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Flammability and Thermal Oxidative Degradation Kinetics of Magnesium Hydroxide and Expandable Graphite Flame Retarded Polypropylene Composites

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The flammability and the thermal oxidative degradation kinetics of expandable graphite (EG) with magnesium hydroxide (MH) in flame-retardant polypropylene (PP) composites were studied by limiting oxygen index (LOI), UL-94 test, and thermogravimetric analysis (TGA). The results show that EG is a good synergist for improving the flame retardancy of PP/MH composite and the effect is enhanced with decreasing EG particle size. The Kissinger method and Flynn-Wall-Ozawa method were used to determine the apparent activation energy (E) for degradation of PP and flame retarded PP composites. The data obtained from the TGA curve indicate that EG markedly increases the thermal degradation temperature of PP/MH composites and improves the thermal stability of the composites. The kinetic results show that the values of E for degradation of flame retarded PP composites is much higher than that of neat PP, especially PP/MH composites with suitable amount of EG, which indicates that the flame retardants used in this work have a great effect on the mechanisms of pyrolysis and combustion of PP.

Keywords: flame retardancy; thermal oxidative degradation; kinetics; polypropylene; magnesium hydroxide; expandable graphite

1. Introduction

Polypropylene (PP) has wide applications in wire and cables, automobiles, housing, electronics, the electric industry, etc. (1, 2). In these applications, the flame retardant improvement of PP is a very important subject. The development of environmentally friendly flame retardant materials to replace the widely used halogenated materials, which produce harmful emissions, is of fundamental importance for the polymer industry and has received extensive research (3, 4). In recent years, the development of halogen-free flame retardant (HFFR) has been promoted for flame retarded polymer materials. In particular, some inorganic fillers, such as alumina trihydrate (ATH) and magnesium hydroxide (MH), as HFFR, have been extensively investigated in detail and have become some of the most popular replacements for halogen-based fire retardants and smoke suppressant fillers (5–7). However, their fatal disadvantages are their low flame-retardant efficiency. Some results (8–10) showed that more than 60 wt% MH loading was required to achieve the desired flame retardancy, whereas high loading levels of MH could be greatly detrimental to the mechanical properties of the filled polymers. In order to solve this problem, an effective route is the incorporation of some HFFR synergistic agents with MH. MH combined with some HFFR synergistic agents, such as red phosphorous (RP), expandable graphite (EG), etc., can improve the flame retardancy of MH and decrease its loading level. However, RP as a flame-retardancy additive has some disadvantages, such as easy spontaneous ignition and absorbing moisture when exposed to air. On the other hand, EG, as a novel intumescent additive, is used in foams and coatings to impart flame retardant properties (11, 12), and has been successfully used as a flame retardant in polyethylene (PE) and ethylene vinyl acetate (EVA) (13, 14).

The pyrolysis and combustion of neat PP and flame retarded PP composites have a close relationship with their thermal oxidative degradation behavior. Thus, it is important

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to evaluate the thermal stability and thermal oxidative degradation of PP and its flame retardant composites so as to ascertain the application and processing window of PP composites. The pyrolysis and combustion of a polymer and its composites is a subject of concern in the research field of flame retardation and smoke suppression (15–18). Several ways have been developed to evaluate the pyrolysis behavior of polymers and their composites (19, 20). The methods of kinetic analysis are based on thermogravimetric analysis. Some valuable parameters, such as apparent activation energy, pre-exponential factor and reaction order, can be calculated from the thermogravimetric curve of a polymer through differential and integral methods. The distinction of the two methods depends on whether they are based on only one heating rate or on more than one heating rate (21).

Some studies have focused on the thermal oxidative degradation of PP (22, 23). It is thought that the thermal degradation of PP occurs by random chain scission, and that the degradation proceeds by a free radical mechanism (24). However, there is a lack of information on the thermal degradation of halogen-free flame retarded PP composites, especially for PP filled with MH and EG. In our previous work (25, 26) we investigated the mechanical properties and combustion characteristics of MH flame retardant PP composites. It was found that incorporation of a suitable amount of EG has good synergistic efficiency with MH in flame retardancy PP composites. In this work, the flammability and thermal oxidative degradation of EG with MH flame retarded PP composites was studied by limiting oxygen index (LOI), UL-94 test and thermogravimetric analysis (TGA). The thermal stability and thermal oxidative degradation kinetics of PP, PP/MH and PP/MH/EG composites were characterized by a series of methods, activation energies of these processes have been determined, and the mechanism of each process has also been discussed.

2. Experimental

2.1 Kinetic Analysis

The application of dynamic TGA methods holds great promise as a tool for unraveling the mechanisms of physical and chemical processes that occur during degradation of a polymer and its composites. For instance, the thermal oxidative degradation kinetics of PP and flame retarded PP composites can be based on TGA results. In TGA measurements, conversion α has been defined as:

$$\alpha = \frac{w_i - w_a}{w_i - w_f} \tag{1}$$

where w_a, w_i and w_f are the actual, initial and final sample weights, respectively. The kinetic information can be extracted from dynamic experiments by means of various methods. All kinetic studies assume that the isothermal rate of conversion (27), $d\alpha/dt$, is a linear function of the reactant concentration loss and of the temperature-independent rate constant, k, and a temperature-independent function of the conversion, α, that is:

$$d\alpha/dt = \beta(d\alpha/dT) = k(T)f(\alpha) \tag{2}$$

where $f(a)$ and $k(T)$ are the functions of conversion and temperature, respectively. $\beta = dT/dt$.

The temperature dependence of the kinetic constant (k) can generally be given by the Arrhenius equation:

$$k(T) = Ae^{-E/RT} \tag{3}$$

where E is the activation energy of the reaction, A is the frequency factor, T is the reaction temperature, and R is the gas constant.

$f(a)$ depends on the particular decomposition mechanism. The simplest and most frequently given model for $f(a)$ in TGA data is:

$$f(\alpha) = (1-\alpha)^n \tag{4}$$

where $(1-\alpha)$ is the dimensionless amount of reactive remaining and n is the reaction order. The combination of Equations (2, 3 and 4) gives the following equation:

$$d\alpha/dt = \beta(d\alpha/dT) = Ae^{-E/RT}(1-\alpha)^n \tag{5}$$

Equation (5) is normally the fundamental base for the kinetic analysis of a solid material from non-isothermal TGA experimental data. In this paper, two methods have been used to analyze the non-isothermal kinetics of PP and flame retarded PP composites.

2.1.1 Kissinger Method (28)

The Kissinger method can be used to determine the activation energy from plots of the logarithm of the heating rate vs. the inverse of the temperature at the maximum reaction rate at constant heating rate. Kissinger assumes that the product $n(1-\alpha_{\max})^{n-1}$ is independent of β and the following expression can be used:

$$\ln\left(\frac{\beta}{T_{\max}^2}\right) = \left\{\ln\frac{AR}{E} + \ln\left[n(1-\alpha_{\max})^{n-1}\right]\right\} - \frac{E}{RT_{\max}} \tag{6}$$

where β is the heating rate, $T_{\max}$ is the temperature corresponding to the inflection point of the thermal oxidative degradation curves which corresponds to the maximum reaction rate, A is the pre-exponential factor, $\alpha_{\max}$ is the extent of conversion at $T_{\max}$, and n is the reaction order. The plot of $(\beta/T_{\max}^2)$ vs. $1/T_{\max}$ can be fitted to a straight line, and the activation energy (E) can be calculated from the slope of the line.

2.1.2 Flynn-Wall-Ozawa Method (29, 30)

This is a relatively simple method of determining activation energy directly from weight loss vs. temperature data obtained at several heating rates. The standard (Eq. (5)) can be given as follows:

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{Ae^{-E/RT}}{\beta} dT \tag{7}$$

which is integrated with the initial condition of $\alpha = 0$ at $T = T_0$ to obtain the following expression:

$$F(\alpha) = \int_0^\alpha \frac{1}{(1-\alpha)^n} d\alpha = \frac{1}{\beta} A \int_{T_0}^T e^{-E/RT} dT \tag{8}$$

where $F(\alpha)$ is the integral function of conversion.

From Equation (8) and the Doyle approximation, the result of the integration can be simplified as:

$$\log\beta = \log\frac{AE}{R} - \log F(\alpha) - 2.315 - 0.457\frac{E}{RT} \tag{9}$$

where β, A, E and T have the known meanings.

This is one of the integral methods that can determine the activation energy without knowledge of reaction order. The activation energy for different conversions can be calculated from a $\log\beta$ vs. $1000/T$ plot.

2.2 Materials

Polypropylene used in this work was a commercial polymer, PP-140, supplied by Baling Petrochemical Ltd (Hunan, China). Expandable graphites (EG), with particle size of 50 mesh (EG1) and 80 mesh (EG2), were supplied by Shandong Zibo Deli Graphite CO., LTD. Magnesium hydroxide, $Mg(OH)_2$, with an average particle size of 2.0–2.5 μm, was provided by Qindao Haida Chemical Ltd (Shandong, China). The surface of MH was treated with stearate.

2.3 Preparation of Samples

The PP composites filled with selected amounts of MH and EG were blended in a twin-screw extruder (Type TSE-40A/400-44-22, L/D = 40, made in Nanjing, China) at 175–215°C and a screw speed of 160 rpm. The extrudate was cut into pellets and injection molded (Type J80M3V, made in China) at 210°C into various specimens for tests and characterization.

2.4 Measurements and Characterization

2.4.1 Limiting Oxygen Index (LOI)

The LOI value was measured using a limiting oxygen index instrument (Type JF-3, manufactured by Jiangning Analysis Instrument Factory, Nanjing, China) on sheets 100 × 10 × 4 mm according to the standard oxygen index test ASTM D2863-77. The test sample is mounted vertically with the ignition point at its upper end. A concentration of O_2 greater than that required to sustain is first determined, from that point, the oxygen is lowered at a slow rate until the flame is extinguished. The concentrations of oxygen and nitrogen are then put into Equation (10) and the limiting oxygen index is determined. LOI is expressed as percent oxygen. The LOI value is calculated according to the equation given below:

$$\text{LOI} = \frac{[O_2]}{[O_2] + [N_2]} \times 100\% \tag{10}$$

where $[O_2]$ and $[N_2]$ are the concentrations of $[O_2]$ and $[N_2]$, respectively.

2.4.2 UL-94 Test

The UL-94 vertical test was carried out using a CZF-1 type instrument (made in China) on sheets 127 × 12.7 × 2.7 mm according to ASTM D635-77. The three ratings (V-2, V-1 and V-0) are defined. The V-0 rating stands for the highest requirements. The criteria for which the materials are rated are based on the time it takes for the burning material to extinguish after the flame source is removed from a vertical specimen, and also if drips fall from the burning specimen. There are five sample bars and two ignitions, each 10 seconds, applied to the each other bar. The test specimen is exposed from a flame source from below for duration of ten seconds. The flame source is then removed. If the specimen extinguishes, the specimen is exposed to the flame for an additional ten seconds.

2.4.3 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was carried out with samples of about 8 mg in air atmosphere with a flow rate of 30 ml/min in a temperature range from 30°C to 600°C at scanning rates of 5, 10, 20 and 30°C/min by a Perkin-Elmer Q 50 thermogravimetric analyzer. Experimental error was about ±5°C and ±1 wt% for thermal oxidative degradation temperature and char yield, respectively.

3. Results and Discussion

3.1 Flammability: the LOI and UL-94 Rating

The LOI and UL-94 tests are widely used to evaluate flame retardancy of polymers, especially for screening flame retardant formulations. Figure 1 compares the changes of LOI values for the PP/MH composites with different particle size of EG. The LOI increases linearly with increasing the EG content, indicating that EG can improve the flame-retardancy of the PP/MH composites. At the same time, it is obvious that the LOI values of the composites with EG2 are higher than those of the composites with EG1. With the addition of 10 phr EG in the composites, the LOI values of the composites with EG1 and EG2 are 30.6 and 31.5, respectively. These data suggest that the addition of EG2 can greatly improve the LOI values of PP/MH composites due to its better synergistic effect with MH.

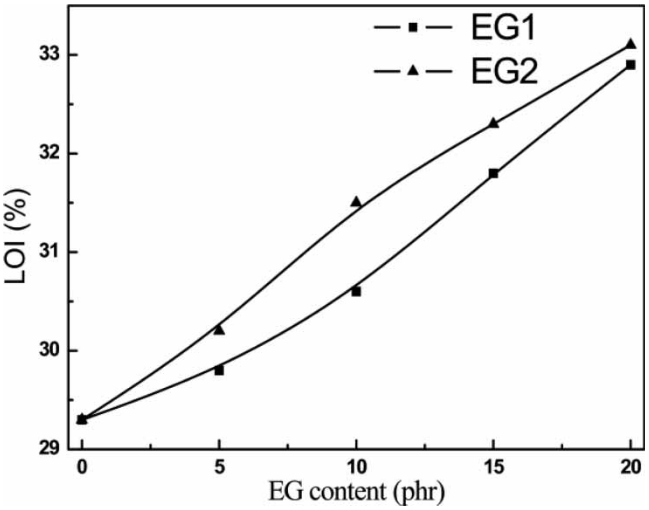

Fig. 1. Effect of expandable graphite on limiting oxygen index of PP/MH/EG composites (MH + EG = 100 phr).

Table 1 lists the UL-94 ratings obtained from the PP/MH/EG composites. The PP composites with only 100 phr MH does not pass the UL-94 rating test. In order to solve this problem, two kinds of EG with different particle sizes were selected as a synergist of MH to improve the flame retardancy of the composites, where the total amount of FR, including both MH and EG, was kept at 100 phr. The data listed in Table 1 show that the particle size of EG has a great effect on the flammability of PP/MH/EG composites. EG2, with smaller particle size, can greatly improve the UL-94 values of PP/MH/EG composites. At the loading of 10 phr EG2, the stringent rating UL-94 V-0 is achieved for the PP/MH/EG2 composites. On the other hand, when the content of EG1 with larger particle size in the PP/MH/EG1 composites is at 10 phr, UL-94 is failed. UL-94 V-0 rating is only reached for the PP/MH/EG1 composites containing 20 phr EG1. This further indicates that EG2, with smaller particle size, has much better synergistic effect than MH with EG1 with larger particle size for the flame retardant improvement of PP/MH composites.

Table 1. Effect of EG content on flammability of PP/MH/EG composites

Formulations		UL-94 Flammability	
MH (phr)	EG (phr)	EG1	EG2
100	0	Fail	Fail
95	5	Fail	V-1
90	10	V-2	V-0
85	15	V-1	V-0
80	20	V-0	V-0

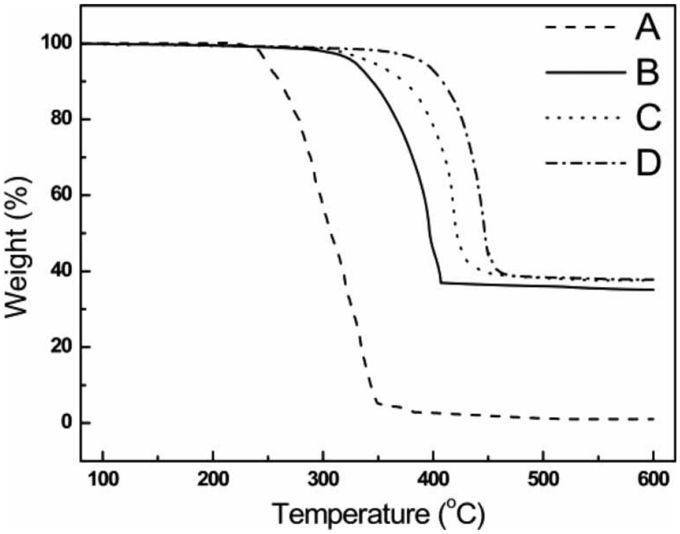

Fig. 2. The TGA curves of PP and flame retarded PP composites in air at the heating rate of 10°C/min: (A) PP; (B) PP/MH (100/100); (C) PP/MH/EG1 (100/90/10); (D) PP/MH/EG2 (100/90/10).

3.2 *Thermal Stability*

TGA curves of PP and the PP composites under a flow of air at a heating rate of 10°C/min are shown in Figure 2. Thermal stability and degradation data of neat PP, PP/MH, PP/MH/EG1 and PP/MH/EG2 composites from the TGA curves are listed in Table 2. The neat PP undergoes complete thermal oxidative degradation at a temperature below 420°C, and there is barely any residue left at the end of the degradation. However, the PP composites filled with fillers degrade with over 35% residue left after the degradation.

It is found from Figure 2 that PP/MH/EG1 and PP/MH/EG2 composites, under a flow of air, show only a one-step decomposition process, the same as that of PP/MH composites. It can be seen that the thermogravimetric curves of the composites are very similar over the whole degradation process and that the decomposition temperatures of the composites with EG are higher than that of the composites without EG. The phenomena revealed that the thermal stability of the PP/MH/EG composites is superior to that of the PP/MH composites by the increase of pyrolysis temperature by about 30–50°C and is improved through decreasing the particle size of the EG. The reason is not clear at present, but it is conceivable that the smaller particle size of EG means that the EG2 has a better synergistic effect with MH than EG1 with large size in the composites. Another observation is that PP/MH/EG composite degrades less than PP/MH composite at the same temperature over almost the whole degradation process. And the residue left after degradation of PP/MH/EG composites at 550°C is higher than that of PP/MH composites. The decomposition temperatures for 5%, 20% and 50% wt loss, the onset temperature (T_i) and peak temperature (T_p) for the whole stage of weight loss, are

Table 2. Thermal properties data of PP and the flame retarded PP composites

Samples	$T_{5\%}$ (°C)	$T_{20\%}$ (°C)	$T_{50\%}$ (°C)	T_i (°C)	T_p (°C)	Residue at 550°C (%)
PP	248.3	278.0	307.2	251.6	316.1	1.0
PP/MH (100/100)	328.5	366.4	396.8	343.6	396.5	35.5
PP/MH/EG1 (100/90/10)	344.3	397.3	421.5	348.2	419.3	37.6
PP/MH/EG2 (100/90/10)	391.1	425.5	446.6	356.7	444.2	38.0

read from the TGA and differential thermogravimetric (DTG) curves are listed in Table 2.

$T_{n\%}$ represents the onset decomposition temperature for 5, 20 and 50% wt loss, respectively; T_i represents initial temperature of TGA; T_p represents peak temperature of DTG.

Figure 3 shows the TGA curves of PP and the flame retarded PP composites heated in air at several heating rates from 5 to 30°C/min. Figure 4 is the corresponding DTG curves of the composites. The thermal oxidative degradation curves of the composites are shifted to higher temperatures with increasing heating rate.

3.3 *Thermal Oxidative Degradation Kinetics*

The TGA results of PP and flame retarded PP composites were obtained under a steady flow of air at different

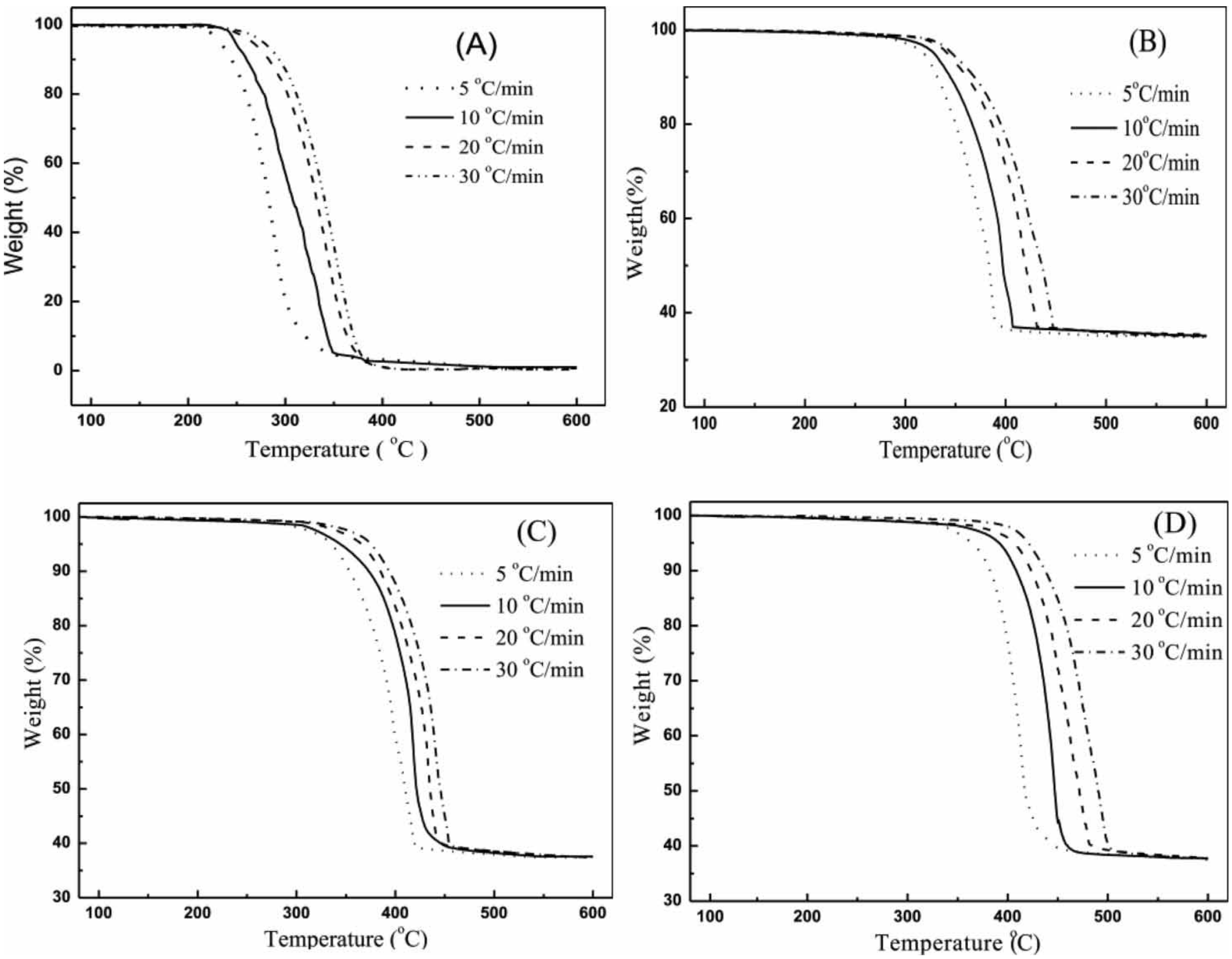

Fig. 3. TGA curves of samples in air at different heating rates: (A) PP; (B) PP/MH (100/100); (C) PP/MH/EG1 (100/90/10); (D) PP/MH/EG2 (100/90/10).

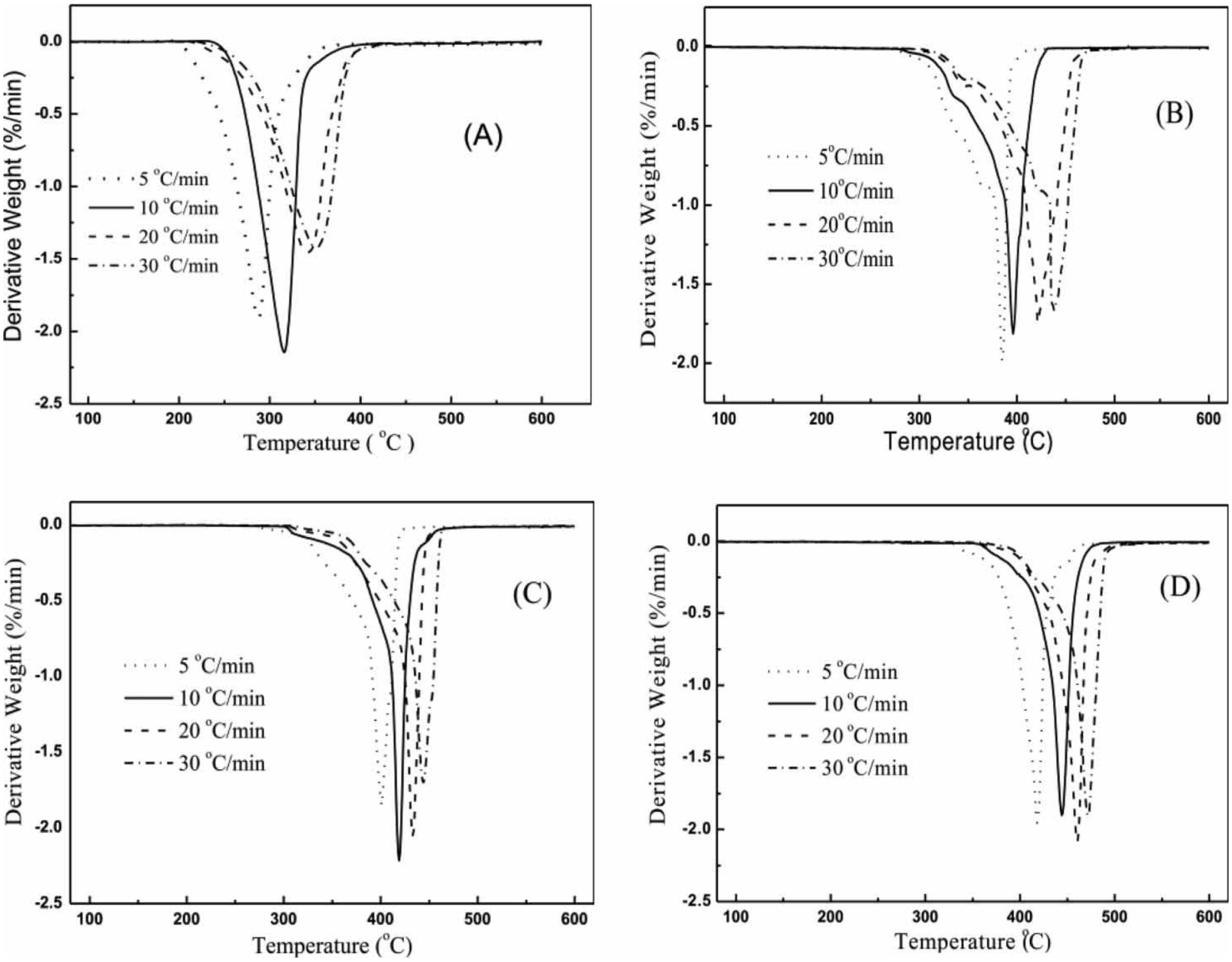

Fig. 4. DGA curves of samples in air at different heating rates: (A) PP; (B) PP/MH (100/100); (C) PP/MH/EG1 (100/90/10); (D) PP/MH/EG2 (100/90/10).

heating rates, 5, 10, 20 and 30°C/min, to evaluate the degradation kinetics parameters. The Kissinger method was employed to analyse the TGA data of PP and flame retarded PP composites. Equation (6) was used to obtain the activation energy which can be calculated from the slope of the straight line of $(\beta/T_{\max}^2)$ vs. $1/T_{\max}$. The peak temperature (T_p) obtained from the DTG curves and the activation energy (E) values for the degradation of PP and its composites are listed in Table 3. The peak temperature (T_p) is shifted to higher temperatures with increasing heating rate. The value of E for the thermal oxidative degradation of neat PP in air is 69.1 kJ/mol. However, the activation energies of PP containing 50% MH (Table 3) are much higher than that of neat PP, and the E value further increases with addition of EG, which means the reaction mechanism of the composites at high temperature was changed.

Another integral method used in this work is the Flynn-Wall-Ozawa method, which is independent of the degradation mechanism (31). Equation (9) is used and the activation energy of neat PP and the flame retarded PP composites can be obtained from a linear fitting of against $1000/T$ for a fixed degree of conversion since the slope of such a line is given by $-0.457E/RT$. From the Doyle approximation, we used the conversion values in the range of 5–60% in this method, so $\alpha = 0.05$, 0.1, 0.2, 0.3, 0.5 and 0.6 were used. The results of the Flynn-Wall-Ozawa analysis are given in Figures 5–8, which are plots of log β vs. $1000/T$ at varying conversions in air. The values of E corresponding to the different conversions are listed in Tables 4–7. The average values of E of neat PP, PP/MH, PP/MH/EG1 and PP/MH/EG2 composites are 37.9, 62.5, 74.7 and 78.6 kJ/mol, respectively, whereas the E values obtained by the Kissinger method are 69.1, 111.4, 134.2, and 137.3 kJ/mol, respectively. There is the same trend of the E values of neat PP and the flame retardant PP composites calculated using the two methods, they follow the order PP/MH/EG2 > PP/MH/EG1 > PP/MH > neat PP, even if there is a discrepancy between the E values obtained by the Kissinger and Flynn-Wall-Ozawa methods.

Table 3. Activation energy of PP and its composites obtained by the Kissinger method

Sample	Heating rate (°C/min)	T_p (°C)	Degradation stage	Activation energy, E(KJ/mol)	Correlation coefficient, γ
Neat-PP	5	287.2	Whole process	69.1	0.9938
	10	316.0			
	20	341.1			
	30	352.3			
PP/MH composite	5	384.9	Whole process	111.4	0.9639
	10	396.1			
	20	421.2			
	30	439.3			
PP/MH/EG1 composite	5	401.2	Whole process	134.2	0.9764
	10	418.6			
	20	432.5			
	30	443.4			
PP/MH/EG2 composite	5	417.9	Whole process	137.3	0.9937
	10	443.8			
	20	460.5			
	30	471.6			

Through analyzing the activation energies obtained by the Kissinger and Flynn-Wall-Ozawa methods above, the E value of the PP/MH/EG composite is higher than that of the composite without EG, no matter what method was used. In other words, the addition of EG can improve the thermal oxidative degradation of the composites in air. The presence of MH in PP affects the E value of the PP degradation, which can be explained by the fact that MH decomposes during the PP degradation. There are some influences of EG on the value of E of PP/MH composite degradation. It is generally accepted that EG exerts its flame retardancy in a polymer in the condensed phase. In EG flame retarded polymer, EG is oxidized to a coherent and dense intumescent char, which can promote forming a protective carbonaceous char on the burning substrate.

The application of a multiple heating rate technique is felt to represent more realistically the variety of heating rates produced during the pyrolysis and combustion reactions occurring when polymer and its composites burn. The two methods, the Kissinger and Flynn-Wall-Ozawa method, present the advantage that they do not require previous knowledge of the reaction mechanism for determining the activation energy (21). The Kissinger method only requires one point, i.e. the point of maximum rate, while the Flynn-Wall-Ozawa method utilizes all points of the TGA curves. This is the primary difference between these

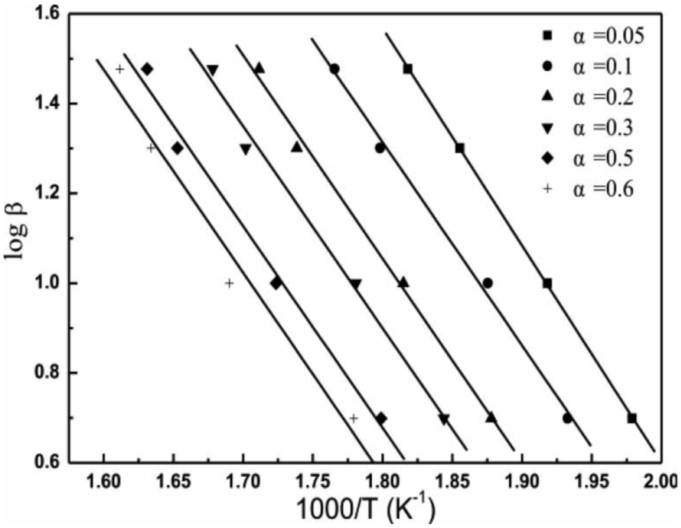

Fig. 5. Ozawa plots of PP at different conversion.

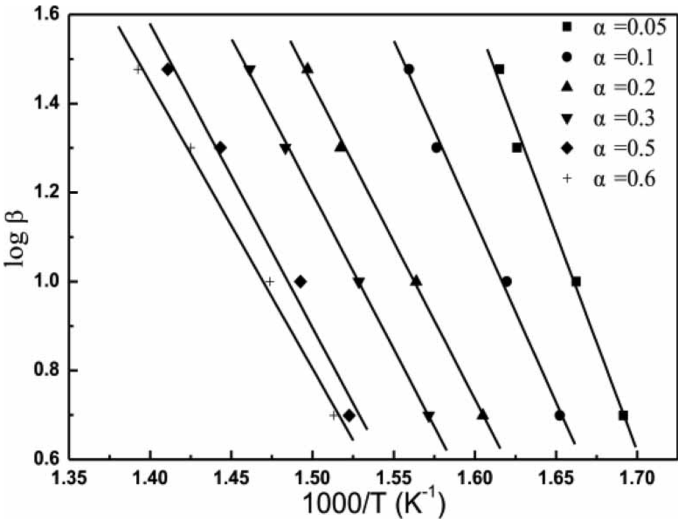

Fig. 6. Ozawa plots of PP/MH (100/100) composite at different conversion.

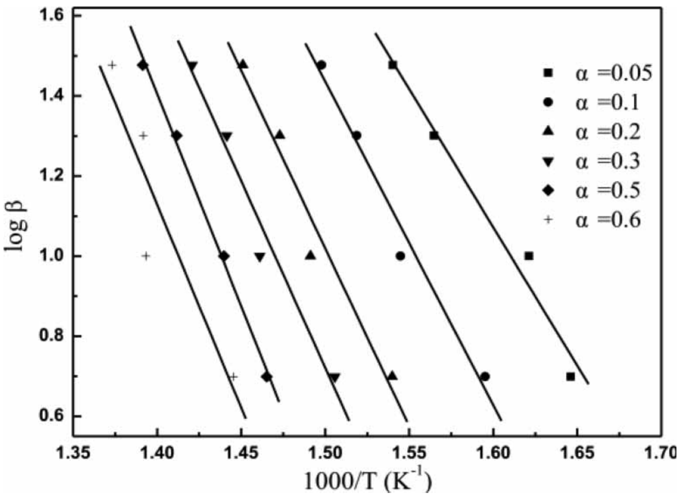

Fig. 7. Ozawa plots of PP/MH/EG1 (100/90/10) composite at different conversion.

two methods. Comparing values of E for the whole process of neat PP and flame retarded PP composites decomposition, as calculated via both the Kissinger and Flynn-Wall-Ozawa methods, we find that there is an evident difference between the two methods. The values of E obtained by Kissinger method are higher than those by Flynn-Wall-Ozawa method. This suggests that the values of the activation energy of neat PP and flame retarded PP composites depend on different mathematical treatment methods during the thermal oxidative degradation. In fact, the actual values of E are dependent not only upon the mathematical treatment used to evaluate the data, but also on such factors as sample size, flow rate, etc. (15), and so the two methods only reveal the trend of the activation energy of samples.

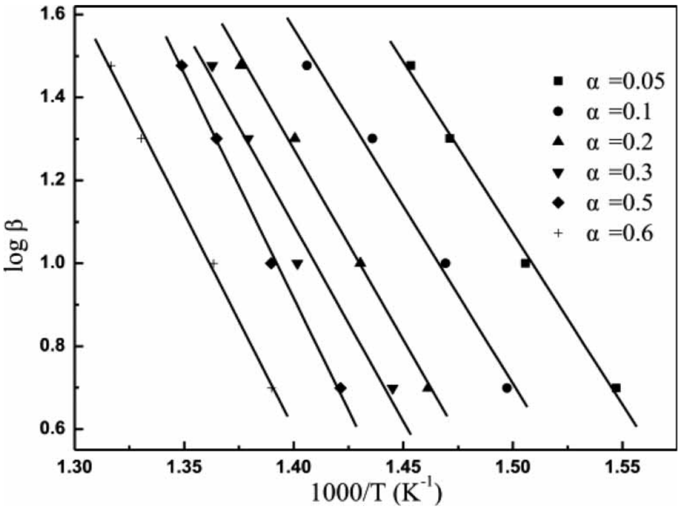

Fig. 8. Ozawa plots of PP/MH/EG2 (100/90/10) composite at different conversion.

Table 4. Activation energy of PP obtained by the Ozawa method

Conversion, α	Activation energy, E(KJ/mol)	Correlation coefficient, γ
0.05	40.2	0.9999
0.1	37.6	0.9979
0.2	37.7	0.9977
0.3	37.4	0.9962
0.5	37.3	0.9946
0.6	37.6	0.9868

Table 5. Activation energy of PP/MH composite obtained by the Ozawa method

Conversion, α	Activation energy, E(KJ/mol)	Correlation coefficient, γ
0.05	81.3	0.9960
0.1	67.6	0.9978
0.2	58.8	0.9991
0.3	58.1	0.9996
0.5	55.5	0.9918
0.6	53.4	0.9976

Table 6. Activation energy of PP/MH/EG1 composite obtained by the Ozawa method

Conversion, α	Activation energy, E(KJ/mol)	Correlation coefficient, γ
0.05	57.4	0.9873
0.1	67.2	0.9896
0.2	73.9	0.9815
0.3	77.5	0.9864
0.5	88.1	0.9983
0.6	84.3	0.9214

Table 7. Activation energy of PP/MH/EG2 composite obtained by the Ozawa method

Conversion, α	Activation energy, E(KJ/mol)	Correlation coefficient, γ
0.05	68.7	0.9981
0.1	71.2	0.9928
0.2	76.6	0.9978
0.3	78.8	0.9882
0.5	89.9	0.9985
0.6	86.2	0.9985

4. Conclusions

The combustion behavior and the thermal oxidative degradation kinetics of PP formulations containing MH in the absence and presence of EG were investigated using the

LOI, UL-94 tests, and TGA in this paper. The results show that expandable graphite has a good synergistic effect with magnesium hydroxide in the PP/MH/EG composites. The EG2, with smaller particle size, usually has the better flame retardant synergistic effect. The TGA results show that the addition of EG can greatly increase the stability of PP/MH/EG composites by increasing the pyrolysis temperature. The thermal oxidative degradation of neat PP and PP/MH and PP/MH/EG composites was investigated by the Kissinger and Flynn-Wall-Ozawa methods. All the results obtained from the methods chosen in this work show that the *E* values for the degradation of the flame retarded PP composites are higher than that of neat PP, especially PP/MH composites with suitable amounts of EG, which indicates that the degradation of the flame retarded PP composites is more difficult than that of neat PP. This suggests that EG with MH used in our work has a beneficial effect on the mechanisms of degradation of neat PP.

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6. References

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