

# Kinetics of Thermal Degradation of Nanometer Calcium Carbonate/Linear Low-Density Polyethylene Nanocomposites

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**ABSTRACT:** To improve the thermal properties of linear low-density polyethylene (LLDPE), the CaCO<sub>3</sub>/LLDPE nanocomposites were prepared from nanometer calcium carbonate (nano-CaCO<sub>3</sub>) and LLDPE by melt-blending method. A series of testing methods such as thermogravimetry analysis (TGA), differential thermogravimetry analysis, Kim-Park method, and Flynn-Wall-Ozawa method were used to characterize the thermal property of CaCO<sub>3</sub>/LLDPE nanocomposites. The results showed that the CaCO<sub>3</sub>/LLDPE nanocomposites have only one-stage thermal degradation process. The initial thermal degrada-

tion temperature  $T_0$  increasing with nano-CaCO<sub>3</sub> content, and stability of LLDPE change better. The thermal degradation activation energy ( $E_a$ ) is different for different nano-CaCO<sub>3</sub> content. When the mass fraction of nano-CaCO<sub>3</sub> in nanocomposites is up to 10 wt %, the nanocomposite has the highest thermal degradation  $E_a$ , which is higher (28 kJ/mol) than pure LLDPE. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** LLDPE; nano-CaCO<sub>3</sub>; nanocomposite; thermal degradation

## INTRODUCTION

Linear low-density polyethylene (LLDPE) with excellent flexibility and ductility is widely used to manufacture utensils, pipes, cables, and so forth.<sup>1,2</sup> However, the application of LLDPE has been limited by its main disadvantages such as less rigidity, poor heat resistance, and low softening point. Therefore, the thermal degradation of LLDPE has received considerable attention in the literature.<sup>3,4</sup> As can be learned from previous studies, the studies were mainly concentrated on blends of polyethylene and other polymers, for instance, high-density polyethylene (HDPE)/LLDPE blends.<sup>5</sup> There are also some reports on polyethylene modified by particles such as wood-LLDPE composites, multiwalled carbon nanotubes/LLDPE nanocomposites, and LLDPE/layered double hydroxide nanocomposites.<sup>6–8</sup> In addition, Gorghiu et al.<sup>9</sup> had reported the effect of metals (Al, Zn, Ti, Mo, Mn, Fe, and Cu) on thermal degradation of polyethylenes. So far, not much

attention has been paid to the effect of the chemical composition, content, and stability of nano-CaCO<sub>3</sub> on the overall thermal stability of LLDPE.

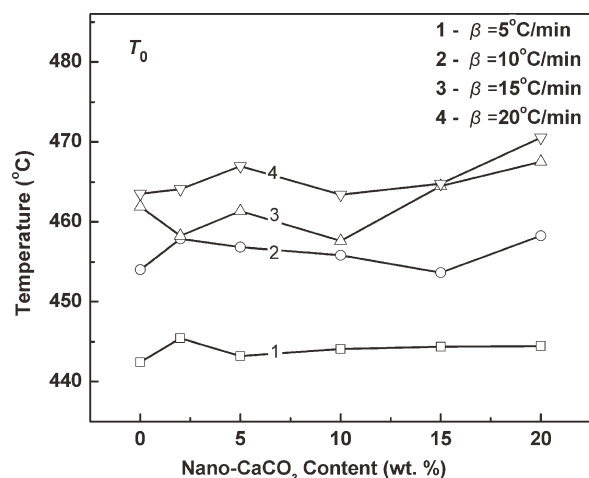
The nano-CaCO<sub>3</sub> as a kind of inorganic nanometer particle, because of its advantages of less surface defects, more unpaired atoms, and large surface area, has large possibility of physically or chemically combining with LLDPE and can make influence of polyethylene thermal decomposition behavior because of single particle effect. In this work, the CaCO<sub>3</sub>/LLDPE nanocomposite was prepared; the kinetics of thermal degradation processes was investigated by the Kim-Park and the Flynn-Wall-Ozawa methods; and the effects of nano-CaCO<sub>3</sub> on the thermal degradation processes of LLDPE were discussed. The results showed that the initial degradation temperature of CaCO<sub>3</sub>/LLDPE nanocomposites rises with increasing the nano-CaCO<sub>3</sub> content, and when the mass fraction of nano-CaCO<sub>3</sub> is up to 10 wt %, it has the highest thermal degradation activation energy  $E_a$ , which is higher (28 kJ/mol) than pure LLDPE. The stability of LLDPE can be increased by adding nano-CaCO<sub>3</sub>.

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## THEORETICAL BACKGROUND

According to the nonisothermal dynamics theory and Arrhenius experience equation, the dynamic equation for degradation of materials is given as follows:



**Figure 1** Relationships of  $T_0$  and nano- $\text{CaCO}_3$  content at different heating rates.

$$\frac{d\alpha}{dt} = A(1 - \alpha)^n \exp\left(-\frac{E_a}{RT}\right). \quad (1)$$

When the heating rate of sample is constant, due to  $\beta = dT/dt$ , the above equation can be changed into the following equation:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} (1 - \alpha)^n \exp\left(-\frac{E_a}{RT}\right). \quad (2)$$

Here,  $A$  is the pre-exponential factor,  $E_a$  is the activation energy, and  $R$  is the gas constant.  $\alpha$ ,  $\beta$ ,  $n$ , and  $T$  are the weight loss rate or conversion rate, heating rate, reaction order, and absolute temperature, respectively.

According to Eq. (2), using different mathematical processing methods, we can get different thermal degradation dynamics calculation method. The thermal decomposition kinetics of  $\text{CaCO}_3/\text{LLDPE}$  nanocomposites was evaluated by two different techniques: Kim-Park method<sup>10</sup> and Flynn-Wall-Ozawa method.<sup>11,12</sup>

### KIM-PARK METHOD

The thermal degradation kinetics equation formulated by Kim-Park is as follows:

$$\ln \beta = \ln A + \ln \left( \frac{E_a}{R} \right) + \ln \left[ 1 - n + \frac{n}{0.9444} \right] - 5.3305 - 1.0516 \left( \frac{E_a}{RT_{\text{md}}} \right), \quad (3)$$

where  $n = (1 - \alpha^m) / [(RT_{\text{md}}^2) (d\alpha/dt)]$ ,  $T_{\text{md}}$  is the largest weight loss temperature, and  $\alpha^m$  is the conversion of weight loss at that time.  $E_a$  can be obtained

from the slope of  $\ln \beta$  versus  $1/T_{\text{md}}$ , and  $\ln A$  can be calculated from the intercept value.

### FLYNN-WALL-OZAWA METHOD

Flynn-Wall-Ozawa method is one of the integral methods that can determine the activation energy without the knowledge of reaction order and differential data of thermogravimetry (TG).

$$\lg \beta = \lg \left( \frac{AE_a}{RG(\alpha)} \right) - 2.315 - 0.4567 \frac{E_a}{RT}. \quad (4)$$

Here,  $A$  and  $R$  are constants for a particular conversion and  $G(\alpha)$  is a constant. Hence, the value of  $E_a$  can be computed by Ozawa's method for any particular decomposition degree or conversion rate,  $\alpha$ , being determined from the linear dependence plot of  $\ln \beta$  versus  $1/T$  at different heating rates without the knowledge of the reaction order.

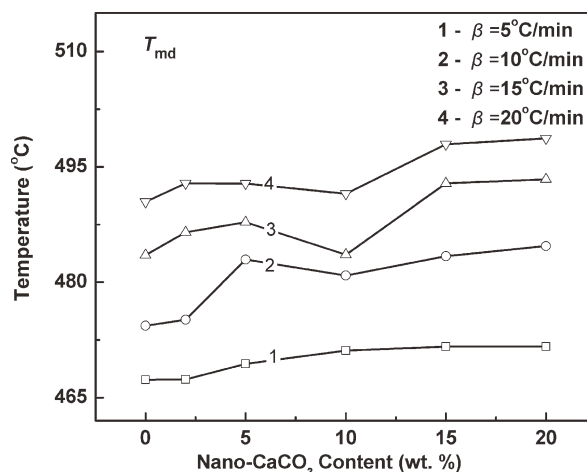
### EXPERIMENTAL

#### Materials and samples

Nano- $\text{CaCO}_3$  was supplied by Shanxi Lanhua Huaming Nano Material, China, with specifications as follows: average diameter is 50–80 nm, the model number is sp-200, and purity >95%. LLDPE was supplied by Sinopec, China, with melt flow index of 2.0 g/10 min at 120°C.

#### Preparation of nano- $\text{CaCO}_3/\text{LLDPE}$ nanocomposites

The  $\text{CaCO}_3/\text{LLDPE}$  nanocomposites were prepared on a two-roll mill [X(S) K-100, Jiangsu Tianyuan Test Equipment, China] at 110–125°C with a screw speed of 20 r/min. After preparation, the samples were



**Figure 2** Relationships of  $T_{\text{md}}$  and nano- $\text{CaCO}_3$  content at different heating rates.

TABLE I  
Physical Parameters of TG Curves

Samples	$\beta$ ( $^{\circ}\text{C}/\text{min}$ ) <sup>a</sup>	$T_0$ ( $^{\circ}\text{C}$ ) <sup>b</sup>	$T_{\text{md}}$ ( $^{\circ}\text{C}$ ) <sup>c</sup>	$R_{\text{md}}$ (%/min) <sup>d</sup>
No. 0	5	442.46	467.33	-0.0746
	10	454.02	474.36	-0.0800
	15	461.91	483.53	-0.1187
	20	463.52	490.46	-0.1503
No. 2	5	445.45	467.38	-0.0411
	10	457.87	475.15	-0.0810
	15	458.26	486.53	-0.0815
	20	464.11	492.85	-0.1273
No. 5	5	443.21	469.41	-0.0449
	10	456.83	482.95	-0.0926
	15	461.36	487.82	-0.1009
	20	466.98	492.83	-0.1584
No. 10	5	444.12	471.13	-0.0761
	10	455.82	480.88	-0.0758
	15	457.63	483.58	-0.1803
	20	463.42	491.48	-0.1976
No. 15	5	444.39	471.65	-0.0429
	10	453.67	483.38	-0.0619
	15	464.49	492.84	-0.1129
	20	464.78	497.96	-0.1087
No. 20	5	444.47	471.65	-0.0454
	10	458.26	484.72	-0.0481
	15	467.53	493.37	-0.1068
	20	470.54	498.70	-0.1250

<sup>a</sup>  $\beta$  is the heating rate of sample.

<sup>b</sup>  $T_0$  is the initial decomposition temperature (5% weight loss).

<sup>c</sup>  $T_{\text{md}}$  is the largest weight loss temperature.

<sup>d</sup>  $R_{\text{md}}$  is the correlation coefficient at the maximal heating rate.

melt pressed at 120 $^{\circ}\text{C}$  and subsequently cooled with pressure under 60 $^{\circ}\text{C}$  to remove the internal stress. The content of nano- $\text{CaCO}_3$  in composites was 0, 2, 5, 10, 15, and 20 wt %, and they were marked as No. 0, No. 2, No. 10, No. 15, and No. 20, respectively.

### Thermogravimetric testing

The thermal degradation analysis of TG and TGA was investigated by using a SETARAM Evolution 24

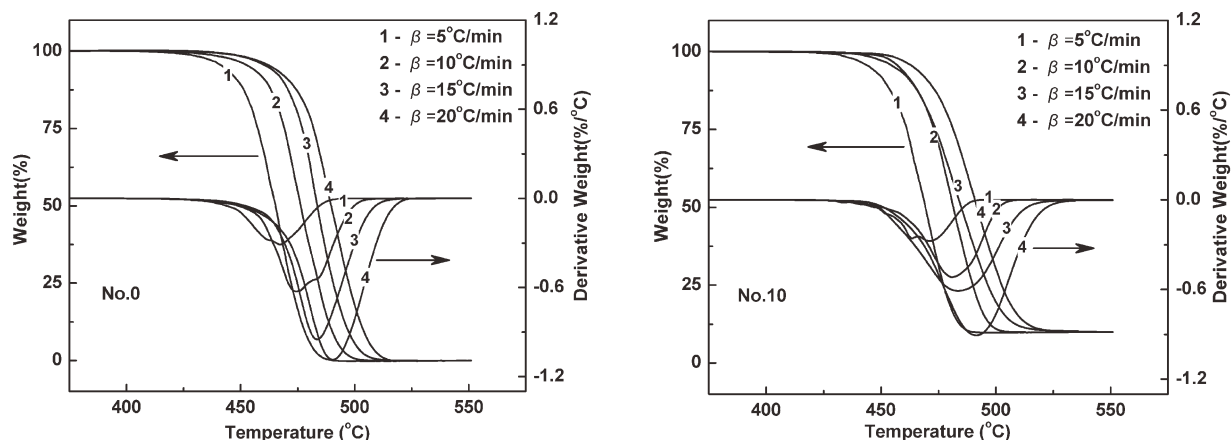


Figure 3 TG and DTG curves of  $\text{CaCO}_3/\text{LLDPE}$  nanocomposites.

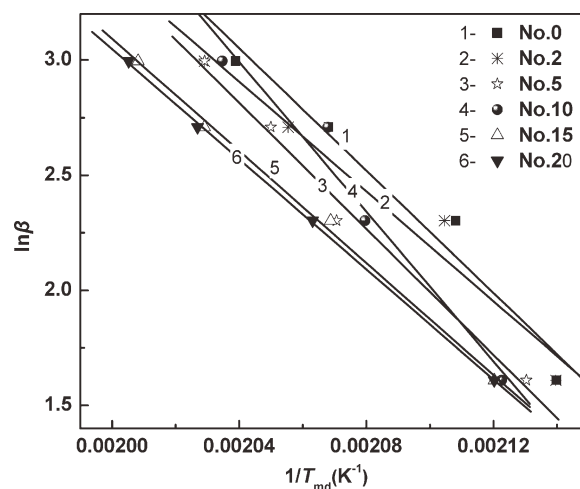


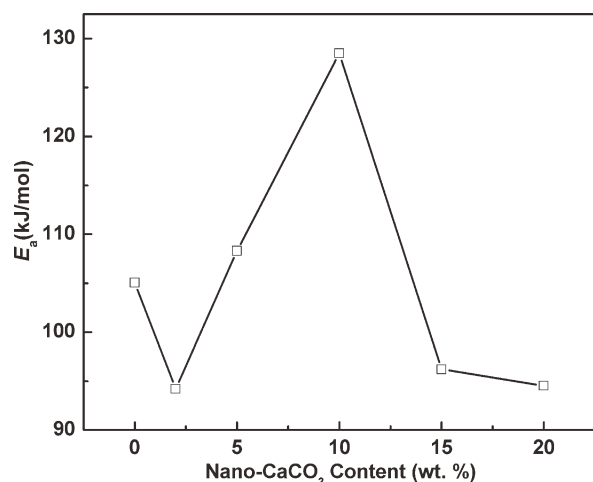
Figure 4 Kim-Park plots of  $\ln \beta$  versus  $1/T$  at maximal decomposition rate.

operated under argon flow rate of 20 mL/min. About 15 mg of samples were heated from 25 to 800 $^{\circ}\text{C}$  at constant heating rates of 5, 10, 15, and 20 $^{\circ}\text{C}/\text{min}$ .

## RESULTS AND DISCUSSION

### Thermogravimetric analysis

Thermogravimetric analysis of all samples was investigated. Figure 1 shows the relationships of initial decomposition temperature  $T_0$  (5% weight loss) and nano- $\text{CaCO}_3$  content at the heating rates of 5, 10, 15, and 20 $^{\circ}\text{C}/\text{min}$ , respectively. Figure 2 shows the relationships of maximal weight loss rate temperature  $T_{\text{md}}$  and nano- $\text{CaCO}_3$  content at same different heating rates, respectively. As seen from Figures 1 and 2,  $T_0$  and  $T_{\text{md}}$  all increase with increasing heating rates for different nano- $\text{CaCO}_3$  content. The physical parameters of TG testing of six samples, which has different nano- $\text{CaCO}_3$  content, are shown in Table I. As seen from Table I, the initial decomposition temperature  $T_0$ , the largest



**Figure 5** Plots of  $E_a$  versus nano-CaCO<sub>3</sub> content at maximal decomposition rate.

weight loss rate, and the maximal temperature of weight loss rate  $T_{md}$  all rise with increasing nano-CaCO<sub>3</sub> content, and they are higher than the pure LLDPE. These results indicate that the thermal stability of LLDPE has been increased due to the addition of nano-CaCO<sub>3</sub>.

TG and differential thermogravimetry (DTG) curves of No. 0 and No. 10 are shown in Figure 3, and all TG curves at different heating rates are smooth against S curves. At constant temperature, the higher heating rate, the bigger weight loss rate is, and every DTG curve has only a single weight loss peak. The  $T_{md}$  increases with the heating temperature rate. The other samples (No. 2, No. 15, and No. 20) all have the same phenomenon as No. 0 and No. 10. The  $T_0$  and  $T_{md}$  all rise with increasing heating rate, which is relative with temperature delaying of samples at faster heating rate.

### Thermal degradation activation energy

The followings are discussions on thermal degradation activation energies ( $E_a$ ) obtained from two dif-

ferent methods. The Kim-Park method only can be used to calculate activation energy of the biggest weight loss rate. The plots of  $\ln \beta$  versus  $1/T$  are shown in Figure 4. The thermal degradation  $E_a$  is calculated by the Kim-Park method, and the relationships of  $E_a$  versus nano-CaCO<sub>3</sub> content are shown in Figure 5 and Table II. The line correlation coefficient  $r$  is all in the range of 0.9797–0.9998. It can be seen from Figure 5 and Table II that the  $E_a$  has the highest value when the nano-CaCO<sub>3</sub> content is 10%. It can be illustrated that the thermal degradation reaction of sample at this nano-CaCO<sub>3</sub> content will be more difficult than other. The  $T_{md}$  in whole process is as same as TGA when the nano-CaCO<sub>3</sub> content is kept constant, and it increases along with the increasing heating rates.

The Flynn-Wall-Ozawa method can be used to calculate thermal degradation  $E_a$  at any conversions in the thermal analysis process. Figure 6 shows the plots of  $\ln \beta$  versus  $1/T$  for No. 0 and No. 10 at different  $\alpha$  by the Flynn-Wall-Ozawa method. The corresponding thermal degradation  $E_a$  of nanocomposites could be obtained according to the slope of fitting line, and the results are listed in Table III. Figure 7 shows the relationships of thermal degradation  $E_a$  and nano-CaCO<sub>3</sub> contents in the nanocomposites at different weight loss rates or conversion rate  $\alpha$ . As seen from Figure 5, the thermal degradation  $E_a$  of samples all changed along with nano-CaCO<sub>3</sub> contents. This result is the same as by the Kim-Park method (Table II). It explains that the addition of nano-CaCO<sub>3</sub> affects the thermal degradation  $E_a$  of nanocomposites and that the thermal degradation  $E_a$  is the biggest when the nano-CaCO<sub>3</sub> content (wt %) is 10%.

As seen from Tables II and III and Figure 7, the thermal degradation  $E_a$  of No. 0 is higher than No. 2 sample, this is due to the fact that pure LLDPE has a higher crystallinity, which has a hindered role for molecular degradation of LLDPE. After the addition of nano-CaCO<sub>3</sub> into LLDPE, the part of LLDPE crystallinity is destroyed, and therefore, the thermal

**TABLE II**  
Kinetic Results Calculated Using the Kim-Park Method

Samples	$T_{md}$ (°C) <sup>a</sup>				$E_a$ (kJ/mol) <sup>b</sup>	$r$ <sup>c</sup>
	$\beta^d = 5^\circ\text{C}/\text{min}$	$\beta = 10^\circ\text{C}/\text{min}$	$\beta = 15^\circ\text{C}/\text{min}$	$\beta = 20^\circ\text{C}/\text{min}$		
No. 0	467.33	474.36	483.53	490.46	100.51	0.9797
No. 2	467.38	475.15	486.53	492.85	94.21	0.9806
No. 5	469.41	482.95	487.82	492.83	108.31	0.9947
No. 10	471.13	480.88	483.58	491.48	128.48	0.9817
No. 15	471.65	483.38	492.84	497.96	96.21	0.9984
No. 20	471.65	484.72	493.37	498.70	94.53	0.9998

<sup>a</sup>  $T_{md}$  is the largest weight loss temperature.

<sup>b</sup>  $E_a$  is the thermal degradation activation energy.

<sup>c</sup>  $r$  is the regression coefficient.

<sup>d</sup>  $\beta$  is the heating rate of sample.

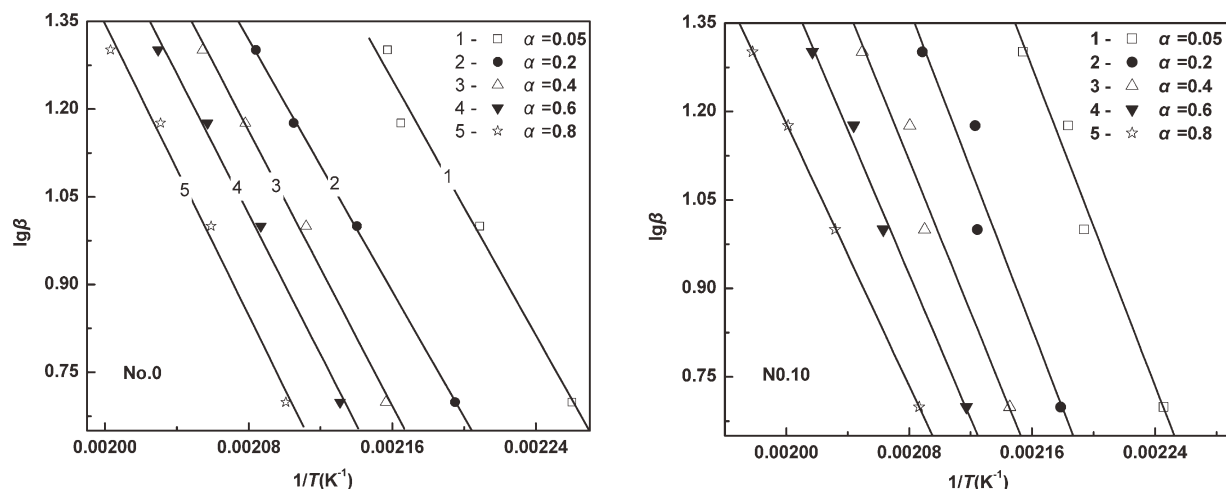


Figure 6 Flynn-Wall-Ozawa plots of CaCO<sub>3</sub>/LLDPE nanocomposites for five different conversions.

degradation  $E_a$  is decreased. However, with increasing the nano-CaCO<sub>3</sub> content, the thermal stability of LLDPE is improved, and it is attributed to the fact that the stronger interaction and hybrid between LLDPE molecules and nano-CaCO<sub>3</sub> confined the ac-

tivity of macromolecule chains and suppressed the emanation of small molecule effectively when degradation reaction originated, resulting in the decrease of degradation velocity of materials. Therefore, the heat stability and thermal degradation  $E_a$  of materials are increased. However, when the content of nano-CaCO<sub>3</sub> is over 10 wt %, the thermal degradation  $E_a$  is decreased with increasing nano-CaCO<sub>3</sub> content. This is due to the fact that the crystallinity of LLDPE will have a larger decrease under this condition.

TABLE III  
 $E_a$  Calculated Using Flynn-Wall-Ozawa Method

Samples	$\alpha^a$	$E_a$ (kJ/mol) <sup>b</sup>	$r^c$
No. 0	0.05	229.16	0.9906
	0.2	260.68	0.9997
	0.4	224.62	0.9975
	0.6	283.12	0.9964
	0.8	257.42	0.9950
No. 2	0.05	211.60	0.9867
	0.2	225.45	0.9976
	0.4	229.82	0.9994
	0.6	216.37	0.9991
	0.8	283.67	0.9973
No. 5	0.05	219.56	0.9949
	0.2	202.19	0.9998
	0.4	246.42	0.9999
	0.6	229.02	0.9997
	0.8	215.45	0.9999
No. 10	0.05	269.36	0.9857
	0.2	213.29	0.9647
	0.4	204.99	0.9834
	0.6	251.33	0.9957
	0.8	231.11	1.0000
No. 15	0.05	215.84	0.9648
	0.2	256.60	0.9898
	0.4	209.58	0.9945
	0.6	217.00	0.9958
	0.8	261.32	0.9939
No. 20	0.05	230.11	0.9958
	0.2	213.90	0.9979
	0.4	233.20	0.9983
	0.6	194.53	0.9974
	0.8	179.77	0.9912

<sup>a</sup>  $\alpha$  is the weight loss rate or conversion rate.  
<sup>b</sup>  $E_a$  is the thermal degradation activation energy.  
<sup>c</sup>  $r$  is the regression coefficient.

It should be noted that this study has examined only the thermal property of CaCO<sub>3</sub>/LLDPE nanocomposites. Other properties such as mechanical strength, heat of fusion, rheology, and flame resistance will be reported in the later investigation. Notwithstanding its limitation, this study suggests that the thermal stability of LLDPE has been improved by the addition of nano-CaCO<sub>3</sub>. This is of great significance for us and others in the research of thermal degradation kinetics of LLDPE and other polymers.

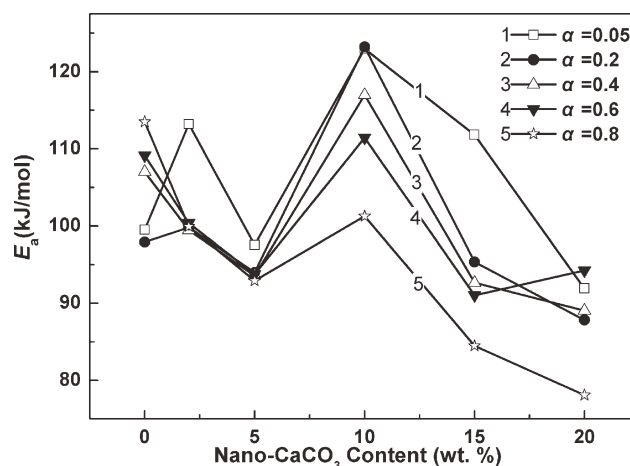


Figure 7 Plots of  $E_a$  calculated using Flynn-Wall-Ozawa method with  $\alpha$  at different nano-CaCO<sub>3</sub> content.



## CONCLUSIONS

In this work, the CaCO<sub>3</sub>/LLDPE nanocomposites can be prepared from nano-CaCO<sub>3</sub> and LLDPE by melt-blending method. The thermogravimetry analysis (TGA) and differential thermogravimetry (DTG) analysis can be used to test the thermal properties of CaCO<sub>3</sub>/LLDPE nanocomposites. The thermal analysis results show that the Kim-Park and the Flynn-Wall-Ozawa methods may be used to analyze the thermal degradation data. The CaCO<sub>3</sub>/LLDPE nanocomposites have one-stage degradation process, and nano-CaCO<sub>3</sub> can increase the initial thermal degradation temperature  $T_0$  and thermal stability of LLDPE. The addition of nano-CaCO<sub>3</sub> has a great effect on the thermal degradation activation energy  $E_a$  of LLDPE. When the mass fraction of nano-CaCO<sub>3</sub> in nanocomposites is up to 10%, it has the highest  $E_a$ , which is higher (28 kJ/mol) than pure LLDPE.

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## References

1. Lu, H. D.; Hu, Y.; Li, M.; Chen, Z. Y.; Fan, W. C. *Compos Sci Technol* 2006, 66, 3035.
2. Weon, J. *Polym Degrad Stab* 2010, 95, 14.
3. Park, J. W.; Oh, S. C.; Lee, H. P.; Kim, H. T.; Yoo, K. O. *Polym Degrad Stab* 2000, 67, 535.
4. Cho, Y.; Shim, M.; Kim, S. *Mater Chem Phys* 1998, 52, 94.
5. Ojeda, T.; Freitas, A.; Birck, K.; Dalmolin, E.; Jacques, R.; Bento, F.; Camargo, F. *Polym Degrad Stab* 2011, 96, 703.
6. Shebani, A. N.; Reenena, A. J.; Meincken, M. *Thermochim Acta* 2009, 481, 52.
7. Qiu, L. Z.; Chen, W.; Qu, B. J. *Polymer* 2006, 47, 922.
8. Bocchini, S.; Frache, A.; Camino, G.; Claes, M. *Eur Polym J* 2007, 43, 3222.
9. Gorghiu, L. M.; Jipa, S.; Zaharescu, T.; Setnescu, R.; Mihalcea, I. *Polym Degrad Stab* 2004, 84, 7.
10. Kim, S.; Park, J. K. *Thermochim Acta* 1995, 264, 137.
11. Ozawa, T. *Bull Chem Soc Jpn* 1965, 38, 1881.
12. Flynn, J. H.; Wall, L. A. *J Polym Sci Part B: Polym Lett* 1966, 4, 323.