

# Kinetics of thermo-oxidative degradation of zinc borate/microcapsulated red phosphorus with magnesium hydroxide in flame retarded polypropylene composites

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**Abstract** The flammability and the thermo-oxidative degradation kinetics of zinc borate (ZB) and microcapsulated red phosphorus (MRP) with magnesium hydroxide (MH) in flame-retardant polypropylene (PP) composites were studied by limiting oxygen index (LOI), TGA, and FTIR spectroscopy. The results show that ZB/MRP is a good synergist for improving the flame retardancy of the PP composites. The Kissinger and Flynn-Wall-Ozawa methods were used to determine the activation energy ( $E$ ) for degradation of PP composites. The results from the TGA curves indicate that the thermal stability of PP/MH/ZB and PP/MH/ZB/MRP composites is better than that of PP/MH composites. The kinetic results show that the values of  $E$  for degradation of PP/MH/ZB/MRP composites is much higher than those of PP/MH and PP/MH/ZB composites. The FTIR spectra data show that the incorporation of MH improves the thermo-oxidative stability of PP, especially for PP/MH composites with suitable content of MRP at higher temperatures. These data indicate that the synergistic flame retardants used in this work have a great effect on the

mechanisms of pyrolysis and combustion of PP/MH composites.

**Keywords** Thermo-oxidative degradation · Kinetics · Zinc borate · Red phosphorus · Magnesium hydroxide · Polypropylene

## Introduction

The degradation of polymer materials is the focus of a lot of research into the management of plastic waste. The analysis of the degradation kinetics of polymeric materials is important for modeling the degradation process. The process of molecule chain scission is very complex and causes various products [1]. Polypropylene (PP) is the major synthetic polymer to achieve industrial importance. However, the relatively low thermal resistance and the flammability of PP matrix limit its usage in many fields of applications. Pyrolysis is the standard technique used for thermally degrading polymer, and much interest has been devoted to the investigation of PP thermal degradation [2–8]. Earlier studies showed that the thermal depolymerization of PP was considered as a radical process, which included initiation, propagation and termination, and which was analogous to the mechanism of polyethylene degradation [1, 4, 9]. After the bond scission into primary and secondary radicals, tertiary radicals are formed *via* rearrangement reactions.

The pyrolysis and combustion of PP and its composites has a close relationship with their thermo-oxidative degradation process. Therefore, it is very important to evaluate the thermal stability and thermo-oxidative degradation of PP and the flame retarded PP composites so as to ascertain the application and processing window of PP composites. The pyrolysis and

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combustion of polymeric materials is a subject of concern in the research field of flame retardancy and smoke suppression [10–13]. Several ways have been developed to evaluate the pyrolysis behaviors of polymer composites [14–16]. The methods of kinetic analysis are based on thermogravimetric analysis. Some valuable parameters, such as pre-exponential factor, reaction order, and apparent activation energy can be calculated from the thermogravimetric curve of 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 [17]. The apparent kinetic parameters for the overall thermal degradation of PP were determined under isothermal conditions using a gradient free reactor with on-line mass spectrometry. For pure PP, different investigators have reported different values of activation energy [4, 8].

However, there is lack of information on the thermal degradation of halogen-free flame retarded PP composites, especially for PP/MH composites with synergistic additives, such as ZB, MRP etc. In our previous work [18–21], we studied the mechanical properties, crystallization behavior, and combustion characteristics of MH flame retarded PP composites. It was found that incorporation of a suitable amount of MRP had good synergistic effect with MH in flame retardant PP composites. In this paper, the flammability and thermo-oxidative degradation of ZB or/and MRP with MH flame retarded PP composites were investigated by limiting oxygen index (LOI), thermogravimetric analysis (TGA), and fourier transform infrared (FTIR) spectra. The thermal stability and thermo-oxidative degradation kinetics of PP/MH, PP/MH/ZB, and PP/MH/ZB/MRP composites were characterized by a series of methods, apparent activation energies of these processes have been determined, and the mechanism of each process has also been discussed in detail.

## Experimental

### Materials

PP used in this work was a commercial polymer PP-140, supplied by Baling Petrochemical Ltd (Hunan, China). zinc borate (ZB) was supplied by Shandong Zibo Zichuan Chemical CO., LTD. Microcapsulated red phosphorus (MRP) was provided by National Engineering Research Center for Compounding and Modification of Polymeric Materials (Guizhou, China). Magnesium hydroxide, Mg(OH)<sub>2</sub>, with an average particle size of 2.0–2.5 μm, was provided by Qindao Haida Chemical Ltd (Shandong, China). The surface of MH particles was treated with stearate according to our previous report [18].

### Preparation of samples

The PP composites filled with the desired amounts of MH, ZB or/and MRP 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 screw speed is 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. The samples for FTIR measurements were obtained from the residue left after the corresponding composites degraded in a muffle oven under different temperatures.

### Measurements and characterization

#### *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.

#### *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°C/min, 10°C/min, 20°C/min and 30°C/min by a Perkin-Elmer Q 50 thermogravimetric analyzer. Experimental error was about ±5°C and ±1 wt.% for thermo-oxidative degradation temperature and char yield, respectively.

#### *FTIR spectroscopy*

The Fourier transform infrared (FTIR) spectra were recorded using a Nicolet MAGNA-IR 750 spectrophotometer. The residues left after degradation of PP/MH, PP/MH/ZB and PP/MH/ZB/MRP composites degraded at different temperatures were mixed with KBr powders, and then the mixture was compressed into plates for FTIR spectra analysis.

### 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 thermo-oxidative degradation kinetics of PP and flame retarded PP

composites can be based on TGA results. In TGA measurements, conversion  $\alpha$  has been defined as:

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

where  $w_\alpha$ ,  $w_i$  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 investigations assume that the isothermal rate of conversion,  $d\alpha/dt$ , 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,  $\alpha$ , 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.  $\beta = dT/dt$ .

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

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

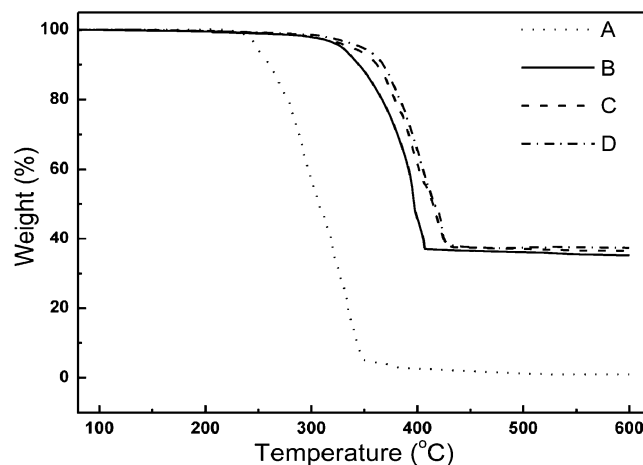
where  $E$  is the activation energy of the reaction,  $A$  is the frequency factor,  $T$  is the reaction temperature, and  $R$  is the gas constant.

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

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



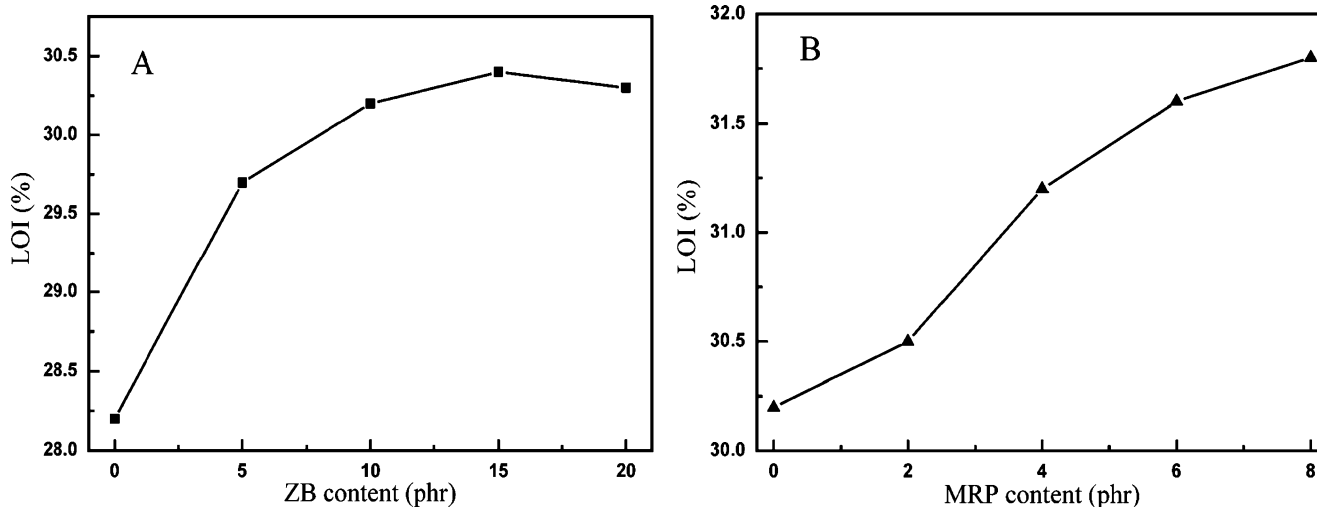
**Fig. 2** The TGA curves of the flame retarded PP composites in air: **a** neat-PP; **b** PP/MH (100/100); **c** PP/MH/ZB (100/90/10); **d** PP/MH/ZB/MRP (100/90/4/6)

Equation 5 is normally the fundamental base for the kinetic analysis of a solid material from nonisothermal TGA experimental data. In present paper, the Kissinger and Flynn-Wall-Ozawa methods [22–25] were used to calculate the activation energy ( $E$ ) of the PP matrix and flame retarded PP composites.

## Results and discussion

### Flammability

Figure 1 presents the changes of LOI values for the PP/MH composites with different synergistic additives. On the one hand, the LOI values of PP/MH/ZB composites increase



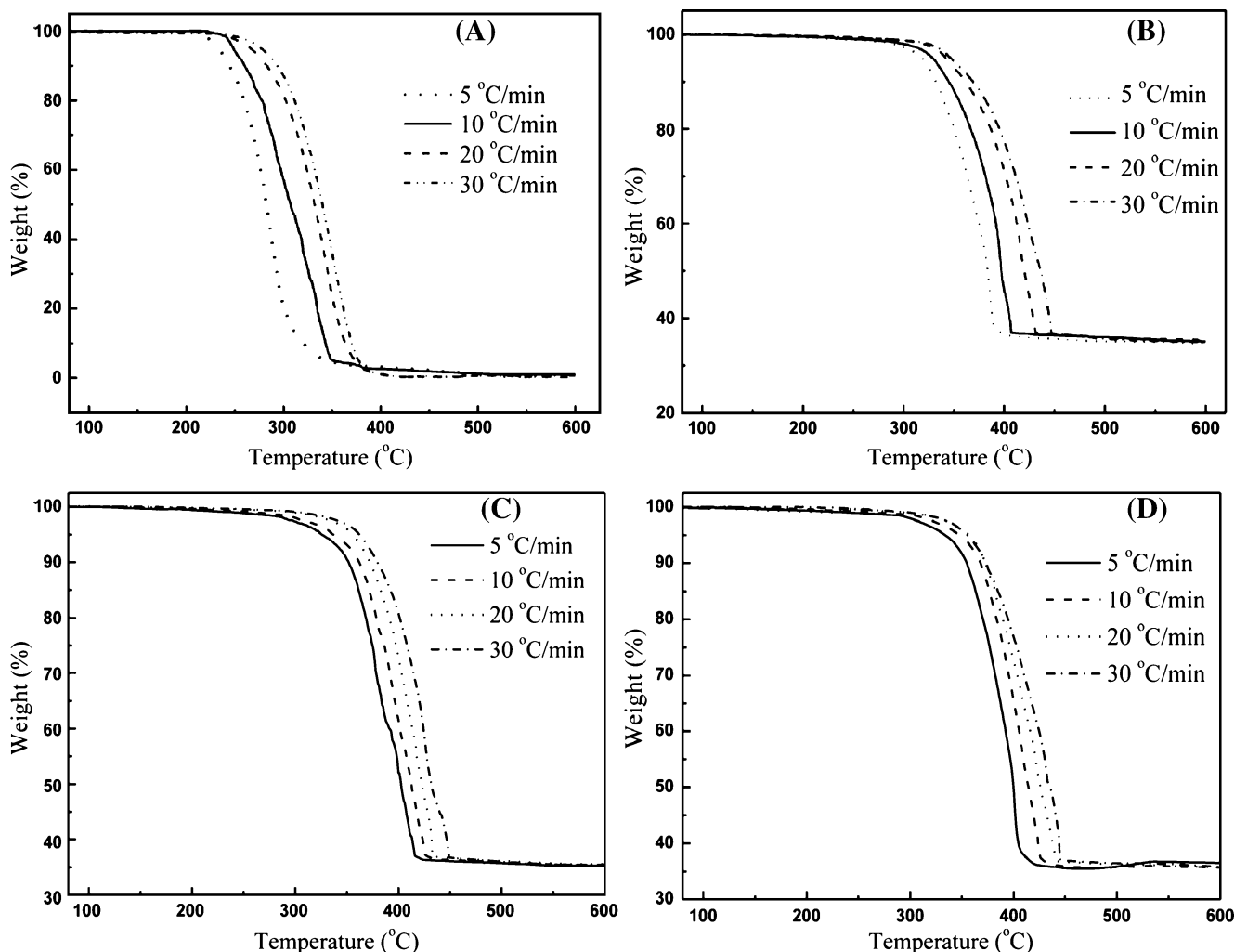
**Fig. 1** Effect of ZB and MRP on LOI values of the flame retarded PP composites: **a** PP/MH/ZB composites (PP=100 phr, MH + ZB=100 phr); **b** PP/MH/ZB/MRP composites (PP=100 phr, MH=90 phr, ZB + MRP=10 phr)

with increasing the loading of ZB and then level off after 10 phr ZB, indicating that ZB can improve the flame retardancy of the PP/MH composites. On the other hand, it is clearly seen that the values of LOI of PP/MH/ZB/MRP composites increase gradually with increasing the concentration of MRP. With the addition of 4 phr MRP instead of partial ZB in the composites, the LOI values of the composites increase from 30.2 to 31.2. These data show that the addition of MRP can greatly improve the LOI values of flame retarded PP composites due to its better synergistic effect with MH. Moreover, the flame retardant mechanism of the system has changed due to the addition of MRP.

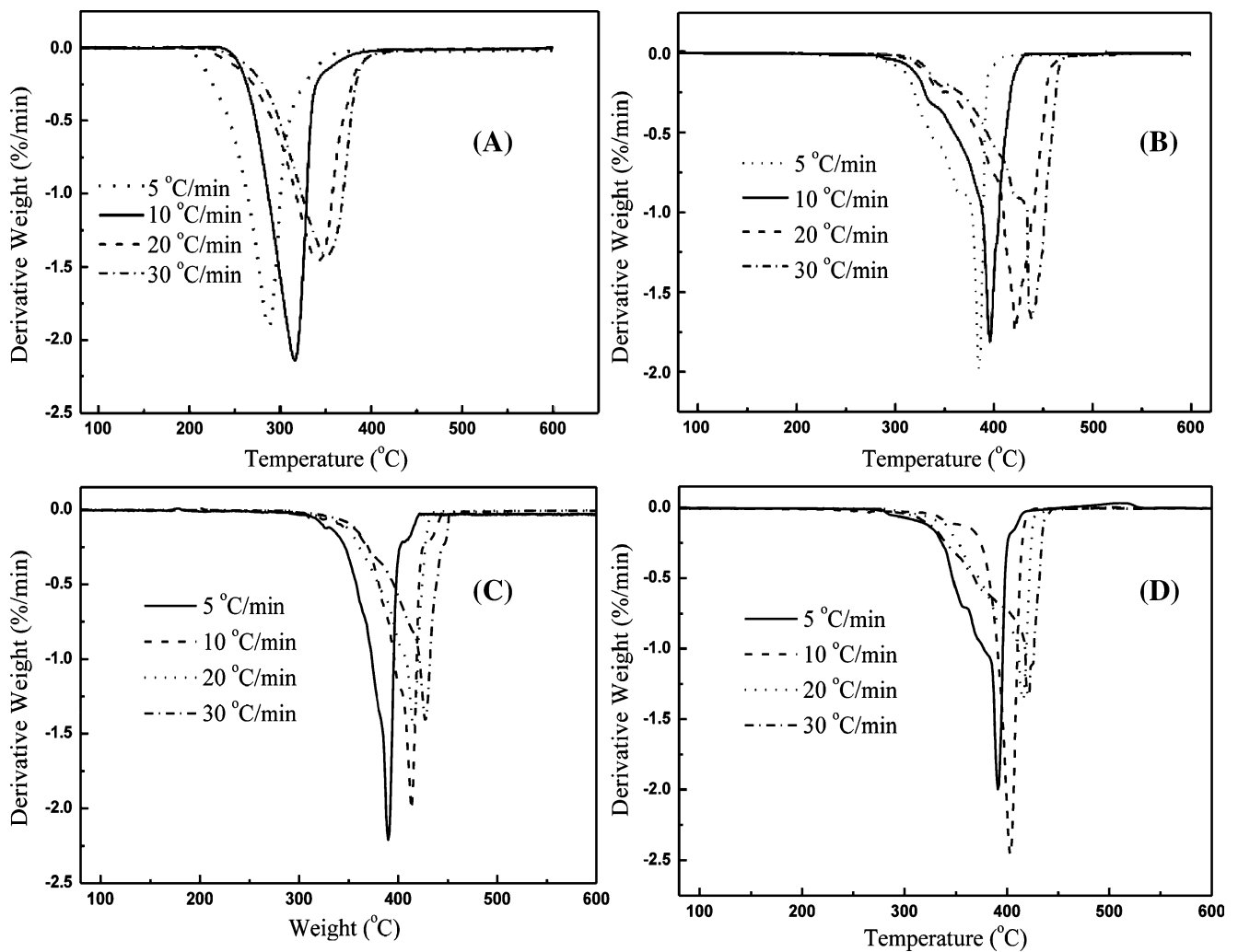
### Thermal stability

TGA curves of the PP composites under a flow of air at a heating rate of 10°C/min are shown in Fig. 2. In our previous studies [8, 18] showed that the addition of MH

greatly improved the thermo-oxidative stability. In this work, the PP/MH/ZB composites with and without MRP both show only one decomposition process as that of PP/MH composites. The thermogravimetric curves of these composites are very similar at whole degradation process and the procedural decomposition temperatures of the composites with MRP are slightly higher than those of the composites without MRP. For example, the decomposition temperatures of neat PP and PP/MH composites at 5% loss weight are 248.3°C and 328.2°C, respectively, whereas those of PP/MH/ZB and PP/MH/ZB/MRP composites are 337°C and 347.1°C, respectively. These results indicate that the thermal stability of the PP/MH/ZB and PP/MH/ZB/MRP composites is greatly superior to that of the PP/MH composites by the increase of pyrolysis temperature. On the other hand, the residue left after degradation of PP/MH composites at 550°C is 35.5 wt.% and those of PP/MH/ZB and PP/MH/ZB/MRP composites are 37.6 wt.% and 38.0 wt.%, respectively, indicating more residue for the



**Fig. 3** TGA curves of PP and PP composites in air at different heating rates: **a** PP; **b** PP/MH (100/100); **c** PP/MH/ZB (100/90/10); **d** PP/MH/ZB/MRP(100/90/4/6)



**Fig. 4** DTG curves of PP and PP composites in air at different heating rates: **a** PP; **b** PP/MH (100/100); **c** PP/MH/ZB (100/90/10); **d** PP/MH/ZB/MRP(100/90/4/6)

**Table 1** 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, $\gamma$
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/ZB composite	5	389.8	Whole process	168.6	0.9419
	10	413.7			
	20	416.8			
	30	427.4			
PP/MH/ZB/MRP composite	5	391.2	Whole process	172.2	0.9553
	10	412.7			
	20	416.3			
	30	425.7			

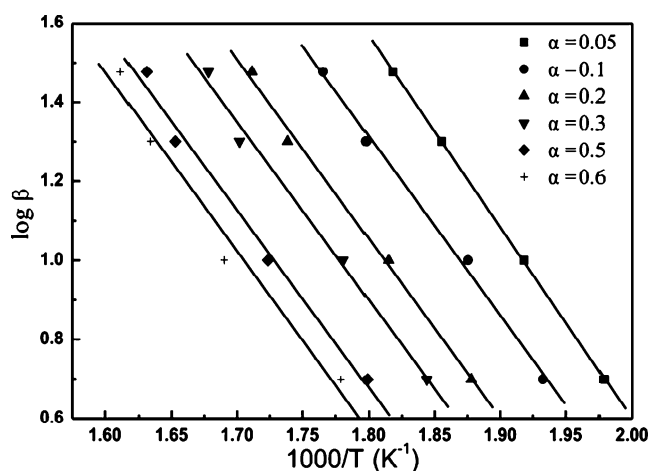


Fig. 5 Ozawa plots of PP at different conversion

composites with ZB/MRP after degradation at high temperature. Higher residue enhances the flame retardancy, reflecting the increase of LOI (Fig. 1).

Figure 3 showed the TGA curves of PP and its composites heated in air at several heating rates from 5°C/min to 30°C/min. Figure 4 was the corresponding DTG curves of the composites. It is clearly found from Figs. 3 and 4 that the thermo-oxidative degradation curves of the above composites are shifted to higher temperatures with increasing heating rate.

#### Thermo-oxidative degradation kinetics

In this work, the activation energy ( $E$ ) values of PP and its composites were calculated using the Kissinger and Flynn-Wall-Ozawa methods. According to the Kissinger method, the values of  $E$  are obtained from the slope of the straight line of  $\ln(\beta/T_{\max}^2)$  versus  $1/T_{\max}$ . The peak temperature ( $T_p$ ) obtained from the DTG curves and  $E$  values for the

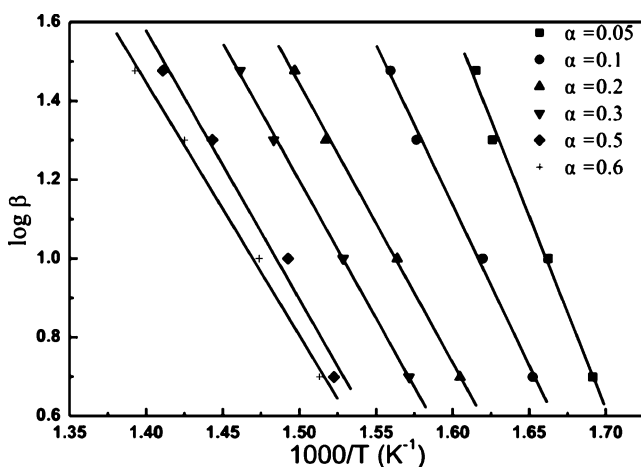


Fig. 6 Ozawa plots of PP/MH (100/100) composite at different conversion

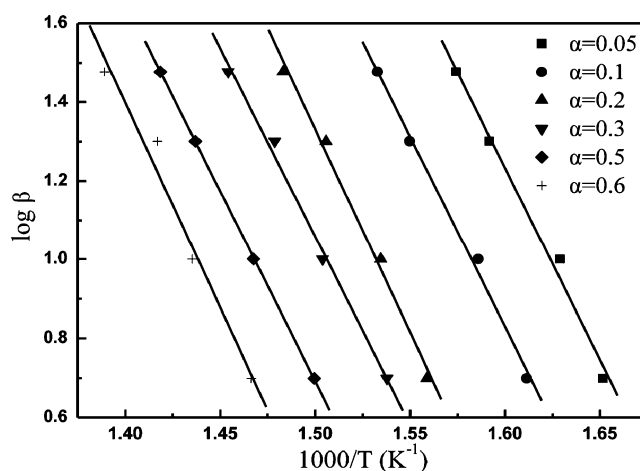


Fig. 7 Ozawa plots of PP/MH/ZB (100/90/10) composite at different conversion

degradation of the above samples were listed in Table 1. The results show that  $T_p$  is shifted to higher temperatures with increasing heating rate. The value of  $E$  of the thermo-oxidative degradation of neat PP in air is only 69.1 kJ/mol. However, the  $E$  values of PP containing various flame retardant additives (Table 1) are much higher than that of neat PP, and the  $E$  values further increase with the incorporation of MRP, indicating the reaction mechanism has changed.

Another kinetic method used in this paper is Flynn-Wall-Ozawa method, which is probably the most general derivative technique [26]. The plot of  $\log \beta$  against  $1,000/T$  at a fixed degree of conversion  $\alpha$  should give a straight whose slope is proportional to  $E$ . 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 method were shown in Figs. 5, 6, 7 and 8, which illustrated the plots of  $\log \beta$  versus  $1,000/T$  at varying conversions in air. And the values of  $E$  corresponding

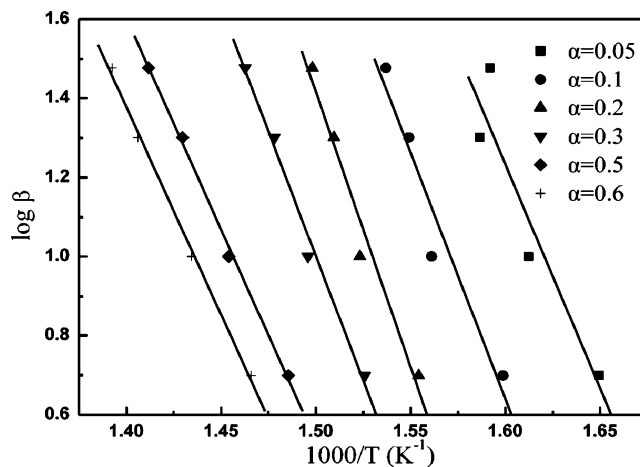


Fig. 8 Ozawa plots of PP/MH/ZB/MRP (100/90/4/6) composite at different conversion

**Table 2** Activation energy of PP obtained by the Ozawa method

Conversion, $\alpha$	Activation energy, $E(\text{KJ/mol})$	Correlation coefficient, $\gamma$
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 3** Activation energy of PP/MH composite obtained by the Ozawa method

Conversion, $\alpha$	Activation energy, $E(\text{KJ/mol})$	Correlation coefficient, $\gamma$
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 4** Activation energy of PP/MH/ZB composite obtained by the Ozawa method

Conversion, $\alpha$	Activation energy, $E(\text{KJ/mol})$	Correlation coefficient, $\gamma$
0.05	80.9	0.9948
0.1	80.3	0.9975
0.2	85.7	0.9959
0.3	79.4	0.9967
0.5	80.1	0.9997
0.6	86.5	0.9879

**Table 5** Activation energy of PP/MH/ZB/MRP composite obtained by the Ozawa method

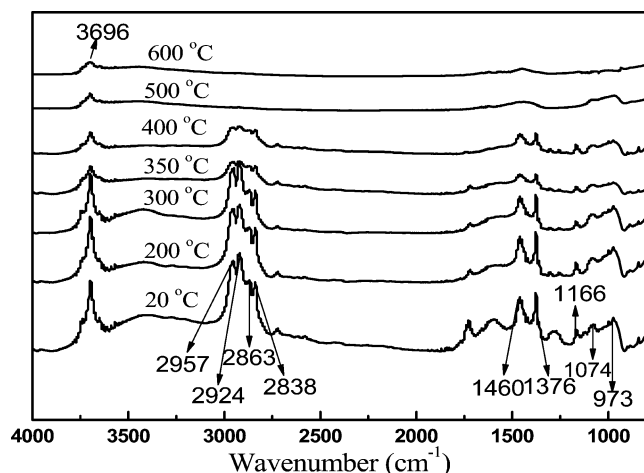
Conversion, $\alpha$	Activation energy, $E(\text{KJ/mol})$	Correlation coefficient, $\gamma$
0.05	94.2	0.9425
0.1	103.4	0.9701
0.2	115.1	0.9833
0.3	104.5	0.9943
0.5	88.2	0.9985
0.6	87.3	0.9985

to the different conversions were listed in Tables 2, 3, 4 and 5. The average values of  $E$  of neat PP, PP/MH, PP/MH/ZB, and PP/MH/ZB/MRP composites are 37.9 kJ/mol, 62.5 kJ/mol, 82.2 kJ/mol, and 98.7 kJ/mol, respectively. The  $E$  values of these composites obtained by Kissinger method are 69.1 kJ/mol, 111.4 kJ/mol, 168.6 kJ/mol, and 172.2 kJ/mol, respectively. It is clearly observed that the same trend of the  $E$  values of neat PP and its composites calculated using the two methods follows the order PP/MH/ZB/MRP > PP/MH/ZB > PP/MH > neat PP, even if there is a discrepancy for the  $E$  values obtained by the Kissinger and Flynn-Wall-Ozawa methods. In addition, it is clearly seen from Table 5 that the  $E$  values of PP/MH/ZB/MRP composites increases with increasing  $\alpha$ , and then decreases. This indicates that the  $E$  values depend on the degree of conversion due to the addition of MRP.

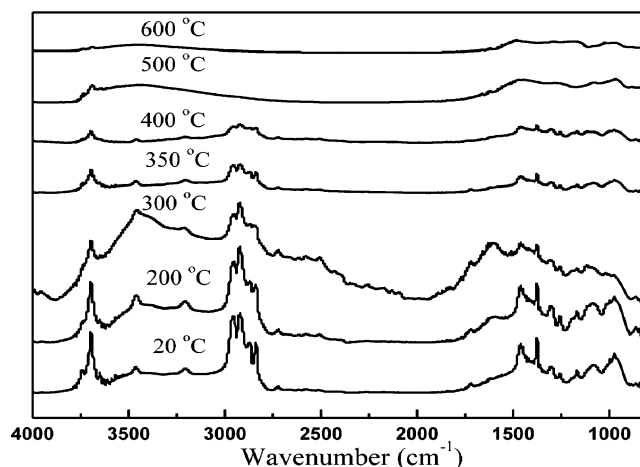
Through analyzing the activation energies obtained by the Kissinger and Flynn-Wall-Ozawa methods, It is found that the  $E$  values of the PP/MH/MRP composites is higher than those of the composites without MRP. In other words, the addition of MRP can improve the thermo-oxidative degradation temperature of the PP composites. The increase of  $E$  value of the PP composites can be explained by the fact that the decomposition of MH does not complete before the polypropylene degradation. And there are some influences of MRP on the value of  $E$  of PP/MH composite. It is generally accepted that MRP exerts its flame retardancy in polymer in the condensed phase. In MRP flame retarded PP, it is oxidized to coherent and dense intumescent char, which can promote forming a protective carbonaceous char on the burning substrate.

#### FTIR analysis of the residue

In general the changes of C-H absorption intensities of aliphatic groups in the 2,400–3,200  $\text{cm}^{-1}$  region are used to

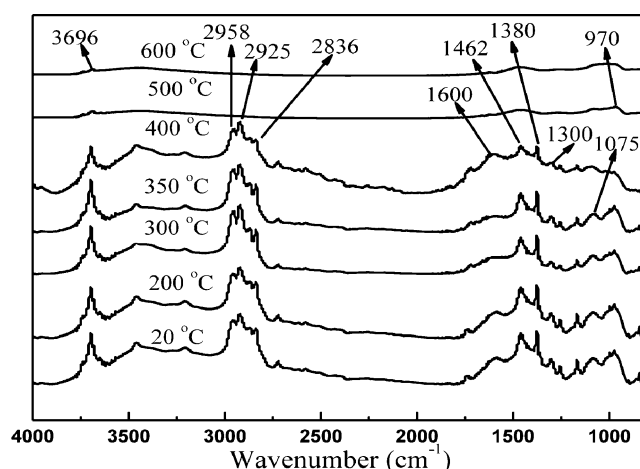


**Fig. 9** Changes in residue left FTIR spectra of PP/MH composite at different pyrolysis temperatures



**Fig. 10** Changes in residue left FTIR spectra of PP/MH/ZB composite at different pyrolysis temperatures

evaluate the thermal stability of polymer materials during thermo-oxidative degradation investigations [27–29]. The changes of FTIR spectra of the PP/MH, PP/MH/ZB, and PP/MH/ZB/MRP composites with increasing the pyrolysis temperature are given in Figs. 9, 10 and 11, respectively. Clearly the relative intensities of characteristic peaks of PP/MH composites almost change below 200°C, but decrease greatly with increase of pyrolysis temperature above 300°C. All peaks nearly disappear at 600°C, indicating that PP in PP/MH composites decomposes completely. Compared with the PP/MH composites, the thermo-oxidative degradation processes of PP/MH/ZB/MRP composites (Fig. 11) are much more complicated. The peaks for PP/MH composites at 2,924, 2,863 and 1,075  $\text{cm}^{-1}$  disappear at about 350°C, whereas the relative intensities of the peaks for PP/MH/ZB/MRP composites still exist when the temperature arrives at 400°C. The intensities of the absorption peaks of the PP/MH/ZB/MRP composites are higher than those of PP/MH composites at the same pyrolysis temperature, which



**Fig. 11** Changes in residue left FTIR spectra of PP/MH/ZB/MRP composite at different pyrolysis temperatures



indicates that the incorporation of MRP increases the thermo-oxidative stability of the PP/MH composites.

There are also some absorption bands in the 1,600–900  $\text{cm}^{-1}$  region. For the PP/MH composites, the intensities of the absorption peaks at 1,460  $\text{cm}^{-1}$ , 1,376  $\text{cm}^{-1}$  and 973  $\text{cm}^{-1}$  decrease with increasing the pyrolysis temperature and even disappear when the temperature increases about over 400°C, however, the relative intensity of the peaks for PP/MH/ZB/MRP composites still exists up to 400°C. The intensity of the carbonyl absorption bands first increases, then decreases, and finally disappears as the pyrolysis temperature increases further. The absorption peaks at 1,462  $\text{cm}^{-1}$ , 1,380  $\text{cm}^{-1}$ , and 970  $\text{cm}^{-1}$  are assigned to  $-\text{CH}_2$ ,  $-\text{CH}_3$  and carbonate, respectively [30, 31]. The peaks at 1,300  $\text{cm}^{-1}$  and 970  $\text{cm}^{-1}$  in Fig. 11 are assigned to the P-O-C and P-O groups [31]. Some studies are focused on the thermo-oxidative degradation of PP [7, 9], which is believed to proceed by a free radical mechanism [32]. When PP is exposed to high temperature, alkyl macroradicals are formed, which reacts with oxygen to form alkyl peroxide radicals.

On the other hand, it can clearly be observed from Figs. 9–11 that the intensity of the absorption peak at 3,696  $\text{cm}^{-1}$  decreases gradually during the thermo-oxidative degradation. This reason is due to the thermal decomposition of  $\text{Mg}(\text{OH})_2$ , resulting in a decrease of  $-\text{OH}$  content.

## Conclusions

The flame retardancy and degradation kinetics of PP formulations containing MH in the absence and presence of ZB or/and MRP were investigated using LOI, TGA, and FTIR. The LOI data indicate that ZB or/and MRP has a good synergistic effect with MH in PP/MH composites. The addition of ZB or/and MRP greatly improves the thermal stability of PP/MH/ZB and PP/MH/ZB/MRP composites by increasing the pyrolysis temperature. The  $E$  values of the degradation of the flame retarded PP composites calculated using the Kissinger and Flynn-Wall-Ozawa methods based on TGA curves are higher than those of neat PP, especially for PP/MH composites with suitable amount of MRP, which indicates that the degradation of the flame retarded PP composites is more difficult than that of neat PP. The FTIR studies show the addition of MRP into PP/MH composites greatly improves the thermal oxidative stability.

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