Thermal Oxidative Degradation Kinetics of PP and PP/Mg (OH)₂ Flame-Retardant Composites

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ABSTRACT: The thermal stability and thermal oxidative degradation kinetics of polypropylene (PP) and flame-retardant PP composites filled with untreated and treated magnesium hydroxide (MH) in air were studied by thermogravimetric analysis (TGA). The effect of the heating rate in dynamic measurements (5°C–30°C/min) on kinetic parameters such as activation energy was also investigated. The Kissinger and Flynn–Wall–Ozawa methods were used to determine the apparent activation energy for the degradation of neat PP and flame-retardant PP composites. The results of TGA showed that the addition of untreated or treated MH improved the thermal oxidative stability of PP in air. The kinetic results showed that the apparent activation energy for degradation of flame-retardant PP composites was much higher than that of neat PP, suggesting that the flame retardant used in this work had a great effect on the mechanisms of pyrolysis and combustion of PP. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 1978–1984, 2007

Key words: thermal oxidative degradation; kinetics; activation energy; polypropylene; magnesium hydroxide

INTRODUCTION

Polypropylene (PP) has a wide range of applications in the wire and cable, automobile, housing electronics and electric industries, among others.[1,2] Improving the flame retardation of PP in these applications is a very profound subject. The pyrolysis and combustion of neat PP and flame-retardant PP composites are closely related to their thermal oxidative degradation behavior. Thus, it is important to evaluate the thermal stability and thermal oxidative degradation of PP and its flame-retardant composites in order to ascertain the application and processing windows of PP and its composites. The pyrolysis and combustion of polymer and flame-retardant polymer composites is a subject of great concern in the field of research of flame retardation and smoke suppression.[3–8]

Several ways have been developed to evaluate the pyrolysis behavior of polymers and their composites.[9–11] The methods of kinetic analysis are based on thermogravimetric analysis. Some valuable parameters such as apparent activation energy, preexponential factor, and reaction order can be calculated from a thermogravimetric curve of polymer through differential and integral methods. The distinction between the two methods lies in whether they are based on one heating rate or more than one heating rate.[12]

Some studies have focused on the thermal oxidative degradation of PP.[13,14] It is believed that thermal degradation of PP occurs by random chain scission and that this degradation proceeds via a free-radical mechanism.[15] However, there is a dearth of information on the thermal degradation of halogen-free flame-retardant PP composites, especially of those filled with MH. In our previous work we investigated the mechanical properties and combustion characteristics of silane-modified MH flame-retardant PP composites. It was found that incorporation of a suitable amount of silane-modified MH could improve the flame retardance of the PP/MH composites. In the present work, the thermal oxidative degradation of PP and flame-retardant PP composites in air at different heating rates was studied by thermogravimetric analysis (TGA). The thermal stability and thermal oxidative degradation kinetics of neat PP, PP/MH, and PP/MH/silane composites, as well as the activation energies of these process, were determined by a series of methods, and the mechanism of each process was considered.

Kinetic analysis

The application of dynamic TGA methods holds great promise as a tool for unraveling the mechanisms of the physical and chemical processes that occur during degradation of polymers and their composites. The thermal oxidative degradation kinetics of PP and flame-retardant PP composites are determined on the basis of TGA results. In TGA measurements, conversion, α, is defined as:

$$\alpha = \frac{w_i - w_a}{w_i - w_f} \quad (1)$$

where w_a, w_i, and w_f are the actual, initial, and final sample weights, respectively. Kinetic information can be extracted from dynamic experiments by various methods. All kinetic studies assume that the isothermal rate of conversion,[16] $d\alpha/dt$, is a linear function of the reactant concentration loss and of the temperature-independent rate constant, k, and a temperature-independent function of conversion, that is:

$$d\alpha/dt = \beta(d\alpha/dT) = k(T)f(\alpha) \quad (2)$$

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

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

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

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.

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

$$f(\alpha) = (1 - \alpha)^n \quad (4)$$

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

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

Eq. (5) is normally the fundamental base for kinetic analysis of a solid material from nonisothermal TGA experiments data. In the present study, two methods were used to analyze the nonisothermal kinetics of PP and flame-retardant PP composites.

Flynn–Wall–Ozawa method

The Flynn–Wall–Ozawa method[17,18] is derived from the integral method. The standard eq. (5) can be given as follows:

$$\frac{d\alpha}{(1 - \alpha)^n} = \frac{Ae^{-E/RT}}{\beta}dT \quad (6)$$

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

$$F(\alpha) = \int_0^\alpha \frac{1}{(1 - \alpha)^n}d\alpha = \frac{1}{\beta}A\int_{T_0}^T e^{-E/RT}dT \quad (7)$$

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

From eq. (7) and the Doyle approximation, the result of the integration can be simplified as:

$$\log\beta = \log\frac{AE}{R} - \log F(\alpha) - 2.315 - 0.457\frac{E}{RT} \quad (8)$$

where β, A, E, and T are as already defined.

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

Kissinger method

The Kissinger method[19] was used in the present study to determine the activation energy from plots of the logarithm of the heating rate versus the inverse of the temperature at the maximum reaction rate at a 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:

$$\ln\left(\frac{\beta}{T_{max}^2}\right) = \left\{\ln\frac{AR}{E} + \ln\left[n(1 - a_{max})^{n-1}\right]\right\} - \frac{E}{RT_{max}} \quad (9)$$

where β is the heating rate, T_{max} is the temperature corresponding to the inflection point of the thermal oxidative degradation curves that corresponds to the maximum reaction rate, A is the preexponential factor, a_{max} is the extent of conversion at T_{max}, and n is the reaction order.

The plot of $\ln(\beta/T_{max}^2)$ versus $1/T_{max}$ can be fitted to a straight line, and the activation energy (E) can be calculated from the slope of the line.

EXPERIMENTAL

Materials

The polypropylene used in this work was a commercial polymer, PP-140, supplied by Baling Petrochemical Ltd. (Hunan, China). 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 coupling agent, silane, was a commercial product from the JinTan Estchina Coupling Agent Factory (Jiangsu, China). Antioxidant 1010 is a commercial auxiliary.

The formulations of the PP and flame-retardant PP composites and their limiting oxygen index (LOI) values are given in Table I.

Thermogravimetric analysis

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

RESULTS AND DISCUSSION

Thermal stability of PP and flame-retardant PP composites

Thermogravimetric analysis (TGA) is widely used to study the thermal stability of polymers and their composites. The TGA results for the neat PP, PP/MH, and PP/MH/silane composites in air at a heating rate of 20°C/min are shown in Figure 1. The thermal oxidative degradation of the neat PP was complete at temperatures up to 420°C, with no residue remaining. However, about 35%–37% of the residue was left after degradation of the flame-retardant PP composites. It is noteworthy that the PP/MH/silane composites degraded less than PP/MH composites at the same temperature over almost the whole degradation process, indicating that the silane-treated MH in the flame-retardant PP composites resulted in increasedthe thermal oxidative stability of the composites. Moreover, the amount of residue remaining at 600°C was in the following order: PP/MH/silane > PP/MH
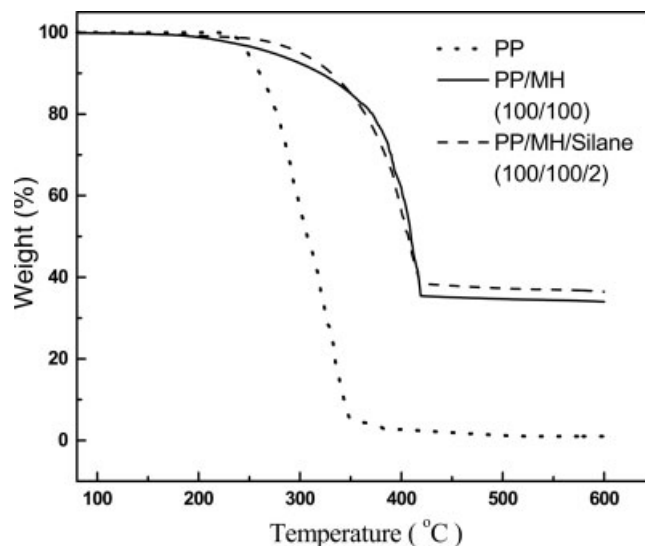
TABLE I
PP and FlameRetardant PP Composites Investigated

Sample	LOI (%)
PP	18.1
PP/MH [100 : 100 (w/w)]	28.2
PP/MH/silane [100 : 100 : 2 (w/w)]	29.6

Figure 1 TGA curves of PP and flame-retardant PP composites in air at a heating rate of 20°C/min.

> PP. Flame resistance can be evaluated from the char residue after pyrolysis. A linear relationship between LOI and char residue for halogen-free polymers was established by Van Krevelen.[20] Increasing char formation can limit the production of combustible carbon-containing gases and decrease the exothermic energy induced by pyrolysis reactions, as well as decrease the thermal conductivity of the surface of burning materials.[21] A higher residue will enhance flame retardation. The LOIs (Table I) of the neat PP, PP/MH, and PP/MH/silane composites were 18.1, 28.2, and 29.6, respectively. This suggests that the addition of MH both untreated and treated can enhance the flame-retardant capability of PP.

The TGA data for the PP and flame-retardant PP composites, including decomposition temperatures of 5%, 20%, and 50% weight loss, onset temperature of TGA, and peak temperature of DTG, are listed in Table II. All the results indicated that the thermal oxidative stability of PP filled with MH composites whether untreated or treated was visibly improved.

Figure 2 shows the TGA curves of the PP and flame-retardant PP composites heated in air at several heating rates from 5°C/min to 30°C/min. Figure 3 shows the corresponding DTG curves of the composites. It can be clearly seen from Figures 2 and 3 that the thermal oxidative degradation curves of the composites shifted to higher temperatures with an increasing heating rate.

Thermal oxidative degradation kinetics of PP and flame-retardant PP composites

TGA of the PP and flame-retardant PP composites was performed under a steady flow in air at heating rates of 5°C/min, 10°C/min, 20°C/min, and 30°C/min in

TABLE II
Thermal Stability and Degradation Data of PP and Flame-Retardant PP

Sample	$T_{5\%}$ (°C)	$T_{20\%}$ (°C)	$T_{50\%}$ (°C)	T_i (°C)	T_p (°C)	Residue at 500°C (%)
PP	248.3	278.0	307.2	251.6	316.1	1.2
PP/MH	272.1	371.2	409.9	343.6	414.8	34.7
PP/MH/silane	300.2	364.5	417.4	348.2	401.7	37.3

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

order to evaluate the degradation kinetics parameters. The Kissinger method was employed to analyze the TGA data of the PP and flame-retardant PP composites. Eq. (9) was used to obtain the activation energy values, which were calculated from the slope of the straight line of $\ln(\beta/T_{max}^2)$ versus $1/T_{max}$. The peak temperatures (T_p) obtained from the DTG curves and the activation energy (E) values for the degradation of PP and its composites are given in Table III. The results show that the T_p increased with increasing heat-

ing rate. The activation energy of the thermal oxidative degradation of neat PP in air was 69.1 kJ/mol, much lower than those of PP containing 50% MH (Table III), indicating a change in the reaction mechanism.[5]

Another derivative method used in the present work was the Flynn–Wall–Ozawa method, which is probably the most general derivative technique.[22] It is an integral method that is also independent of the degradation mechanism. Using eq. (8), the activation
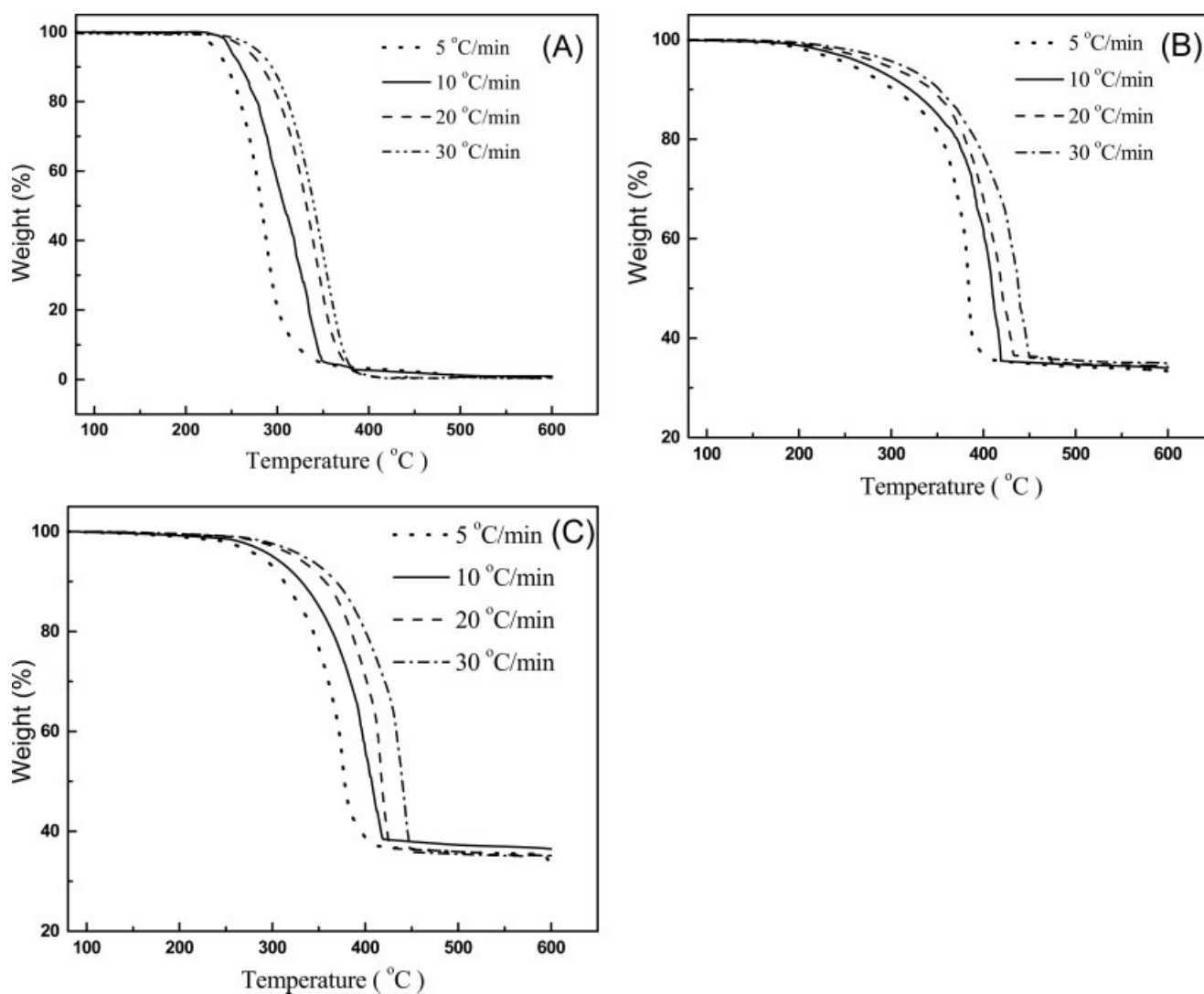

Figure 2 TGA curves of samples in air at different heating rates: (A) PP; (B) PP/MH; (C) PP/MH/silane.
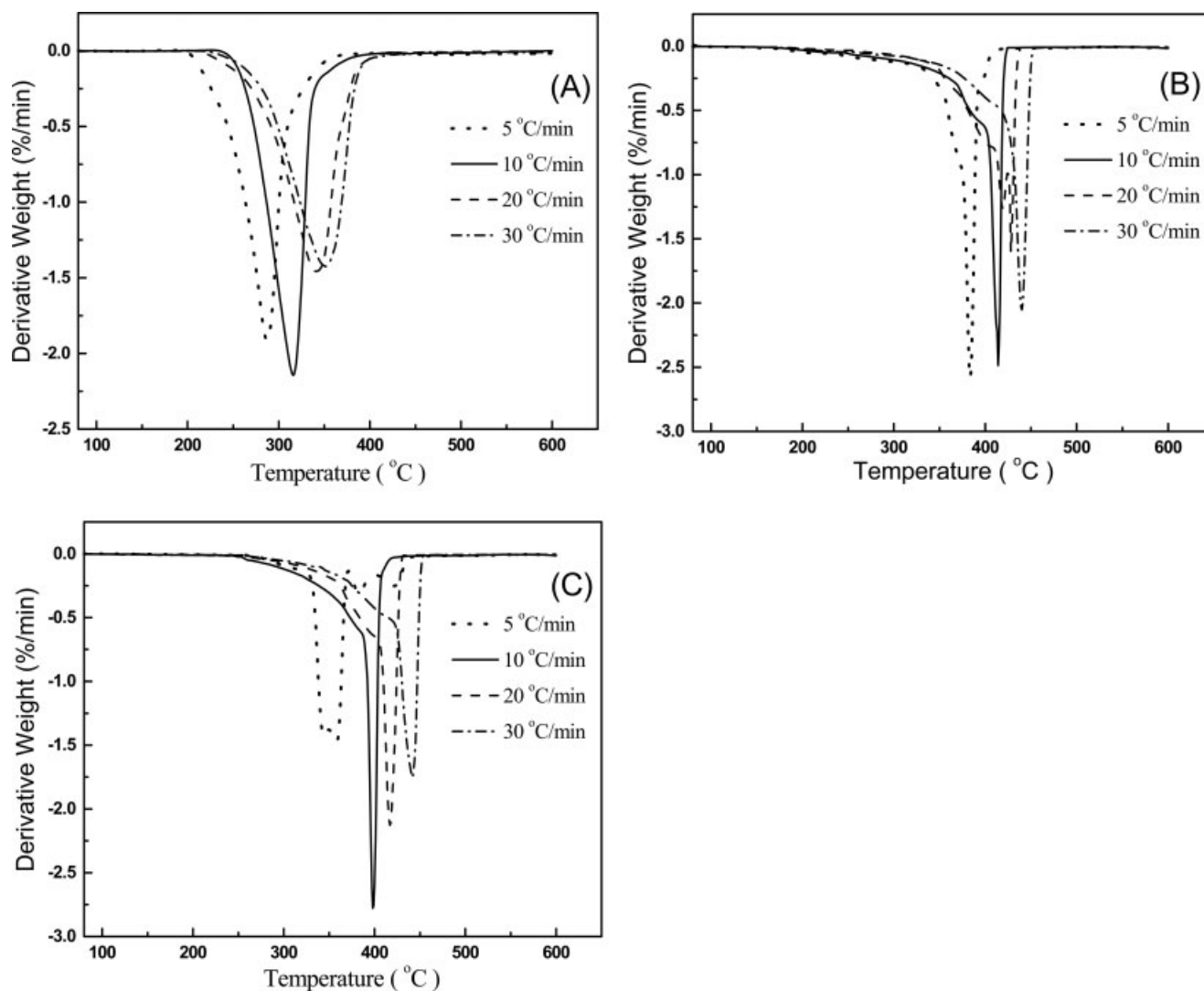
Figure 3 DTG curves of samples in air at different heating rates: (A) PP; (B) PP/MH; (C) PP/MH/silane.

energy values of neat PP and flame-retardant PP composites could be obtained from a linear fitting of log β against 1000/T for a fixed degree of conversion because the slope of such a line is given by $-0.457 E/RT$.

From the Doyle approximation, we used conversion values in the range of 5%–60% with this method, so α values of 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

TABLE III
Activation energy of PP and Its Composites Obtained by Kissinger Method

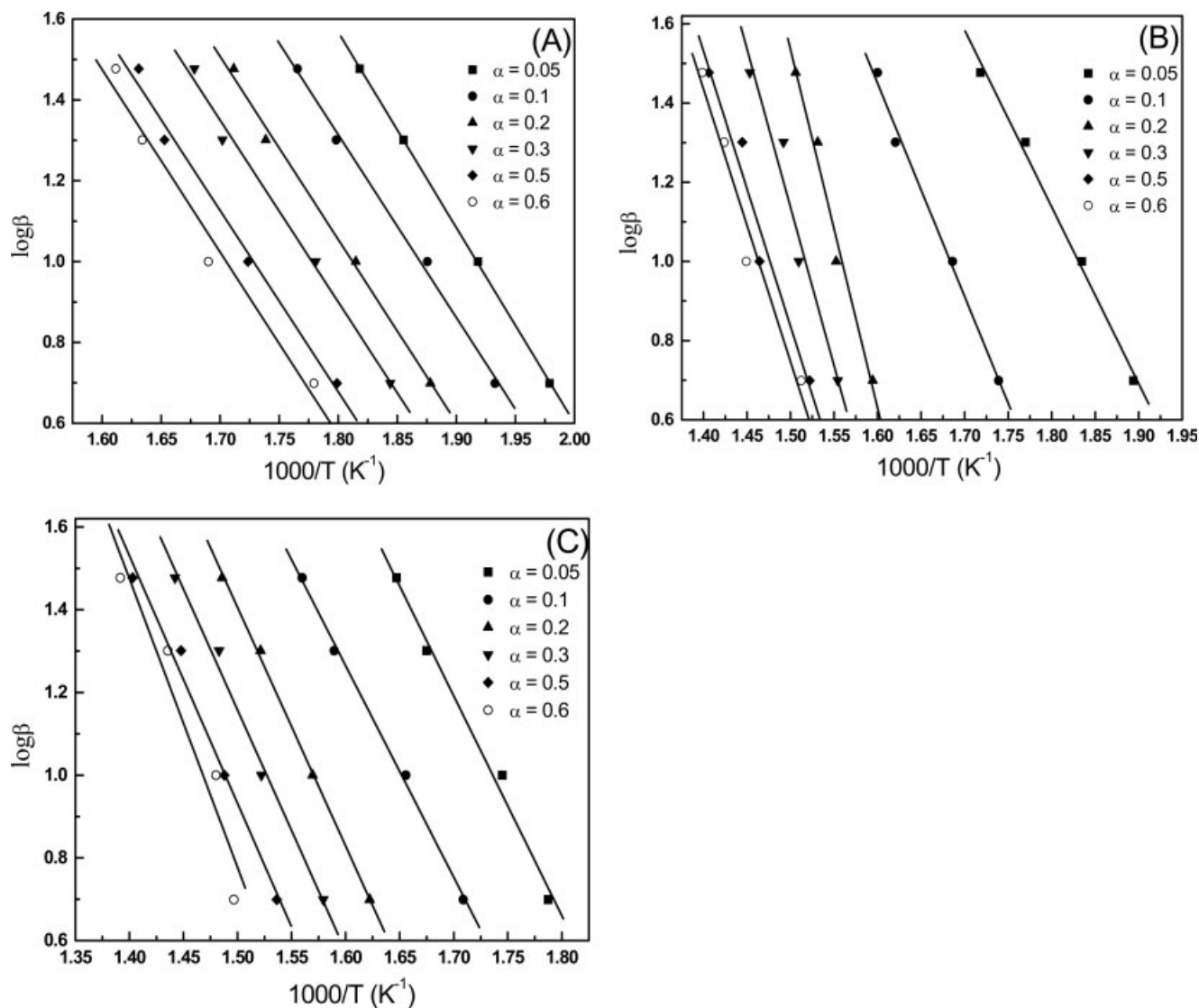| Sample	Heating rate (°C/min)	T_p (°C)	Degradation stage	Activation energy, E (kJ/mol)	Correlation coefficient (γ)
PP	5	287.2	Whole process	69.1	0.9938
	10	361.0			
	20	341.1			
	30	352.2			
PP/MH	5	383.4	Whole process	110.0	0.9791
	10	414.1			
	20	427.9			
	30	440.2			
PP/MH/silane	5	358.4	Whole process	95.4	0.9813
	10	398.4			
	20	417.0			
	30	442.2			

Figure 4 Ozawa plots of PP and flame-retardant PP composites in air at different conversions: (A) PP; (B) PP/MH; (C) PP/MH/silane.

Figure 4, which shows the plots of log β versus 1000/T at varying conversion in air. The activation energies (E) corresponding to the different rates of conversion are listed in Tables IV–VI, which show that the neat PP, PP/MH, and PP/MH/silane composites, respectively, had an average activation energy of 37.9, 55.6,

and 48.8 kJ/mol, respectively. The corresponding activation energy values obtained by the Kissinger method were 69.1, 110.0, and 95.4 kJ/mol, respectively. It was clearly observed that the activation energies of neat PP and flame-retardant PP composites calculated using the two methods followed the same

TABLE IV
Activation Energy of PP Obtained by Flynn–Wall–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 V
Activation Energy of PP/MH Composites Obtained by Flynn–Wall–Ozawa Method

Conversion, α	Activation energy, E (kJ/mol)	Correlation coefficient, γ
0.05	37.1	0.9969
0.1	44.7	0.9966
0.2	75.2	0.9907
0.3	66.5	0.9785
0.5	56.6	0.9804
0.6	57.3	0.9821

TABLE VI
Activation Energy of PP/MH/Silane Composites Obtained by Flynn–Wall–Ozawa Method

Conversion, α	Activation energy, E (kJ/mol)	Correlation coefficient, γ
0.05	44.2	0.9948
0.1	43.3	0.9988
0.2	48.0	0.9994
0.3	48.6	0.9956
0.5	49.8	0.9932
0.6	58.0	0.9924

trend, in the order PP/MH composites > PP/MH/silane composites > neat PP, even if there were differences in the E values obtained by the Kissinger and Flynn–Wall–Ozawa methods.

Through analyzing the activation energies obtained by the Kissinger and Flynn–Wall–Ozawa methods, we found that the E of neat PP was much lower than that of flame-retardant PP, no matter what method was used. In other words, MH could improve the thermal oxidative degradation of neat PP in air. The increase in the apparent activation energy of the polypropylene thermal oxidative degradation can be explained by the decomposition of MH not being complete before polypropylene degradation.

The application of a multiple heating rate technique was believed to more realistically represent the variety of heating rates produced during the pyrolysis and combustion reactions occurring when polymer and its composites burn. The primary difference between the two methods is that the Kissinger method is only suitable for one point on a TGA curve, the maximum rate, whereas the Flynn–Wall–Ozawa method is applicable to all points on a TGA curve. Comparing E values for all stages of neat PP and flame-retardant PP composite decomposition as calculated by both the Kissinger and Flynn–Wall–Ozawa methods, we found obvious differences between the two methods. E values obtained by the Kissinger method were higher than those by obtained by the Flynn–Wall–Ozawa method. These two methods have the advantage of not requiring previous knowledge of the reaction mechanism to determine the activation energy.[12] This suggests that the activation energy of neat PP and flame-retardant PP composites depend on different mathematical treatment methods during thermal oxidative degradation. At the same time, we think the actual apparent activation energies are dependent not only on the mathematical treatment used

to evaluate the data but also on such factors as sample size and flow rate.[5]

CONCLUSIONS

TGA results showed the thermal stability of flame-retardant PP composites was much better than that of neat PP. The thermal oxidative degradation of neat PP and PP/MH and PP/MH/silane composites was investigated by the Kissinger and Flynn–Wall–Ozawa methods. The results showed that the apparent activation energies of the degradation of the flame-retardant PP composites were higher than that of neat PP, indicating it was much more difficult to degradate the flame-retardant PP composites than the neat PP. This suggested that the filler used in our work had a great effect on the mechanisms of the degradation process of neat PP.

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