The Pyrolysis of Inorganic Fire Retardant Polyolefin Cable Materials

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Abstract

The Inorganic Fire Retardant Polyolefin Cable Materials is analyzed with thermogravimetric and differential scanning calorimetry (TG-DSC) in this paper. The result indicates that there are three stages in the pyrolysis process: 260～330℃，330～400℃, and 400～500℃. Active energy E and antecedent A in each stage are calculated. And reaction in the first and third stages can be treated as first order reaction.

Nomenclature

A	antecedent(s^{-1})
E	active energy(kJ /mol)
R	gas constant(8. 315J•mol^{-1}•K^{-1})

Greek symbols

β	heating rate(K/min)
w	the percentage of weight loss of the sample at temperature T

1. Introduction

With the rapid economic growth, electrical fire has been a major type of fire disaster in China. Since 2007, the occurrence rate of electrical fire has exceeded 30% of the total in China each year, and seems to be increasing [1-2]. Electrical fire has been mostly seen in places with dense population such as shopping mall, hotel, and restaurant, and will cause heavy casualties and property loss [1,3-4]. It is known that the high temperature of the local part of cables might be incurred due to short circuit or overload, which will then lead to chain reaction and fire accident. Therefore, the resistance to elevated temperatures is very important to cable insulation layer.

The pyrolysis behavior of the polyvinyl chloride and rubber which are used as the coating materials of cable has been sufficiently studied [5-7], yet that of polyolefin and especially inorganic fire retardant polyolefin requires further research. Normally, additives such as phosphorus and metal hydroxide [8] are added to polyolefin to increase its fire retardancy. The pyrolysis behavior of inorganic fire retardant polyolefin cable materials with metal hydroxide (primarily magnesium hydroxide and aluminium hydroxide) as its fire-retardant additive will be studied in this paper.

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2. Experiment

2.1. Experimental apparatus

Thermogravimetric differentia scanning calorimetry (DSC-TGA) is an analytical method that can measure the change of properties (mainly including mass, temperature, and heat) under the program-control temperature. The measurement in this paper is conducted with STA 409 PC produced by the German company Netzsch.

3. Result and discussion

3.1. Pyrolysis process

The curves for the thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTG) of the inorganic fire retardant polyolefin sample in nitrogen with different heating rates are seen in Fig. 1. According to the data in the figure, there are three stages for the pyrolysis of the material in nitrogen between 40℃ and 900℃. (1) In the first stage when the temperature is between 260℃ and 330℃, two crystal waters are lost by the aluminium hydroxide for thermal decomposition considering that metal hydroxide (mainly magnesium hydroxide and aluminium hydroxide) is used as the fire retardant for the inorganic fire retardant polyolefin. (2) In the second stage when the temperature is between 330℃ and 400℃, the third crystal water is lost by the aluminium hydroxide, and aluminium hydroxide is dehydrated for thermal decomposition. The additives such as plasticizer, stabilizer, and colorant are volatilized and part of the polymer materials might be degraded. (3) In the third stage when the temperature is between 400℃ and 500℃, it is mainly the backbone of the cross-linked polymer that experiences thermal decomposition, because of which a large amount of small molecular substances such as ethylene and propylene are produced and then volatilized with the airflow and the quantity decreases sharply. Then the quantity will decrease gradually at the temperature between 550℃ and 650℃ on the TGA curve because the small molecules from the polymer will form new compounds under high temperature. The new compounds have higher thermal stability, which means that their decomposition needs higher temperature and longer period of time.
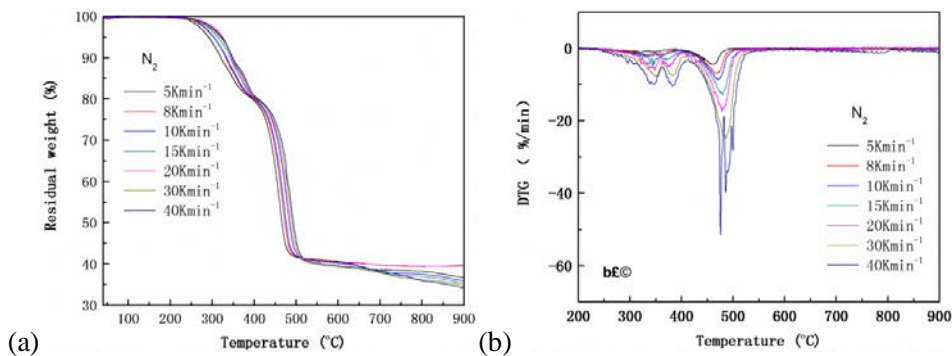

Fig. 1 TGA and DTG curves for the material in nitrogen with different heating rates (a. TGA; b.DTG)

The trends of the TGA and TG curves for the pyrolysis of the sample cable show little difference by comparing the different heating rate curves. With the increase of the heating rate, the initial and final temperatures of each stage rise, because during the pyrolysis, the diffusion of medium and heat transfer need a certain period of time—the pyrolysis shows retardance which will be more obvious with the increase of the heating rate [9].

The detailed data of the pyrolysis of the material in nitrogen are shown in Table 1, 2, and 3 where β indicates the heating rate; t_{on1}, t_{on2} and t_{on3} the initial degradation temperature at each stage; t_{max1}、t_{max2} and t_{max3} the temperature with the maximum weight loss rate at each stage; V_{max1}、V_{max2} and V_{max3} the maximum weight loss rate at each stage; α_1、α_2 and α_3 the percentage of weight loss at each stage; and w the remaining mass at 900 ℃.

It can be seen by comparing the different heating rates that the weight loss rate of the sample at each stage of the pyrolysis grows with the increase of heating rate. In the first two stages, the weight loss rate does not increase significantly with the growth of heating rate—the weight loss rates are 1 %/min and around 10%/min respectively when the heating rates are 5 ℃/min and 40 ℃/min. The reason is given above: the first two stages mainly see the dehydration and decomposition of aluminum hydroxide, magnesium hydroxide, and other additives. The reaction rate does not change significantly with the increase of heating rate. In the third stage the weight loss rate of the sample changes greatly with the increase of heating

rate—the weight loss rates are 4.58 %/min and 39.75 %/min respectively when the heating rates are 5℃/min and 40 ℃/min. It is because that the backbone of the cross-linked polymer experiences thermal decomposition in this stage, and the increase of heating rate will significantly quicken the reaction rate.

Table 1 physical parameters of the sample in nitrogen during the first stage of pyrolysis

Heating rate β/ ℃·min^{-1}	t_{on1}/℃	t_{max1}/℃	Vmax1/%/min	α 1/%	w/ % （Amount of remaining coke at 900℃）
5	273.5	319.7.	1.15	11.82	36.69
8	293.9	332.0	2.08	13.20	39.61
10	287.1	336.6	2.17	12.87	35.89
15	307.7	344.3	5.13	13.20	35.28
20	314.1	350.2	6.20	12.42	39.41
30	313.8	353.4	7.73	12.88	34.77
40	308.4	348.7	10.02	12.30	34.15

Table 2 physical parameters of the sample in nitrogen during the second stage of pyrolysis

Heating rateβ/ ℃·min^{-1}	t_{on2}/℃	t_{max2}/℃	Vmax2/%/min	α 2/%
5	331.5	348.0	1.07	8.24
8	349.1	354.0	1.69	6.26
10	349.8	366.1	2.03	6.48
15	353.6	370.6	3.18	6.59
20	358.3	377.6	5.06	7.11
30	364.8	385.0	7.58	6.84
40	363.9	385.7	10.29	7.89

Table 3 physical parameters of the sample in nitrogen during the third stage of pyrolysis

Heating rateβ/ ℃·min^{-1}	t_{on3}/℃	$t_{max\,3}$/℃	Vmax3/%/min	α 3/%
5	396.3	459.1	4.58	43.25
8	391.9	469.4	6.98	40.96
10	395.0	472.6	8.64	44.79
15	403.3	479.9	12.93	44.97
20	403.5	480.1	17.47	41.07
30	402.9	486.9	24.84	45.46
40	413.9	487.4	39.75	45.67

3.2. Kinetic analysis of pyrolysis

To further understand the reaction of the sample, FWO method (integral method) and Kissinger method (differential method) are adopted to calculate the active energy E and antecedent A of the material in nitrogen during each stage of pyrolysis.

As for FWO method, its active energy E for thermal decomposition is obtained according to the percentage of weight loss as shown in Formula 1:

$$lg\beta= lg \; [\; - AE \,/\, Rln \; (\; 1 - w \;) \;] - 2.315 - 0.4567 \; (\; E \,/\, RT \;) \tag{1}$$

Fig. 2 shows the relation between lg β and 1/ T. Straight lines are shown during each of the three stages with different percentage of weight loss (w). The active energy for thermal decomposition at each stage is obtained from the slope of each straight line as shown in Table 4. The straight lines in the first and third stages of the thermal decomposition of the sample are basically parallel to one another using FWO method, and the active energies are essentially consistent. The averages in the first and third stages are 155.243 kJ.mol^{-1} and 328.964 kJ.mol^{-1} respectively. In addition, that the little difference between the active energies for the two stages with different percentages of weight loss indicates that the kinetic parameter of pyrolysis has no apparent relevance with its conversion rate. Therefore, it can be regarded that the reaction in the two stages of thermal decomposition is one-step and can be described with only one kinetic parameter. But the straight lines in the second stage are not parallel; the active energy seems to be larger when the percentage of weight loss is larger and the maximum difference is 56% (when the percentage of weight loss is 13% and 18%). It indicates that the thermal decomposition in the second stage is more complicated with multiple reactions, which cannot be described with a single kinetic parameter.
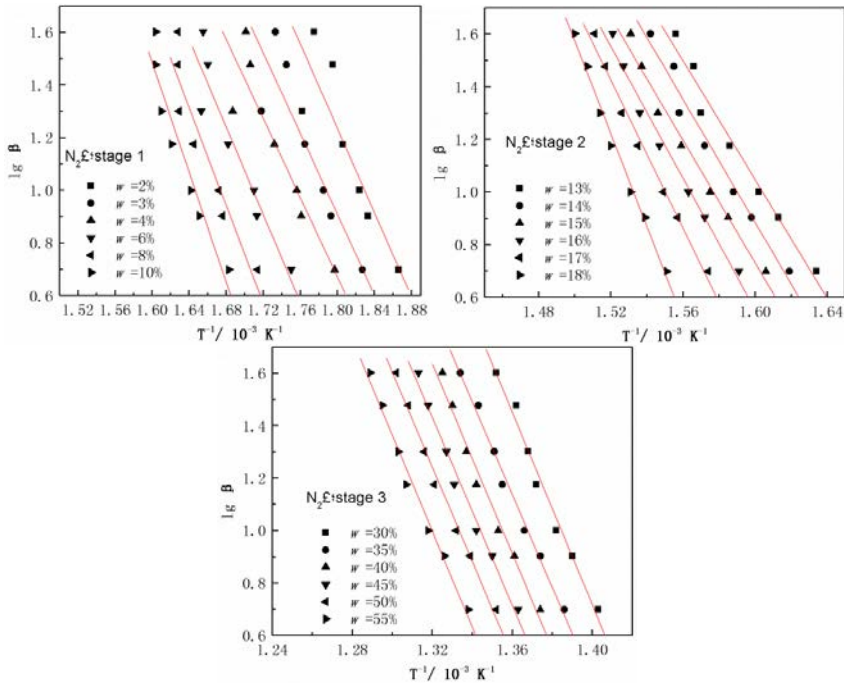
Fig. 2 Isoconversional curves for the thermal decomposition of the material in nitrogen

Table 4 active energies for the thermal decomposition of the material in nitrogen during the three stages

	stage 1			stage 2			stage 3	
w / %	E kJ.mol^{-1}	Average kJ.mol^{-1}	w / %	E kJ.mol^{-1}	Average kJ.mol^{-1}	w / %	E kJ.mol^{-1}	Average kJ.mol^{-1}
2	145.683		13	205.248		30	333.869	
3	139.316		14	213.159		35	322.145	
4	136.786	155.243	15	212.182	239.160	40	329.981	328.964
6	151.084		16	227.692		45	325.653	
8	168.735		17	255.981		50	328.532	
10	189.855		18	320.699		55	333.605	

As for Kissinger method, the active energy E and antecedent A for thermal decomposition are obtained according Formula 2 as shown below:

$$lg(\beta / Tp\ 2)= lg\ (AR /E\ ) - (E / 2.303\ RT) \tag{2}$$

As similar to the result from FWO method, there are three straight lines in the $lg(\beta / Tp^2)$-1 / Tp figure, as shown as in Fig. 4. The active energy E and antecedent A at each of the three stages are obtained according to the slope and intercept of the straight line.
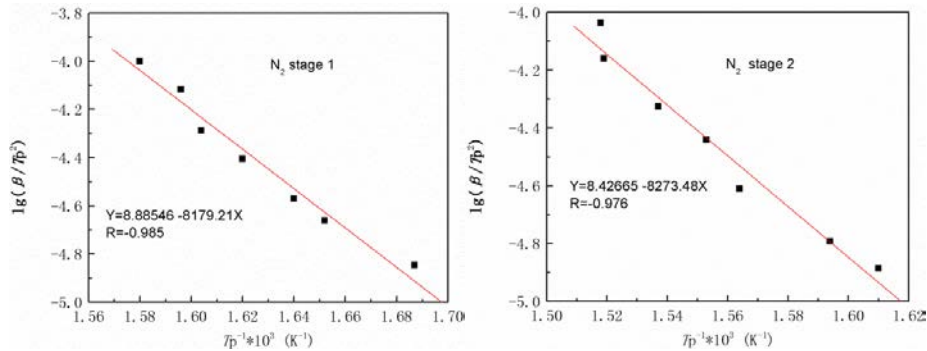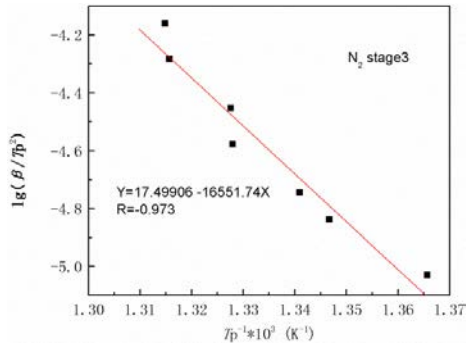
Fig. 3 lg (β/Tp^2) -1 /*Tp* curve for the material in nitrogen calculated with Kissinger method

With the linear regression analysis of Fig. 3 three straight lines and their numerical equations are obtained. According to Formula 2: slope=E/2.303R, and intercept= lg (*AR /E*), the active energy and antecedent for the thermal decomposition during each of the three stages are shown as follows:

First stage: E_1=156.608 kJ/mol，A_1=1.447×10^{13};

Second stage: E_2=158.413 kJ/mol，A_2=5.089×10^{12};

Third stage: E_3=316.918 kJ/mol，A_3=1.203×10^{22}.

It is known by comparing the results from the two methods that the active energies in the first and third stages respectively show little difference and the active energies in the second stage are quite different. That means the thermal decomposition of the sample in the second stage is not a single reaction but with multiple processes.

3.3. Order of reaction

As discussed above the pyrolysis in the first and third stages are simple, but that in the second stage consists of multiple processes. Therefore the order of reaction during each stage of pyrolysis shall be discussed. The basic formula for thermal decomposition kinetics which describes the thermal decomposition process of polymer in inert gas is shown as follows [10]:

$$d\,w\,/\,d\,T = (\,A\,/\beta)\,exp\,(\,-\,E\,/\,R\,T)\,(1\,-\,w)^{\,n} \tag{3}$$

where, *w*—percentage of weight loss at the moment of *t*, *β*—heating rate, *A*—antecedent, *E*—active energy, *R*—gas constant, *T*—absolute temperature.

In the lg(-ln(1-w))-1/*T* figure, if there is a straight line, then it is a first order reaction; if not, then it is not a first order reaction.

The relation between lg(-ln(1-w)) and 1/*T* for the sample in nitrogen with different heating rates is shown in Fig. 4. In the first and third stages, the lg(-ln(1-w))-1/*T* lines with different heating rates are straight which indicates that they are first order reactions. The lines in the second stage are not straight; therefore, a non-linear relationship is suggested between the two parameters.
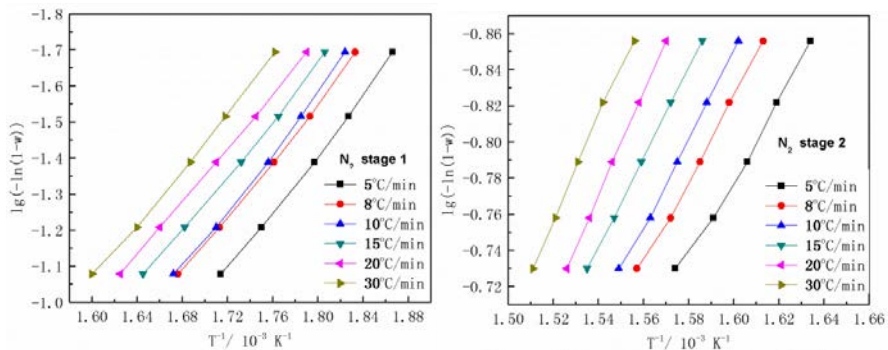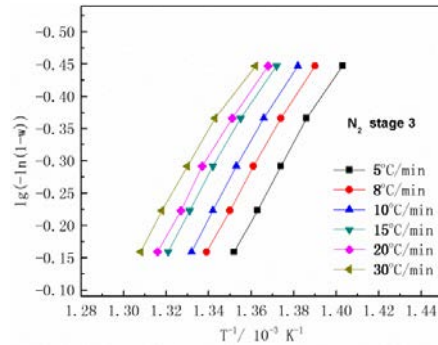
Fig.4 relation between lg(-ln(1-w)) and $1/T$ for the material in N_2 with different heating rates

4. Conclusion

The kinetic analysis of the pyrolysis behavior of inorganic fire retardant polyolefin is conducted in this paper with thermogravimetric (TGA) and differential thermogravimetric (DTG) methods with the conclusion as follows:

(1) The pyrolysis of inorganic fire retardant polyolefin can be divided into three stages: between 260℃ and 330℃, two crystal waters are lost by the aluminium hydroxide for thermal decomposition; between 330℃ and 400℃, the third crystal water is lost by the aluminium hydroxide, aluminium hydroxide is dehydrated, and the additives such as plasticizer, stabilizer, and colorant are volatilized and part of the polymer materials is degraded; between 400℃ and 500℃, it is mainly the backbone of the cross-linked polymer that experiences thermal decomposition for which small molecular substances such as ethylene and propylene are produced.

(2) With FWO method and Kissinger method, the active energy E and antecedent A for the cable sample at each of the three stages of pyrolysis are obtained. The active energies in the first and third stages obtained with different methods do not appear to be much different, which are around 155 kJ.mol^{-1} and 320 kJ.mol^{-1} respectively. The active energies in the second stage vary substantially, which means that the process cannot be described with a single thermokinetic parameter.

(3) According to the lg(-ln(1-w))-$1/T$ figure, the sample in nitrogen in the first and third stages experiences first order reaction.

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