2)$ versus $1/T_{\max}$ for different systems at four different heating rates can be drawn according to eq 1. The slopes of the straight lines of EP, EP/PEPSQ, EP/DBAMP, and EP/PEPSQ/DBAMP were 7.22×10^3 , 7.49×10^3 , 7.93×10^3 , 8.88×10^3 , respectively, and the calculated kinetic parameters were compared and summarized, as shown in Table 2.

The activation energies for the thermal degradation process predicted by the Kissinger kinetics theory are shown in Table 2. It can be seen that the kinetic parameters changed with additives. The activation energies of the EP/PEPSQ and EP/DBAMP systems (62.28 and 65.90 kJ/mol) were both slightly higher than that for blank EP (60.00 kJ/mol). This indicated that the addition of flame retardants can effectively improve the thermal stability of the EP system. Moreover, comparing the four EP systems, the highest activation energy was the EP/PEPSQ/DBAMP system, reaching 73.84 kJ/mol. It can be seen that the synergistic effect of PEPSQ and DBAMP greatly increased the activation energy of thermal degradation of EP and slowed down its thermal degradation rate. Finally, the flame retardancy of the system was improved by forming an insulating char layer.

These results provide data support for the thermal stability analysis of flame-retardant EP systems. However, the Kissinger method can only obtain the information data of the system at the peak rate. Therefore, the Flynn–Wall–Ozawa method is needed for further analysis of TGA data, so as to obtain more comprehensive thermal stability data of the system.

The equation of the Flynn–Wall–Ozawa method is as follows:³⁷

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

It can be seen from the above equation that $\lg(\beta)$ is linearly proportional to $1/T$. The activation energy at any conversion degree can be obtained by calculating the slope of the $\lg(\beta) - 1/T$ plots.

Based on the datum of Figures 1–4 and the equation of $a = \frac{w_0 - w_t}{w_0 - w_\infty}$ (w_0 is the initial weight of the sample, w_t is the sample weight at any temperature t , w_∞ is the final sample weight), the degree of conversion as a function of temperature relative to the degradation of both EP and flame-retardant EP (FREP) systems can be obtained (Figures S3–S6).

Equation 2 was used to process TGA data, and Figure 5 shows the $\lg(\beta)$ versus $1/T$ plots of the conversion degree for the EP and FREP systems from 2 to 90%, indicating a good linear relationship. Then, the activation energy of any particular conversion degree was obtained by calculating the slope of the fitting straight line.

Figure 6 shows the results calculated from these plots by the Flynn–Wall–Ozawa method as values of the activation energy at various conversions. Obviously, three different stages can be marked. In the first stage, the conversion degree ranged from 0 to 10%. This can be due to mass loss of some volatile components and/or mass loss of the light degradation compounds. The E values were slowly increased in the second stage within 0–80% for three samples, which was mainly due to the degradation reaction of the main chain of EP. Polymer molecules had the same degradation mechanism and lasted for a long time. The third stage thermal degradation of EP was within the range of 80–100%. At this time, the main reaction was the breakage of strong linkages after the principal reaction.³⁸

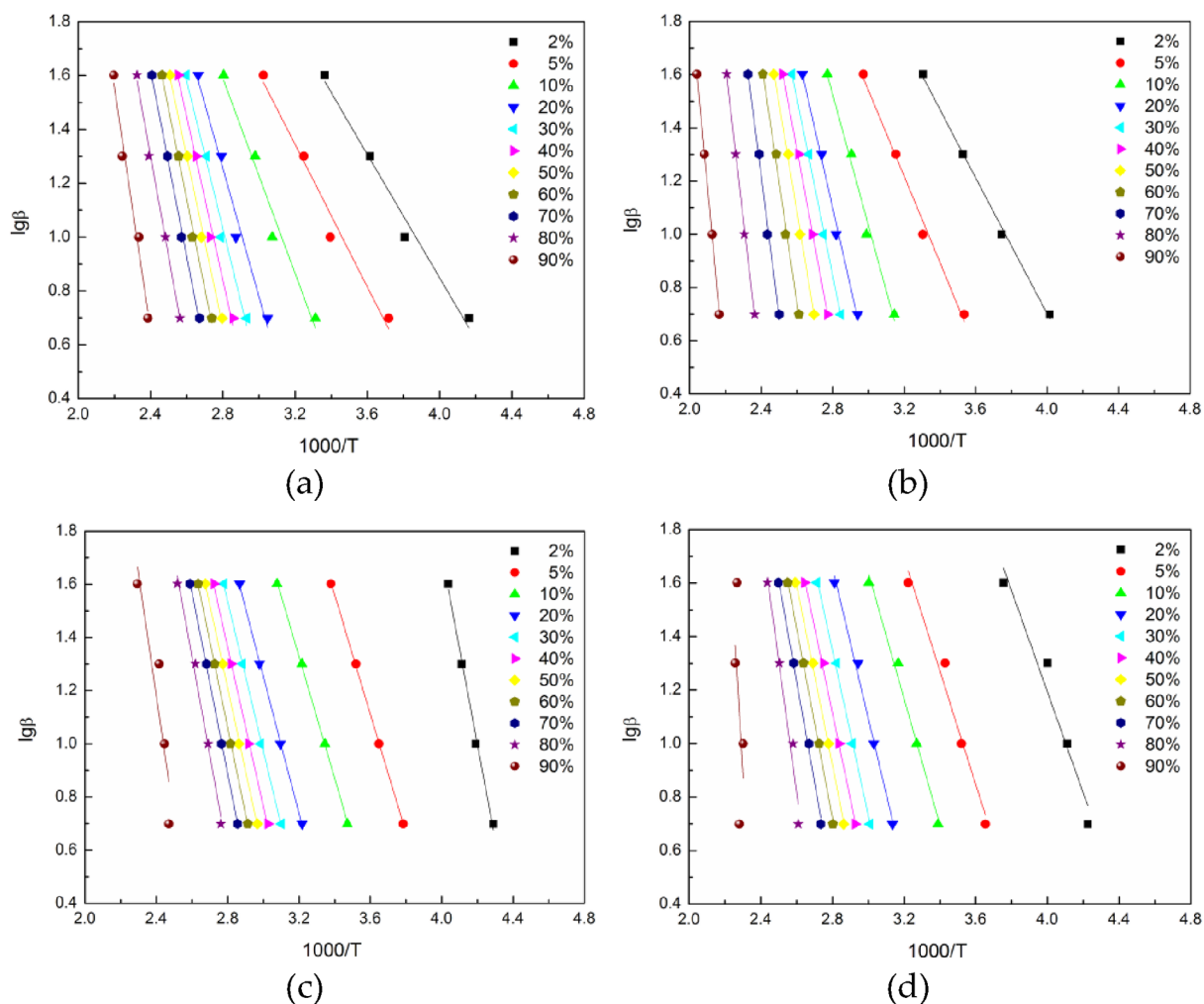


Figure 5. The plots of $\lg(\beta)$ vs $1/T$ of EP (a), EP/PEPSQ (b), EP/DBAMP (c), and EP/PEPSQ/DBAMP (d).

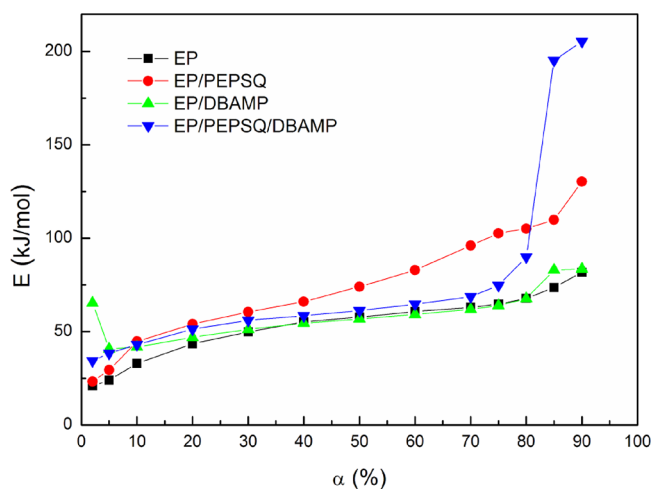


Figure 6. Activation energy curves of EP systems by the Flynn–Wall–Ozawa method.

When the conversion degree was 5%, the activation energies of EP, EP/PEPSQ, EP/DBAMP, and EP/PEPSQ/DBAMP were 24.03, 29.44, 40.40, and 38.46 kJ/mol, respectively. It can be obtained that the activation energy of blank EP was the lowest and EP/DBAMP the highest. With the increase in the conversion degree, the activation energies of the four systems

were gradually increased. When the conversion degree reached 50%, the activation energies of EP, EP/PEPSQ, EP/DBAMP, and EP/PEPSQ/DBAMP were 57.79, 74.06, 56.79, and 61.27 kJ/mol, respectively. At this point, the activation energy of blank EP was still the lowest, but EP/PEPSQ became the highest of all. This is because the EP/DBAMP and EP/PEPSQ/DBAMP systems contain the DBAMP flame retardant. The catalytic degradation of the phosphorous-containing flame retardant retarded the improvement of activation energy. When the conversion degree increased to 85%, the activation energy of the EP/PEPSQ/DBAMP system increased significantly and became the maximum value among the four systems.

By analyzing the above data, it can be found that both the Kissinger and Flynn–Wall–Ozawa methods can obtain the thermal degradation activation energies of the EP and FREP systems. The value law of the two methods was consistent. Moreover, the activation energies of the FREP system were higher than those of the EP system. Furthermore, the addition of PEPSQ and DBAMP further increased the activation energy in the thermal degradation process, indicating that the flame retardant retarded the thermal degradation behaviors of EP. In fact, the formation of the char layer is one of the important processes for the condensed phase flame retardancy of the polymer. When the polymer burns, the char layer can prevent the polymer from contacting with combustible gas and oxygen,

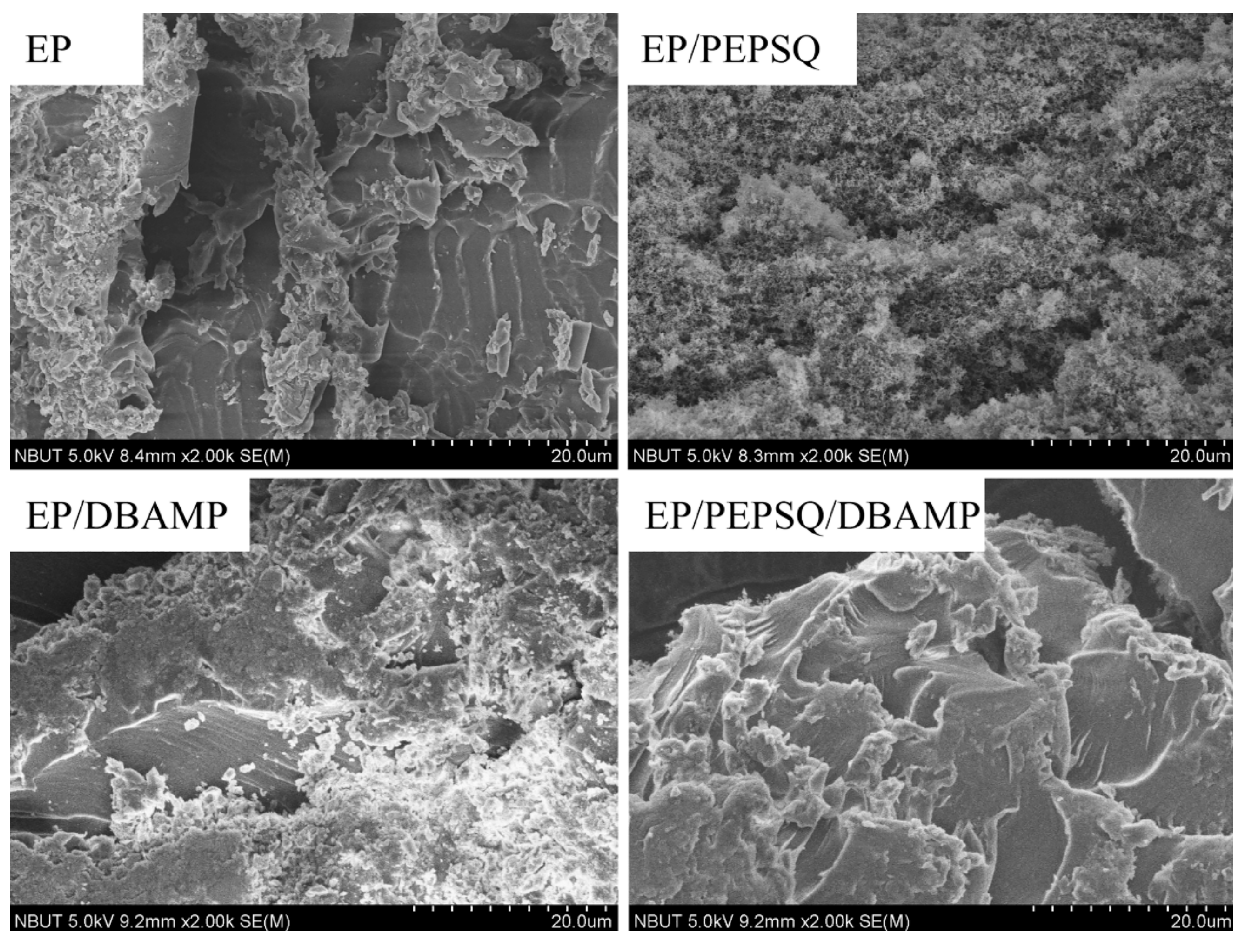


Figure 7. Residual char morphologies of EP systems.

so as to achieve the purpose of flame retardancy. In the mechanism of flame retardancy, some types of flame retardants can increase the density of the char layer and amount of the char residue through the reaction process and play a role in stabilizing the char layer. In this study, it was revealed that PEPSQ and DBAMP had the function of stabilizing the char layer and improving the flame retardancy of EP in the final period of the thermal degradation process. Therefore, the flame-retardant behaviors of PEPSQ and DBAMP on EP were synergistic.

3.3. Morphology Analyses. In generally, the char layer played an important role as a physical barrier in preventing the spread of fires. It effectively prevented the passage of heat, oxygen, and combustible volatiles.³⁹ Therefore, the structure and quality of the char layer would directly affect the flame retardancy of the system. In order to study the relationship between the microstructure of the char layer and the flame retardancy, the char layer morphology of the EP systems after combustion was measured by SEM (Figure 7).

For the blank EP, the surface of the burning residue was a discontinuous char layer, and cracks can also be seen. After the introduction of 10% PEPSQ as a flame retardant, the char layer morphology obviously became much more continuous and the quantity of char residues increased. However, the char layer of the EP/PEPSQ system also had some drawbacks. The main problem was compactness. In the char layer of the EP/PEPSQ system, a lot of holes can be found, which may affect the effect of the physical barrier. Compared with EP/PEPSQ, the char layer formed by EP/PEPSQ/DBAMP systems is more

continuous, dense, and uniform. Moreover, this just confirmed the activation energy relationship between them. Since EP/PEPSQ was easy to form a char layer on the combustion surface of the polymer, its activation energy was relatively high in the middle stage of combustion. However, the formed char layer was relatively loose, which made it difficult to reach the highest flame retardancy. When an appropriate amount of DBAMP was added to the EP/PEPSQ system, the synergistic effect between PEPSQ and DBAMP was generated, which made the char layer formed more excellent. With the enhancement of activation energy, the thermal degradation process became difficult, which significantly improved the flame retardancy of the EP system. Compared to the above systems, it can be easily concluded that the flame retardant DBAMP had a very positive catalytic effect on the formation of better char layer for the EP/PEPSQ system during the degradation process. The continuous, compact, and uniform burning char layer in the EP/PEPSQ/DBAMP system indicated a synergistic effect between PEPSQ and DBAMP.

4. CONCLUSIONS

In this article, the LOI and UL94 test results showed that the flame retardants PEPSQ and DBAMP had a synergistic effect on the flame retardancy in EP systems. The non-isothermal degradation behaviors of EP containing PEPSQ and DBAMP were studied by TGA. The Kissinger and Flynn–Wall–Ozawa methods both showed that PEPSQ and DBAMP have been confirmed to be effective to enhance the thermal stability for

EP by the kinetics analysis. The addition of PEPSQ and DBAMP further improved the activation energy in the final stage of the thermal degradation process, revealing that the flame retardant delayed the thermal degradation of EP. It indicated that PEPSQ and DBAMP have the function of stabilizing the char layer and improving the flame retardancy of EP in the final stage of the thermal degradation process. The morphology analysis of the polymer char layer further confirmed the above conclusion. When an appropriate amount of DBAMP was added to the EP/PEPSQ system, the synergistic effect between PEPSQ and DBAMP was generated, which made the char layer formed more excellent.

Data Availability Statement. The data used to support the findings of this study are available from the corresponding author upon request.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c05817>.

DSC curves of EP systems; the plots of $\ln\left(\frac{\beta}{T_{\max}^2} \text{ vs } \frac{1}{T_{\max}}\right)$ of EP systems; the conversion of EP, EP/PEPSQ, EP/DBAMP, and EP/PEPSQ/DBAMP (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Jiangbo Wang – School of Materials and Chemical Engineering, Ningbo University of Technology, Ningbo 315211, China; Zhejiang Institute of Tianjin University, Ningbo 315201, China; orcid.org/0000-0002-0528-7325; Email: jiangbowang@nbut.edu.cn

Authors

Rongfan Zhou – School of Materials and Chemical Engineering, Ningbo University of Technology, Ningbo 315211, China

Xintong Wu – School of Materials and Chemical Engineering, Ningbo University of Technology, Ningbo 315211, China

Xiaohui Bao – School of Materials and Chemical Engineering, Ningbo University of Technology, Ningbo 315211, China

Fangyi Wu – School of Materials and Chemical Engineering, Ningbo University of Technology, Ningbo 315211, China

Xiaoshuai Han – Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, International Innovation Center for Forest Chemicals and Materials, College of Materials Science and Engineering, Nanjing Forestry University, Nanjing 210037, China

Complete contact information is available at: <https://pubs.acs.org/10.1021/acsomega.2c05817>

Notes

The authors declare no competing financial interest.

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