Research Article

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Zheng-Huan Wu*, Bin Zhou, Qi-Xiang Fan and Yu-Jun Cai

Thermal degradation kinetics investigation on Nano-ZnO/IFR synergetic flame retarded polypropylene/ethylene-propylene-diene monomer composites processed via different fields

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Abstract: In the field of polymer processing, disperse phase exhibited better dispersion and distribution performance in elongational field rather than shearing field. This property commonly brought a better functional feature for polymer composites. It could also be applied to Nano-ZnO/IFR synergetic flame retarded polypropylene/ethylene-propylene-diene monomer composites. An experiment was designed to study the mechanism of improving flame retardant properties. In the experiment, the same formulas of composites were extruded by vane extruder (represents elongational field) and three-screw extruder (represents shearing field). Then Kissinger method and Flynn-Wall-Ozawa method were used to mutually proved

that Nano-ZnO with better dispersion condition catalysed a more intense esterification of IFR in the whole thermal degradation process.

Keywords: thermal degradation kinetics; elongational and shearing field; nano-ZnO/IFR/PP composites; Kissinger method; Flynn-Wall-Ozawa method

Nomenclature: VE—vane extruder; TSE—three-screw extruder; α —reaction degree; β (K/min)—heating rate; A (s^{-1})—pre-exponential factor; E (kJ/mol)—activation energy for Kissinger method; R (8.314J/(K·mol))—gas constant; n —reaction order; T_p (K)—temperature corresponding to the maximum weightlessness rate; θ —char yield; T_{max} (°C)—temperature corresponding to the maximum weightlessness rate ($T_p = T_{max} + 273.15$); V_{max} —maximum weightlessness rate. r —correlation coefficients for Kissinger method; E_o (kJ/mol)—activation energy for Flynn-Wall-Ozawa method.

* **Corresponding author: Zheng-Huan Wu**, National-Local Joint Engineering Laboratory of Intelligent Manufacturing Oriented Automobile Die & Mould, Tianjin University of Technology and Education, Tianjin 300222, China; National Mold Product Quality Supervision & Inspection Center (Guangdong), NO.10 lianhu road, Chang'an town, Dongguan city, Guangdong 523841, China; Key Laboratory of Tianjin Automobile Injection Mold Enterprise, Tianjin 300222, PR China; College of Mechanical Engineering, Tianjin Key Laboratory of High Speed Cutting and Precision Machining, Tianjin University of Technology and Education, Tianjin 300222, China, e-mail: wzh46817@163.com.

Bin Zhou, National Mold Product Quality Supervision & Inspection Center (Guangdong), NO.10 lianhu road, Chang'an town, Dongguan city, Guangdong 523841, China.

Qi-Xiang Fan, College of Mechanical Engineering, Tianjin Key Laboratory of High Speed Cutting and Precision Machining, Tianjin University of Technology and Education, Tianjin 300222, China.

Yu-Jun Cai, National-Local Joint Engineering Laboratory of Intelligent Manufacturing Oriented Automobile Die & Mould, Tianjin University of Technology and Education, Tianjin 300222, China; Key Laboratory of Tianjin Automobile Injection Mold Enterprise, Tianjin 300222, PR China; College of Mechanical Engineering, Tianjin Key Laboratory of High Speed Cutting and Precision Machining, Tianjin University of Technology and Education, Tianjin 300222, China.

1 Introduction

Polypropylene (PP) is considered as one of the five most abundantly produced plastics in the worldwide (1). The outstanding advantages of tensile property, impact performance, and chemical resistance make PP used broadly in fields like automobile, architecture, food packing, and so on (2). However, its intrinsic flammability severely limits its application (3). Over the past two decades, the study on intumescent flame retardants (IFRs) have been attracting considerable attention (4). The IFRs are usually composed of the acid source, carbonization agent, and blowing agent (4,5). But, the addition of IFR in PP matrix is around 30 wt% (6), it means that the IFR is not so efficient. The synergists such as metallic oxide, Boron compounds are used to improve the efficiency of IFR.

As we all known, formula is not the only essential factor to determine the flame retardancy property of flame retarded PP nanocomposites, but the processing method is also assignable during preparation. Researchers always use screw extruders that can produce shearing field to melt blend polymer composites (7). While we use VE, which developed by Qu (8), to melt blend flame retardant PP nanocomposites by producing elongational field. According to a large number of research reports, elongational field improves the dispersion and distribution effect of additives in polymer matrix better than shearing field (7,9,10). The more homogeneous dispersion performance of additives basically implies better polymeric properties, of which can be reflected from the ameliorative polymeric properties of polymer composites (7-10).

Among these polymeric properties, the flame retardancy properties of flame retarded PP nanocomposites are closely related to their pyrolysis (11), thus exploring on their thermal decomposition kinetics, including activation energy and pre-exponential factor, are of great significance (12). Kissinger method is a method of differentiation. It is very suitable for processing data without the order of thermal degradation, and the solved activation energies represent the average values during the whole degradation phase (13). Meanwhile, Flynn-Wall-Ozawa method is a method of integration. It is very suitable for processing data of thermal degradation with different types of phases and high degradation degree. The information of activation can be acquired in a wider temperature range, and the average activation calculated directly is very reliable (14). In the light of such properties, the two methods not only can be applied to analyse the synergistic thermal degradation mechanism of Nano-ZnO with different dispersion condition in IFR/PP composites from different aspects, but also can be mutual verification, to ensure that the conclusions are credible.

In this research, a synergist of Nano-ZnO with an IFR prepared by us were served to improve the flammability efficiency of PP composites (15). Above all, the same formulas of composites were separately processed by the elongational field (VE) and shearing field (TSE) to define which one possesses higher thermal stability.

2 Experimental

2.1 Materials and devices

The polypropylene (PP-T30S) was obtained from Sinopec Maoming. Co., Ltd. China. The ethylene-propylene-diene monomer (EPDM-2504N) was obtained from Exxon Mobil

Co., Ltd. USA. Both the poly ammonium phosphate (APP-101) and the dipentaerythritol (DPER-HY) were obtained from Yiju Chemical Co., Ltd. Guangzhou, China. The melamine (MEL-AR) was supplied by Kemiou Chemical Reagent Co., Ltd. Tianjin, China. Furthermore, The ZnO (ZnO-DZZn-01) with the particle size of 20 nm was supplied by Dezhao Chemical Co., Ltd. Guangzhou, China. The silane coupling agent (SCA-A172) was supplied by Shouzheng Chemical Technology Co., Ltd. Guangzhou, China. The polyethylene wax (H110) was supplied by S.Q.I Co., Ltd. Thailand.

2.2 Preparation of flame retardant PP nanocomposites

Firstly, the SCA was weighed and dissolved in an appropriate amount of methanol. The solution of SCA was sprayed onto the surface of IFR and Nano-ZnO, and the mixture was stirred in a high-speed mixer for 30 min. Then the mixture was placed in a drying oven for 2 h at 100°C. Afterwards, PP, EPDM, IFR, Nano-ZnO, and PE wax in different ratios were extruded using the vane extruder (VE) and three-screw extruder (TSE) separately. To ensure the credibility of the contrast, the rotational speeds of VE and TSE were respectively 7 r/min and 25.5 r/min, so that the yields were the same. The processing temperatures from feeding section to the extrusion section were shown as follows. VE: 160°C, 175°C, 185°C, 185°C; TSE: 160°C, 175°C, 185°C, 185°C, 185°C, 185°C, 185°C, 185°C, 185°C. Formulations of the specimens are presented in Table 1. The IFR contained APP, DPER, and MEL was prepared by us. After extruding, the polymer composite samples were pressed under 15 MPa for 20 min at 185°C

Table 1: Formulations of flame retardant PP nanocomposites.

Sample code		PP/ EPDM (wt%)	IFR (wt%)	ZnO (wt%)	SCA (wt%)	PE wax (wt%)
VE	TSE					
Lγ5 ^a /10 ^b /15 ^c /20 ^d	Sγ5/10/15/20	70	24	6	0.5	0.5
Lδ5/10/15/20	Sδ5/10/15/20	70	25	5	0.5	0.5
Lε5/10/15/20	Sε5/10/15/20	70	26	4	0.5	0.5
Lζ5/10/15/20	Sζ5/10/15/20	70	27	3	0.5	0.5
Lη5/10/15/20	Sη5/10/15/20	70	28	2	0.5	0.5

^a5 defined as the heating rate of 5°C/min.

^b10 defined as the heating rate of 10°C/min.

^c15 defined as the heating rate of 15°C/min.

^d20 defined as the heating rate of 20°C/min.

into laminates with suitable thickness and size, and they were kept under the condition of 50% relative humidity and 25°C for at least 48 h before testing.

2.3 Thermogravimetric test

All the samples were examined under nitrogen flow in a thermogravimetric analysis apparatus (model 209, Netzsch, Germany), which was used with crucible sample holders, at the heating rate of 5°C/min, 10°C/min, 15°C/min, 20°C/min, separately. Whereas the final temperature was set to be 600°C.

All thermal degradation kinetics methods were based on non-isothermal kinetic theory combined with Arrhenius equation (16), the thermal degradation kinetics was expressed as:

$$d\alpha/dT = (A/\beta) \exp(-E/RT) (1-\alpha)^n \quad (1)$$

Based on Eq. 1 and the thermogravimetric curves, the activation energy E , pre-exponential factor A of the thermal decomposition kinetics were calculated by Kissinger method and Flynn-Wall-Ozawa method (17).

3 Results and discussion

3.1 Thermogravimetric analysis

Figure 1 and Figure 2 present the TG curves of the flame retardant PP nanocomposites processed via VE and TSE at different heating rates. Combining with data in Table 2, it was found that with the increasing content of Nano-ZnO, the decomposition temperature at 0.05% weightlessness first rose then fell at a heating rate of 5°C/min; The decomposition temperature at 0.05% weightlessness kept falling at the heating rates of 10°C/min and 15°C/min; While the decomposition temperature at 0.05% weightlessness exhibited a disorder state at a heating

Figure 1: TG curves of flame retardant PP nanocomposites processed via VE at different heating rates.

Figure 2: TG curves of flame retardant PP nanocomposites processed via TSE at different heating rates.

rate of 20°C/min. Among them, the decomposition temperature at 0.05% weightlessness was basically inversely proportional to the heating rate. Took data from samples that processed by VE for instance, the maximum and minimum temperatures were separately 248.5°C and 155.7°C at the heating rate of 5°C/min, and the maximum and minimum temperatures were separately 140.3°C and 32.3°C at the heating rate of 20°C/min. However, this principle was not applicable for samples which processed by TSE. All the decomposition temperatures at 0.05% weightlessness appeared at a rather low temperature with an average number of 75.9°C except for the five temperatures with a heating rate of 5°C/min. All of them maintained at rather high values which around 240°C, and it seemed that they were not even influenced by the content variation of IFR and Nano-ZnO.

Besides, the decomposition temperature at 0.1% weightlessness for VE presented the same principle, which first rose then fell at the heating rates of 5°C/min and 10°C/min. Afterwards, it went into a mess

with heating rates of 15°C/min and 20°C/min. For TSE, the same situation occurred as well as the decomposition temperature variation at 0.05% weightlessness. The weight loss between 99.9% and 99.95% was so tiny that the tendency wouldn't change.

In addition, referring to VE, the decomposition temperature at 0.5%, 0.7%, and 5% weightlessness with a heating rate of 5°C/min showed the same tendency, though the temperature gap became smaller and smaller with the increasing content of Nano-ZnO. Then it obeyed a principle of temperature falling continuously with the heating rates of 10°C/min and 15°C/min. The temperatures exhibited irregular mess with the heating rate of 20°C/min. On the other hand, referring to TSE, the decomposition temperature at 0.5%, 0.7%, and 5% weightlessness showed a weak tendency of first rising then falling with a heating rate of 5°C/min. The former two values were very close which owing to the small decomposition amplitude. The tendency altered to first falling then rising with the heating rates of 10°C/min and 15°C/min. Again, the

Table 2: Characteristic points of TG and DTG curves of all components.

Sample code	Decomposition temperature at different weightlessness rates/°C						θ /%	T_{max} /°C	V_{max} /%.°C ⁻¹
	0.05%	0.1%	0.5%	0.7%	5%	50%			
Lγ5	167.1	171.3	190.9	199.6	280.3	454.1	17.43	460.0	-1.97
Lδ5	248.5	249.1	254.5	256.4	333.7	455.2	21.17	457.2	-2.33
Lε5	241.8	242.6	247.7	250.0	316.5	457.2	22.45	449.8	-1.37
Lζ5	222.1	224.2	235.3	239.1	319.9	458.8	17.75	461.6	-2.47
Lη5	155.7	158.4	175.4	185.3	307.1	456.9	13.62	463.5	-2.23
Lγ10	187.2	201.1	243.7	250.2	331.6	468.9	16.14	469.4	-3.31
Lδ10	136.9	147.4	222.5	234.3	317.9	469.8	15.38	469.7	-3.08
Lε10	111.9	118.6	218.5	233.1	335.4	470.5	12.95	478.4	-3.18
Lζ10	113.8	127.2	190.0	210.4	301.3	472.1	16.02	473.0	-2.15
Lη10	87.4	98.2	181.9	210.4	310.8	473.2	18.69	478.3	-2.15
Lγ15	115.4	126.7	230.9	244.1	342.7	480.5	29.83	480.0	-1.91
Lδ15	109.7	127.6	224.4	237.7	318.3	479.8	15.87	482.6	-2.05
Lε15	55.7	64.2	118.6	163.8	298.6	481.8	18.25	485.4	-2.06
Lζ15	63.2	72.3	175.6	220.1	313.9	480.7	15.77	483.5	-2.08
Lη15	59.4	67.0	163.8	218.3	338.7	479.4	12.45	480.3	-2.99
Lγ20	97.5	109.3	214.3	241.5	230.2	486.2	16.01	481.6	-2.57
Lδ20	140.3	151.8	223.5	240.4	325.0	486.3	15.34	481.9	-2.68
Lε20	94.3	105.7	132.0	136.1	186.2	484.3	11.48	490.7	-2.34
Lζ20	104.2	125.5	224.6	239.9	326.8	490.0	15.71	493.7	-2.30
Lη20	32.3	32.3	102.0	135.4	323.6	487.1	11.56	489.7	-3.06
Sγ5	243.5	244.4	249.5	251.6	314.0	455.6	22.74	458.1	-2.30
Sδ5	240.2	241.2	247.9	250.5	317.5	456.3	20.42	459.0	-2.27
Sε5	248.9	249.8	255.2	257.3	349.0	453.9	16.57	457.6	-2.26
Sζ5	251.9	252.5	257.9	261.0	331.1	461.4	23.64	463.6	-1.99
Sη5	230.0	231.1	238.1	241.5	324.7	460.2	19.54	463.2	-2.04
Sγ10	70.5	81.5	203.0	229.6	319.9	473.0	21.36	464.5	-3.08
Sδ10	41.1	74.1	202.8	225.9	306.2	471.5	20.78	471.0	-3.82
Sε10	41.2	49.6	206.6	230.3	318.8	474.4	20.13	477.2	-2.27
Sζ10	46.7	106.0	211.4	232.0	320.1	473.3	18.50	473.7	-3.39
Sη10	102.2	117.5	214.8	226.9	323.0	472.5	17.17	472.5	-10.72
Sγ15	81.2	105.3	228.7	239.9	302.2	477.9	20.47	480.8	-1.98
Sδ15	58.2	181.8	234.8	244.6	277.2	477.4	18.48	481.0	-2.26
Sε15	57.8	80.7	231.0	243.0	333.5	477.9	13.53	481.3	-2.28
Sζ15	62.4	209.2	238.2	242.9	301.6	479.6	20.20	482.0	-2.12
Sη15	56.4	105.4	221.6	233.9	312.3	479.9	17.72	481.3	-2.25
Sγ20	30.1	32.6	74.8	91.2	281.0	458.8	17.00	490.6	-2.21
Sδ20	106.1	180.4	252.2	258.6	341.1	488.5	14.92	487.2	-3.31
Sε20	99.8	105.1	234.6	246.3	315.9	488.8	19.89	484.2	-2.50
Sζ20	213.8	229.2	254.0	258.7	326.4	489.7	18.72	491.9	-2.08
Sη20	71.4	111.1	221.8	241.4	328.3	489.2	17.55	490.8	-2.24

temperatures exhibited irregular mess with the heating rate of 20°C/min, which was the same phenomenon as the data of VE.

Finally, regardless of the heating rate or content of flame retardant, the decomposition temperatures at 50%

weightlessness for VE were nearly the same and showed no obvious rule as well as that for TSE. Such phenomenon reflected that all the decomposition reactions were in an intense stage which mainly dominated by the esterification of IFR (18).

Figure 3: DTG curves of flame retardant PP nanocomposites processed via VE at different heating rates.

According to the results above, the decomposition procedure presented certain rules in VE at 5°C/min, 10°C/min, and 15°C/min, meanwhile it presented certain rule in TSE only at 5°C/min. Considering the same formula of flame retardant processed respectively by VE and TSE, the only reason can be confirmed that the different dispersion characteristics which endowed by different devices. In other words, the better dispersion and distribution of Nano-ZnO/IFR particles in PP/EPDM blend by VE (19), the lower decomposition rate and a longer time to reach the decomposition peak.

Figure 3 and Figure 4 present the DTG curves of flame retardant PP nanocomposites processed via VE and TSE at different heating rates. Combining with Table 2, there were not so much difference with the values of θ and T_{max} between VE and TSE. Meanwhile, the value of θ declined with the rising of the heating rate, the value of T_{max} was just the opposite. $d\alpha/dt$ increased with the rising of the heating rate, namely more heat energy released in unit time, which produced more char layer at the beginning

of the esterification, the char layer separated oxygen and heat from the composites and atmosphere to postpone the process of complete combustion (20). The longer of the ignition time, the higher temperature of the composites at the most intense degradation reaction, and the more exhaustive ignition.

Moreover, the average values of V_{max} for VE were a little lower than that for TSE, which meant that the esterification reaction peaks for VE were milder than that for TSE. It can be inferred that better dispersion and distribution of synergistic flame retardants make a relatively moderate reaction rate.

3.2 Thermogravimetric kinetics

3.2.1 Kissinger method

Kissinger method is a method of differentiation. Activation energies E were calculated according to different

Figure 4: DTG curves of flame retardant PP nanocomposites processed via TSE at different heating rates.

temperatures which corresponding to peaks of DTG curves at four heating rates (21). Function equation is expressed as follow:

$$\ln \beta / T_p^2 = \ln (AR/E) - E/RT_p \quad (2)$$

According to the relationship between T_p and β , curve fitting is undertaken. We plotted straight lines based on $\ln \beta / T_p^2$ and $1/T_p$ with gradients of $-E/R$ to calculate the activation energy E , and to obtain the pre-exponential factor A in line with intercept $\ln(AR/E)$. All the curves and data are shown in Figure 5 and Table 3.

In Figure 5, each straight line is fitted by four data points, the gradient of $-E/R$ and intercept $\ln(AR/E)$ are shown in it with exact values. Moreover, in Table 3, all the correlation coefficients r are very close to 1, especially for VE, which represented high reliabilities of E and A (3).

The activation energy of $L\eta 5/10/15/20$ is higher than that of $S\eta 5/10/15/20$ by 20.41 kJ/mol, the percentage difference reaches 9.26%. Besides, the activation energy

of $L\zeta 5/10/15/20$ is higher than that of $S\zeta 5/10/15/20$ also by 20.41 kJ/mol, the percentage difference reaches 12.15%. Furthermore, the activation energy of $L\gamma 5/10/15/20$ is higher than that of $S\gamma 5/10/15/20$ by 99.14 kJ/mol, the percentage difference reaches 62.58%. While the activation energy of $L\epsilon 5/10/15/20$ is less than that of $S\epsilon 5/10/15/20$ by 8.09 kJ/mol, the activation energy of $L\delta 5/10/15/20$ is less than that of $S\delta 5/10/15/20$ only by 6.14 kJ/mol. For most synergistic flame retardants, the best flame retardancy performance appeared when the content of synergist was 1-3 wt% (4,6,22). It can be inferred that more homogeneous samples owned higher thermal stability, namely VE endowed samples with 2, 3, 5 wt% Nano-ZnO better dispersion and distribution effects in processing.

The pre-exponential factor A , which represented the effective collision times among activated molecules, has a positive correlation exponential function relationship with the activation energy E (23). It can also be proved in Table 3 that the tendency of A was the same as E .

Figure 5: Plots of $\ln \beta/T_p^2$ and $1/T_p$ of flame retardant PP nanocomposites processed via VE and TSE.

Table 3: Activation energies and pre-exponential factors of all components.

Sample code	Activation energy (E) kJ/mol	Pre-exponential factor (lgA)	Correlation coefficient (r)
Lγ5/10/15/20	257.56	17.83	0.95219
Lδ5/10/15/20	211.21	14.49	0.91662
Lε5/10/15/20	193.14	13.08	0.97818
Lζ5/10/15/20	188.40	12.75	0.95510
Lη5/10/15/20	240.73	16.50	0.92772
Sγ5/10/15/20	158.42	10.69	0.79893
Sδ5/10/15/20	217.35	14.93	0.98227
Sε5/10/15/20	201.23	13.74	0.81770
Sζ5/10/15/20	167.99	11.22	0.54710
Sη5/10/15/20	220.32	12.08	0.92189

3.2.2 Flynn-Wall-Ozawa method

Flynn-Wall-Ozawa method is a method of integration. Activation energies E_o were calculated according to different temperatures which corresponding to the same degree of reactivity α in curves with different heating rates. We used integral transformation and Doyle approximation to change Eq. 1 into Eq. 3, in which, T was separately T_1 , T_2 , T_3 , and T_4 that corresponding to the heating rates of 5°C/min, 10°C/min, 15°C/min, and 20°C/min. The activation energy E_o was confirmed by the linear relation between $\lg \beta$ and $1/T$, there was no need to consider the difference of reaction mechanism (24).

$$\lg \beta = \lg \left(AE_o / Rg(\alpha) \right) - 2.315 - 0.4567 E_o / RT \quad (3)$$

All the values of E_o were calculated according to the gradients from Figure 6. It can be seen from Figure 6 that the

Table 4: Activation energies of all components.

Range of α	Activation Energy (kJ/mol)				
	η	ζ	ϵ	δ	γ
$0.2 \leq \alpha \leq 0.4$ (VE)	144.58	179.80	195.46	183.69	168.04
$0.2 \leq \alpha \leq 0.4$ (TSE)	188.13	186.66	177.01	180.02	179.35
$0.5 \leq \alpha \leq 0.8$ (VE)	195.77	203.18	151.74	175.51	210.63
$0.5 \leq \alpha \leq 0.8$ (TSE)	219.51	204.74	149.23	184.90	243.06

linear fitting degree was high, which implied the method was feasible and the results were reliable. Referring to VE, As for 2, 3, 4, 5, 6 wt% Nano-ZnO/IFR, when $0.2 \leq \alpha \leq 0.4$, the average values of E_o were respectively 144.58 kJ/mol, 179.80 kJ/mol, 195.46 kJ/mol, 183.69 kJ/mol, 168.04 kJ/mol; While $0.5 \leq \alpha \leq 0.8$, the average values of E_o were respectively 188.13 kJ/mol, 186.66 kJ/mol, 177.01 kJ/mol, 180.02 kJ/mol, 179.35 kJ/mol. Referring to TSE, As for 2, 3, 4, 5, 6 wt% Nano-ZnO/IFR, when $0.2 \leq \alpha \leq 0.4$, the average values of E_o were respectively 195.77 kJ/mol, 203.18 kJ/mol, 151.74 kJ/mol, 175.51 kJ/mol, 210.63 kJ/mol; While $0.5 \leq \alpha \leq 0.8$, the average values of E_o were respectively 219.51 kJ/mol, 204.74 kJ/mol, 149.23 kJ/mol, 184.90 kJ/mol, 243.06 kJ/mol.

According to data above, the activation energy of VE first rose then fell with the increasing content of Nano-ZnO when $0.2 \leq \alpha \leq 0.4$, and it showed a peak with 4 wt% addition of Nano-ZnO. While the activation energy of VE was not only much higher than that above, but also expressed just the opposite when $0.5 \leq \alpha \leq 0.8$. This was due to the Nano-ZnO might break the C=O bond of DPER and P-N bond between APP and PP at early stage (25), which destroyed the stability of initial esterification reaction of IFR. However, the increasing concentration of

Nano-ZnO started to catalyze the esterification until the addition reached its critical value 4 wt%. Afterwards, the excessive and overweight Nano-ZnO broke the char layer that reduced the reaction rate. The activation energy maintained at a high level when $0.5 \leq \alpha \leq 0.8$ compared with $0.2 \leq \alpha \leq 0.4$, and the peak appeared when the addition of Nano-ZnO was 2 wt%. The high level of activation energy was not only ascribed to the polyphosphoric acid, volatile phosphorus oxides, and network polymers with P-N bond, all of which were derived from high temperature decomposed IFR (4,9), but also ascribed to the dehydration, cross-linking, catalytic carbonization by Nano-ZnO, heat, oxygen, and molten drop isolation of char layer (3,4,9,25). These made polymer molecular chain need more energy during thermal degradation. The totally different high activation energy ranges from Figure 6 proved the analysis above. In addition, the concentration of IFR and Nano-ZnO increased so gradually that the activation energies maintained around 200 kJ/mol except for ones with 4, 5 wt% Nano-ZnO in them. It can be inferred that overweight Nano-ZnO migration to the bottom of char layer because of gravity, which destroyed the integrity and compactness of char layer during its formation.

On the other hand, the activation energy of TSE (Figure 7) declined gradually but maintained at a high level with the increasing content of Nano-ZnO when $0.2 \leq \alpha \leq 0.4$, it showed a peak with 2 wt% addition of Nano-ZnO. While the activation energy of TSE was much higher than that above, and exhibited the same rule when

$0.5 \leq \alpha \leq 0.8$. This is due to the reason that the dispersion and distribution of Nano-ZnO is not so well as in VE, the esterification of IFR at early stage is not disturbed so much as samples processed via VE. Furthermore, with a good foundation that formed by the synergistic flame retardant, the flame retardant effects that described above reach the most intense stage, which make the polymer molecular chains need more activation energy to break. The activation energies of samples that processed via TSE fluctuated much more than samples processed via VE. The reason may due to the heterogeneous of Nano-ZnO/IFR particles in the matrix.

4 Conclusions

Based on TG and DTG data with four different heating rates, Kissinger method and Flynn-Wall-Ozawa method were used not only to analyze the synergistic flame retardancy mechanism of Nano-ZnO and IFR in PP/EPDM matrix, but also to compare the effects of elongational field and shearing field applied on samples with five identical formulas.

As for Kissinger method, it indicated that the activation energy declined obviously with the increasing content of Nano-ZnO, and 2-3 wt% Nano-ZnO with IFR exhibited the best thermal stability during intense decomposition phase. Referring to Flynn-Wall-Ozawa method, it basically proved the conclusion of Kissinger method. Moreover, it also proved that the thermal degradation of

Figure 6: Plots of $\lg\beta$ and $1/T$ of flame retardant PP nanocomposites processed via VE.

Figure 7: Plots of $\lg\beta$ and $1/T$ of flame retardant PP nanocomposites processed via TSE.

Nano-ZnO/IFR should be divided into initial phase and intense phase. While the Nano-ZnO played a catalytic role mainly in the initial phase.

Both two methods proved that the thermal stability was higher, and the decomposition process was more orderly for samples processed via VE. It should be attributed to the elongational field of VE, which produced a better dispersion and distribution condition of the synergistic flame retardant.

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