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Thermal Decomposition Kinetics of Poly(L-lactic acid) after Heat Treatment

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Abstract: Thermal decomposition behavior of Poly(L-lactic acid) (PLLA) and PLLA composites after different heat treatment were investigated using thermogravimetric analysis. Firstly, the thermal decomposition results of neat PLLA showed that the decomposition of PLLA was a first-order kinetic reaction, and thermal decomposition kinetics indicated that the heat treatment significantly affected activation energy of thermal decomposition of PLLA. The measurement results also exhibited that the onset decomposition temperature of PLLA treated below 115 ºC was lower than that of the pristine PLLA. Then, the effect of additive $CaCO_3$ on the thermal decomposition behavior of PLLA was evaluated. The addition of $CaCO_3$ could significantly improve the crystallization performance of PLLA, but the $CaCO_3$ did not change the decomposition trend of PLLA, and the thermal decomposition behavior of PLLA/$CaCO_3$ composites after isothermal heat treatment was similar to that of PLLA. However, the thermal decomposition activation energy of PLLA/$CaCO_3$ is lower than that of PLLA.

Keywords: Calcium carbonate, composites, crystallization, poly(L-lactic acid), thermal decomposition kinetics.

1. INTRODUCTION

Poly(L-lactic acid) (PLLA) is one of the most important biodegradable polymers [1]. There exist many literatures about PLLA and its composites based on PLLA [2, 3], and the addition of a functional additive can significantly improve the properties of PLLA. For example, Fan *et al.* [4] reported that *N*, *N′*-bis(benzoyl)sebacic acid dihydrazide was synthesized and used as a nucleating agent for PLLA. The addition of *N*, *N′*-bis(benzoyl)sebacic acid dihydrazide enhanced the crystallization rate of PLLA, and thermogravimetric analysis showed that the thermal stability of PLLA with *N*, *N′*-bis(benzoyl)sebacic acid dihydrazide was enhanced, indicating that there were strong hydrogen bonds between *N*, *N′*-bis(benzoyl)sebacic acid dihydrazide and PLLA matrix.

Thermal stability is key factor used to evaluate the application field of materials. Thus, the thermal stability of polymer and composites need to be investigated to meet application requirements. As to the PLLA and its composites, the decomposition behavior of PLLA and composites including decomposition process and kinetics had been reported in some papers. Yeng-Fong Shih *et al.* [5] prepared the PLA/banana fiber composites though melt blending technologies, the thermogravimetric analysis showed that the decomposition temperatures of PLLA reinforced by the banana fiber were smaller than those of the pristine PLA. However, the decomposition temperatures of PLLA reinforced by the char yields of banana fiber were larger than those of pristine PLA. Meng *et al.* [6] reported that the addition of montmorrilonite considerably decreased the thermal decomposition rate and shifted the peak rate to a higher temperature compared to that of PLA composites with wood. Similarly, the incorporation of the montmorrilonite resulted in a significant improvement in the initial thermal stability of the both PLA and PLA/LLDPE nanocomposites [7].

There exists relevant literature to investigate the thermal decomposition kinetics of PLLA composites. However, in this article, we focus on the thermal decomposition behavior of PLLA and PLLA/$CaCO_3$ composites after heat treatment at different temperatures to illustrate the role of heating rate, heat treatment process and additive in decomposition behavior of PLLA. The related results can be used to help us further investigate the properties of PLLA to widen the application field of PLLA and composites.

2. EXPERIMENTAL SECTION

2.1. Materials

Poly(L-lactic acid) (2002D) from Nature Works LLC was purchased from the Kunshan Longyuan Plastic Company (JiangSu Province, China). The calcium carbonate ($CaCO_3$) of analytical grade was purchased from the Chengdu Kelong Chemical Reagents Company (Sichuan Province, China).

2.2. Preparation of PLLA/$CaCO_3$ Composites

Blending of PLLA and $CaCO_3$ was performed on counter-rotating mixer from the Shanghai Kechuang Rubber Plastic Mechanical Equipment Co., Ltd., and the preparation

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process of PLLA/$CaCO_3$ composites is similar to that of our previous paper [8].

2.3. Characterization

The thermal decomposition behaviors of PLLA and PLLA/$CaCO_3$ composites were measured using Q500 thermogravimetric analysis (TGA) from TA Instruments-Waters LLC with a different heating rate under air flow (60 ml/min) from room temperature to 600 ºC.

The isothermal crystallization behavior of PLLA and PLLA/$CaCO_3$ composites was evaluated by GJY-Ⅲoptical depolarizer from the Donghua University in China in the region from 100 ºC to 120 ºC.

3. RESULTS AND DISCUSSION

3.1. Thermal Decomposition Behavior of PLLA

Thermal decomposition of PLLA after heat treatment at different temperatures for 1 h is shown in Fig. (**1**). As shown in Fig. (**1**), there exists only one platform on the TGA curves, indicating that the decomposition of neat PLLA is a first-order kinetic reaction. At the same time, it is clear that the thermal decomposition temperature of PLLA went through the same heat treatment technology and increases with increasing of heating rate, resulting from thermal inertia. The larger heating rate makes the decomposition of PLLA not achievable at the set temperature, resulting in the decomposition occurring at a higher temperature. It is clear from Table **1** that the onset decomposition temperature of PLLA after heat treatment below 115 ºC is lower than that of the pristine PLLA, this is an interesting phenomenon, the possible reason is that there exists a substantial random macromolecule segment in PLLA without heat treatment. This will impede the macromolecular segment active ability during the heating process. Meantime, the crystallization degree of PLLA could improve though heat treatment, but the crystallization ability of neat PLLA was very limited in the low temperature region, resulting in the easy formation of free molecular chain during the heat process. However, above 115°C, the onset decomposition temperature of PLLA after heat treatment is higher than that of the pristine PLLA.

According to first-order kinetic reaction, thermal decomposition kinetics of PLLA can be described by the following Coats-Redfern equation [9]:

$$\lg[-\frac{\ln(1-\alpha)}{T^2}] = \lg[\frac{AR}{\beta E_a}(1-\frac{2RT}{E_a})] - \frac{E_a}{2.303R} \bullet \frac{1}{T} \qquad (1)$$

where, α is the mass loss rate, β is the heating rate, A is the frequency factor, R is the gas constant, E_a is activation energy. From this data we can easily obtain the temperature for the different mass loss rate at a different heating rate based on the TGA curves, and the relationship curves of $\lg[-\ln(1-\alpha)/T^2]$ against 1/T are displayed in Fig. (**2**). As seen in Fig. (**2**), $\lg[-\ln(1-\alpha)/T^2]$ and 1/T keep a favorable linear relationship, and the thermal decomposition kinetics parameters of PLLA after heat treatment are listed in Table **2**. Apart from 3 ºC/min, upon the same heating rate, E_a of PLLA after heat treatment is higher than that of the pristine PLLA, indicating that the heat treatment significantly affects the E_a of thermal decomposition of PLLA. In addition, it is observed that the heating rate can also slightly affect the E_a,. The reason is that different heating rates make the decomposition of PLLA occurs at a different temperature.

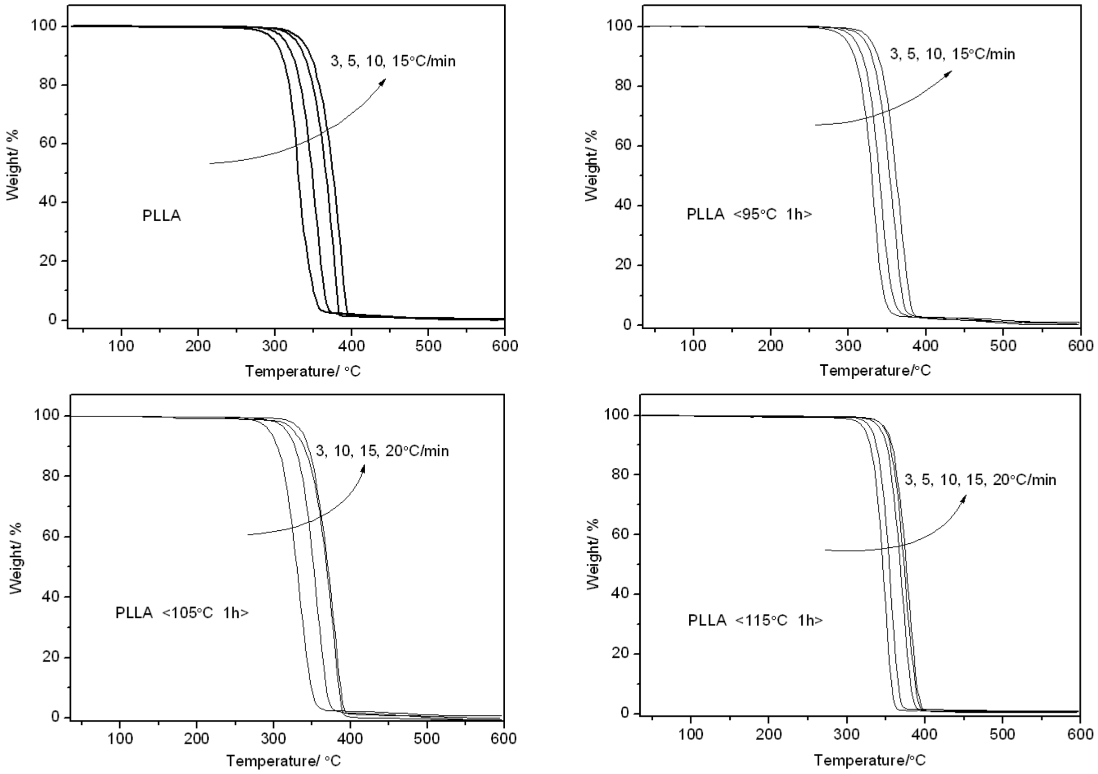

Fig. (1). Thermal decomposition of PLLA after heat treatment at different temperatures for 1 h.

Table 1. The onset decomposition temperatures of PLLA after heat treatment.

Sample	β	Onset Temperature/ °C
PLLA	3	317.8
	5	332.0
	10	349.8
	15	353.4
	20	355.4
PLLA (95°C 1 h)	3	314.6
	5	324.5
	10	334.5
	15	352.0
PLLA (105°C 1 h)	3	308.5
	10	334.3
	15	357.0
	20	349.3
PLLA (115°C 1 h)	3	333.4
	5	341.8
	10	353.6
	15	357.9
	20	359.6

Table 2. Thermal decomposition kinetics parameters of PLLA.

Sample	β	E_a/ KJ/mol
PLLA	3	66.778
	5	61.007
	10	62.215
	15	63.431
	20	66.187
PLLA (95°C 1 h)	3	62.347
	5	71.144
	10	75.113
	15	72.740
PLLA (105°C 1 h)	3	55.473
	10	65.388
	15	55.964
	20	72.547
PLLA (115°C 1 h)	3	100.779
	5	103.432
	10	109.742
	15	113.673
	20	108.418

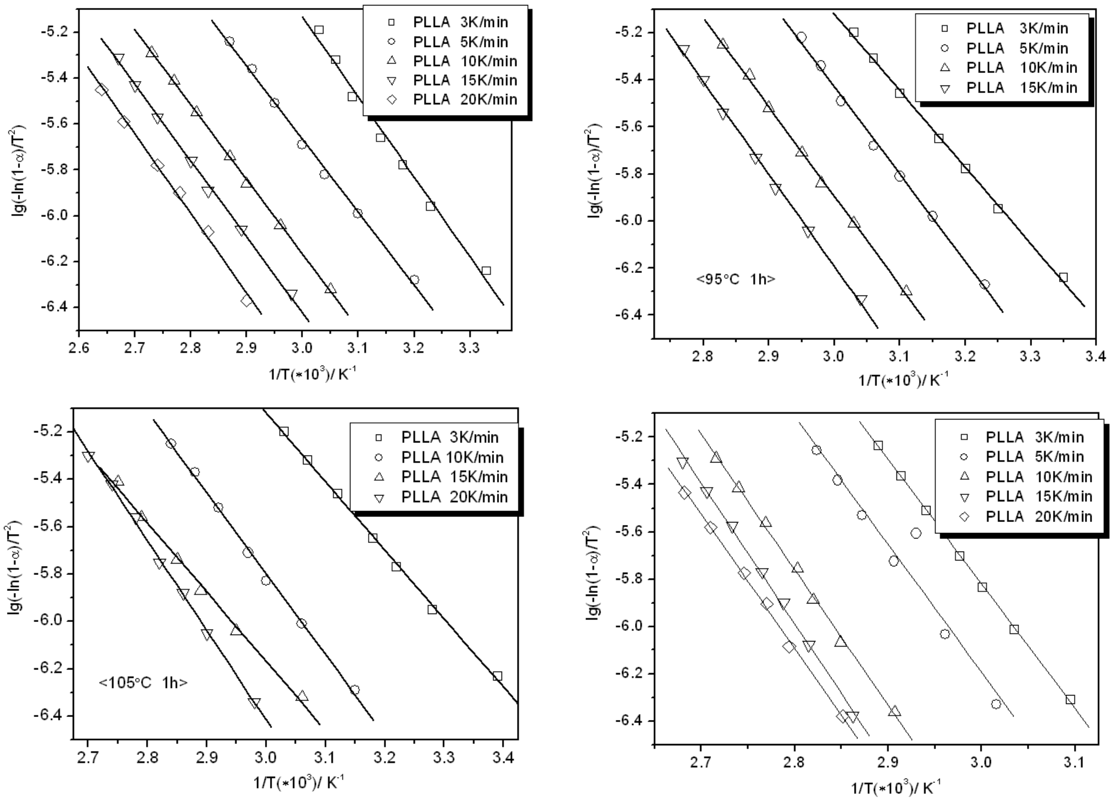

Fig. (2). Coats-Redfern curves of PLLA.

3.2. Thermal Decomposition Behavior of PLLA/$CaCO_3$ Composites

Usually, the addition of an additive would more or less affect the physical and chemical performance of polymer. Thus, the effect of the additive on the thermal decomposition of the polymer matrix is also interesting for future research in enabling an understanding the role of additives. $CaCO_3$ is a common commercial inorganic compound, and widely used to improve the mechanical properties of polymer materials [10-12]. Moreover, $CaCO_3$ as a nucleating agent is used to improve the crystallization behavior of PLLA [13]. Similarly, the nucleating ability of $CaCO_3$ for PLLA was firstly investigated before studying the thermal decomposition of PLLA/$CaCO_3$ composites. Fig. (**3**) shows the effect of $CaCO_3$ and the crystallization temperature (T_c) against the half time of overall PLLA crystallization $t_{1/2}$. The addition of $CaCO_3$ makes the $t_{1/2}$ of PLLA decrease, indicating that the $CaCO_3$ as a heterogeneous nucleating agent can promote the crystallization of PLLA. In addition, the $t_{1/2}$ of PLLA/5%$CaCO_3$ composites firstly decreases, then increases with an increase of T_c. while 5% $CaCO_3$ makes the $t_{1/2}$ of PLLA decreases to the minimum value 352.52 s at 105 ºC.

Similarly, the thermal decomposition behavior of PLLA/5%$CaCO_3$ composites after heat treatment (isothermal crystallization) at different temperatures (See Fig. **4**) is similar to that of PLLA. With increasing of heating rate, the onset decomposition temperature of PLLA/5%$CaCO_3$ composites still increases. However, the addition of $CaCO_3$ does not change the trend of decomposition curves of PLLA, resulting from the higher decomposition temperature of $CaCO_3$.

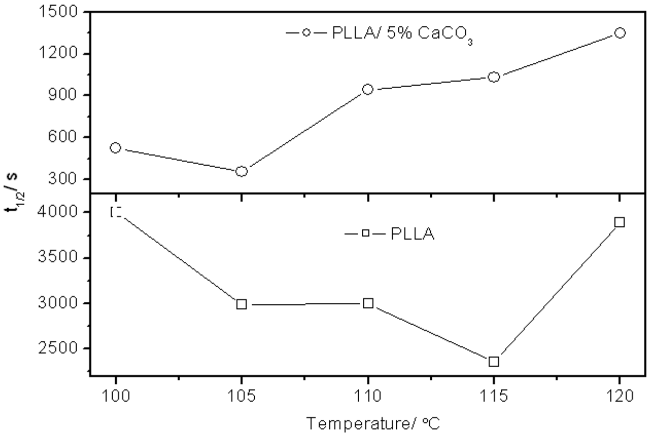

Fig. (3). The $t_{1/2}$ of PLLA and PLLA/5%$CaCO_3$ with T_c.

Compared to neat PLLA, the dates from Table **3** obtained though the Coats-Redfern equation (See Fig. **5**) shows that the thermal decomposition activation energy of PLLA/5%$CaCO_3$ composites is lower than that of PLLA. This result indicates that it could affect the thermal decomposition activation energy of PLLA/$CaCO_3$ composites and it is possibly affected by the additive $CaCO_3$. This is because the addition of $CaCO_3$ may lead to more defects in the PLLA matrix. However, the thermal decomposition activation energy of PLLA/5%$CaCO_3$ composites increases with increasing heat treatment temperature.

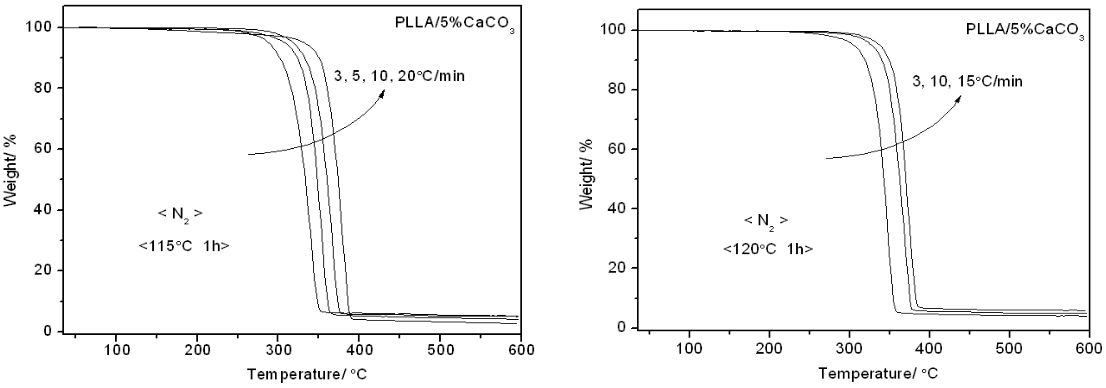

Fig. (4). Thermal decomposition of PLLA/5%$CaCO_3$ after heat treatment at different temperature for 1 h.

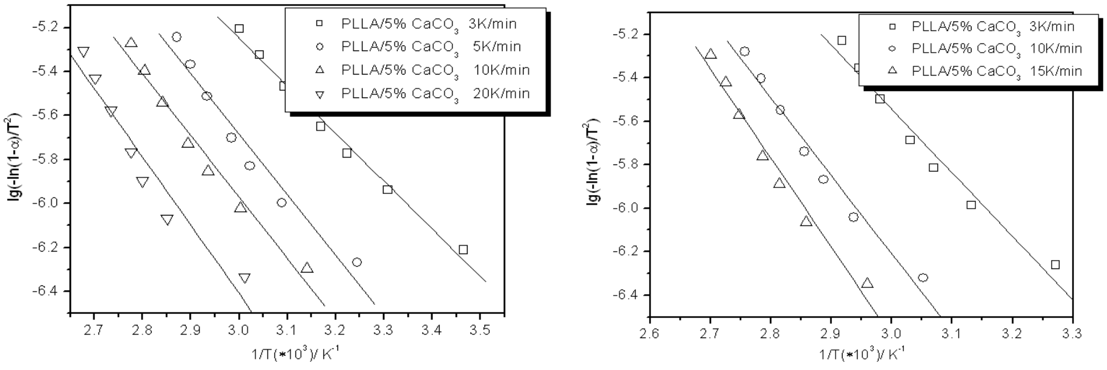

Fig. (5). Coats-Redfern curves of PLLA/5%$CaCO_3$ composites.

Table 3. Thermal decomposition kinetics parameters of PLLA/5%CaCO$_3$ composites.

Sample	β	E_a/ KJ/mol
PLLA/5%CaCO$_3$ (115°C 1 h)	3	41.514
	5	52.469
	10	53.574
	20	59.493
PLLA/5%CaCO$_3$ (120°C 1 h)	3	56.137
	10	68.747
	15	78.385

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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