

Thermal Stability and Degradation of Poly (Lactic Acid) / Hexamoll® DINCH / Montmorillonite Composites

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The effects of the plasticizer 1,2-cyclohexane dicarboxylic acid diisononyl ester (Hexamoll® DINCH) on the thermal stability and degradation of poly (lactic acid) were investigated and compared with tributyl citrate and montmorillonite. A series of poly (lactic acid) composites were prepared *via* melt blending before being hot pressed into 0.3 mm films. Along with the increase of the content of MMT, the agglomeration degree rise and the MMT content for this study was determined. The addition of Hexamoll® DINCH could efficiently decrease the T_g of PLA and improve the crystallinity of poly (lactic acid) composites. The addition of DINCH or TBC could deteriorate the thermal stability of PLA composites. The addition of montmorillonite could improve the thermal stability of PLA/TBC and PLA/DINCH composites. The kinetic parameters including activation energy of decomposition (E), reaction order (n), and pre-exponential factor ($\ln A$) of PLA/DINCH/MMT composites are 180.2 kJ/mol, 0.863, and 36.8, respectively by using Freeman-Carroll method.

Keywords: Poly (lactic acid); Thermal stability; Hexamoll® DINCH; Kinetic parameter; Montmorillonite

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INTRODUCTION

Poly (lactic acid) (PLA) is a thermoplastic aliphatic polyester derived from renewable resources, such as corn starch (in the United States), tapioca roots, chips or starch (mostly in Asia), or sugarcane (in the rest of the world). It is the most extensively researched and utilized biodegradable polymer, with potential to replace conventional petrochemical-based polymers. In 2010, PLA was the second most important bioplastic of the world in regard to consumption volume (Lepitre 2012). The development of economically feasible industrial production processes has made PLA the most promising biodegradable polymer for environment-friendly applications such as packaging field (Rahaman and Tsuji 2013; Rasal *et al.* 2010). Poly (lactic acid) is a bio-based polymer that accomplishes the double benefit of coming from renewable resources and being biodegradable once discarded, within a rational time. This polymer can provide good strength and is easy to process in most equipment. However, it needs further modification for many practical applications due to its brittleness, low impact strength, and low ability to resist thermal deformation (Badia *et al.* 2012; Qu *et al.* 2010).

Poly (lactic acid) was chosen as the matrix for the current study, which aimed to develop a composite suitable for packaging applications. Numerous studies have focused on the PLA composites reinforced with various materials (Johansson *et al.* 2012; Rasal *et al.* 2010; Tee *et al.* 2013).

Brittleness is the major drawback of PLA. Blending is probably the most extensively used methodology to improve PLA mechanical properties. Poly (lactic acid) has been blended with different plasticizers and polymers (biodegradable and non-

biodegradable) to achieve desired mechanical properties (Rasal *et al.* 2010). Citrate esters have been used as plasticizers with PLA and were found to be effective in reducing the glass transition temperature and improving the elongation at break. It was observed that the plasticizing efficiency was higher for the intermediate molecular weight plasticizers (Labrecque *et al.* 1997). Researchers used glycerol, citrate ester, PEG, PEG monolaurate, and oligomeric lactic acid to plasticize PLA and found that oligomeric lactic acid and low molecular weight PEG gave the best results, while glycerol was found to be the least efficient plasticizer (Martin and Avérous 2001; Rasal *et al.* 2010).

Another approach to improve the mechanical properties of PLA is through the incorporation of organic/inorganic fillers. For example, PLA-clay solvent cast blends exhibited improved Young's modulus (Ogata *et al.* 1997). Poly (lactic acid)-organically modified montmorillonite (MMT) clay composites showed a strain at break increase to 15.9% at 2.5 wt% MMT content, which increased to 67 MPa at 5 wt% MMT content (Jiang *et al.* 2007). The addition of hydroxyapatite also promotes the crystalline of poly (lactic acid) (Wei *et al.* 2011).

The thermal stability of a polymeric material is of significance because this property determines its processing conditions and further applications. The thermal stability (Fortunati *et al.* 2010; Liu *et al.* 2010; Zhao *et al.* 2011; Chen *et al.* 2012; Hughes *et al.* 2012) and the mechanical strength of the composite material, which is a mixture of different additives or other materials, have been researched; investigators have also studied the impact of cross-linking on the thermal stability and crystalline properties of the poly (lactic acid) (Yang *et al.* 2008; Cheng *et al.* 2009; Abdelwahab *et al.* 2012; Al-ltry *et al.* 2012).

The activation energy of decomposition (E) and pre-exponential factor (A) of poly (lactic acid) have been studied by some researchers, but the results have been shown to follow different degradation mechanisms (Wang *et al.* 2010; Badia *et al.* 2012). The incorporation of nanoclays into a polymeric matrix can improve its thermal stability. It is widely accepted that this improvement is due to the dispersed silicate layers that hinder the diffusion of volatile decomposition products out of the materials, delaying the release of thermal degradation products in comparison to the pure polymer (Zhang and Loo 2009; Corres *et al.* 2013).

It has been shown that the thermal stability of the nanocomposites depends significantly on the thermal stability of the organic modifiers (Corres *et al.* 2013). 1,2-cyclohexane dicarboxylic acid diisononyl ester (Hexamoll® DINCH) is a plasticizer for the manufacture of flexible plastic articles in sensitive application areas such as toys, medical devices, and food packaging. Hexamoll® DINCH is the most widely used phthalate substitute in the world. However, there is little literature regarding the combination of PLA and Hexamoll® DINCH. Wang and associates have studied PLA modification by using TBC and DINCH, and shown that the TBC and DINCH can improve the plasticity of PLA. While there is a lack of compatibility between PLA and DINCH, the study results show that the organic montmorillonite (DK-2) can improve their compatibility (Wang 2009; Wang *et al.* 2009). To the best of our knowledge, the effect of Hexamoll® DINCH on the thermal degradation behavior of PLA composites has yet to be reported. The PLA/Hexamoll® DINCH composite materials were prepared by a melt blending method. Since montmorillonite can improve the plasticizer's compatibility with PLA (Wang *et al.* 2009), we have developed PLA/Hexamoll® DINCH/MMT composites suitable for packaging applications. Thus, the thermal

properties of PLA/Hexamoll® DINCH/MMT were investigated and compared with tributyl citrate and montmorillonite.

EXPERIMENTAL

Materials

Poly (lactic acid) (PLA) resin (AI-1001, with an MFI of 2 to 3 g/10 min (190 °C/2.16 kg), a bulk density of 1.25 g/cm³, and a melting temperature of about 175 °C) was purchased from Shenzhen Bright China Industrial Corporation Ltd. (China). Reagent-grade tributyl citrate (TBC, C₁₈H₃₂O₇, with a boiling point of 217 °C) was purchased from J&K Scientific Ltd. (China). Hexamoll® DINCH (C₂₆H₄₈O₄, with a boiling point of 186 °C) was purchased from BASF Corporation (China). The boiling points of these two plasticizers are higher than the melting temperature of PLA, which ensures they cannot be gasified during the melt processing. Montmorillonite (DK-2, with a bulk density of 1.8 g/cm³, an apparent density of 0.35 g/cm³, and a layer thickness below 25 nm) was purchased from Zhejiang Feng Hong Clay Chemical Co., Ltd., China. Its typical molecule structure is shown in Fig. 1 (Alexandre and Dubois 2000).

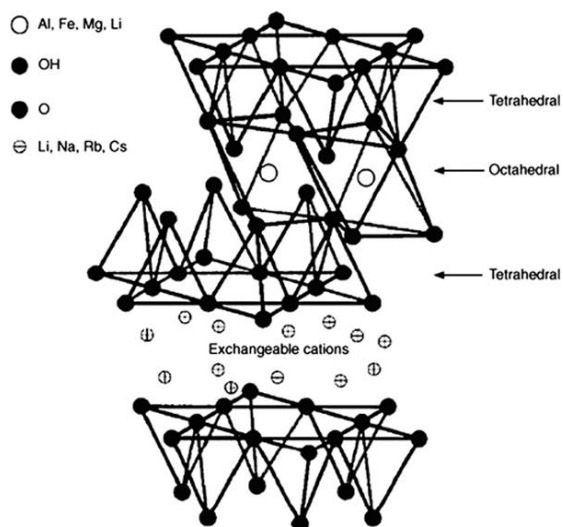


Fig. 1. Molecule structure of montmorillonite (Alexandre and Dubois 2000)

Sample Preparation

Poly (lactic acid) and montmorillonite were dried for 24 h at 60 °C in a DZF 6020 vacuum dryer (Shanghai Fengling Laboratory Instrument Co., Ltd., China) in order to remove as much moisture as possible from PLA and montmorillonite material. The mixture of PLA, montmorillonite, and plasticizer were prepared via melt blending using an internal mixer at a screw speed 50 rpm and an operating temperature of 170 °C for 15 min. The pallets were then pressed into 0.3-mm composite films with a hot and cold press machine at 160 °C. The content of MMT was 2, 4, and 6 parts per hundred (phr). The content of TBC and DINCH was 16%.

Morphological Characterization

The morphology of PLA/DINCH/MMT composites was observed using a Hitachi SU-70 field emission scanning electron microscope (FESEM; Japan) operating at an

accelerating voltage of 10 kV. Before scanning, the samples were mounted on an aluminum stub and sputter-coated with gold.

Differential Scanning Calorimetry (DSC)

The PLA and composite films were subjected to thermal analysis using a differential scanning calorimeter (DSC Q100 V9.7 Build 291; TA Instruments Company, USA). Samples weighing 4 to 10 mg were sealed in sample pans and then introduced into the heating cell of the DSC and heated from 30 to 180 °C at 10 °C/min under a nitrogen atmosphere at a flow rate of 10 mL/min. During the process, the enthalpy changes along with the temperature variations were recorded and the crystallinity calculated with Eq. 1:

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} \times 100 \% \quad (1)$$

where $\Delta H_m^0 = 93.7 \text{ J/g}$ (Garlotta 2001).

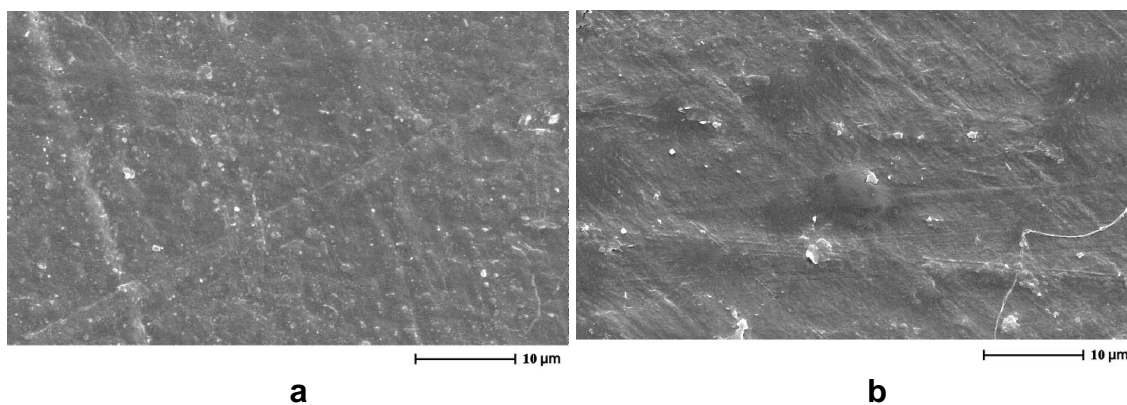
Thermogravimetric Analysis (TGA)

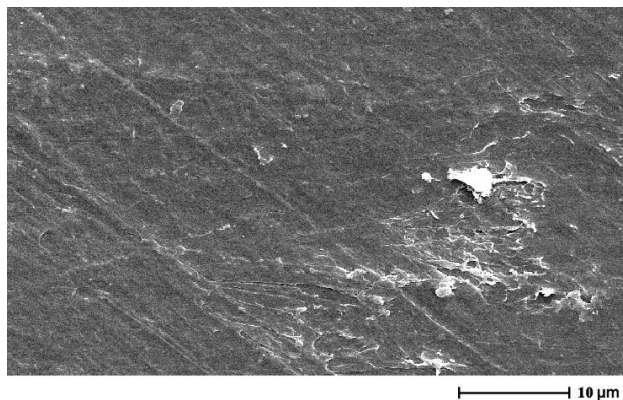
Poly (lactic acid) and the composite films were subjected to thermal analysis using a thermal gravimetric analyzer (SDT Q600 V8.2 Build 100; TA Instrument Company, USA). Samples weighing 4 to 10 mg were placed in appropriate pans and heated from 30 to 500 °C at 10, 15, 20, and 30 °C/min under a nitrogen atmosphere at a flow rate of 50 mL/min.

RESULTS AND DISCUSSION

Morphology Analysis

Figure 2 shows micrographs of PLA/DINCH/MMT composites with the MMT





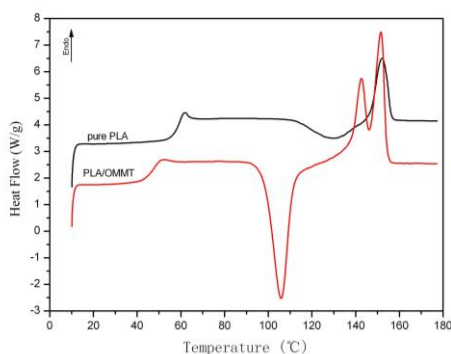
c

Fig. 2. FESEM images of PLA composites. (a) 2 phr MMT, (b) 4 phr MMT, and (c) 6 phr MMT

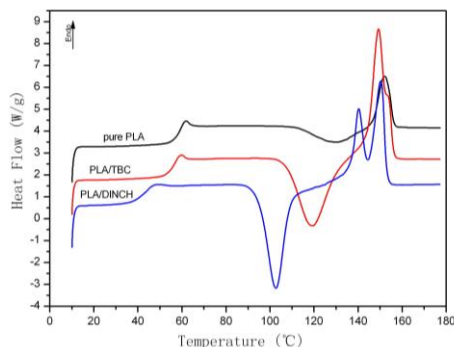
content of 2 phr, 4 phr, and 6 phr, respectively. From Fig. 2a it can be seen that MMT can be uniformly dispersed in the PLA substrate. Along with the increase of the content of MMT, the degree of agglomeration rose. Figure 2b shows some reunion phenomenon. When the MMT content reached 6 phr, agglomeration phenomena were observed in the PLA composites (Fig. 2c). Since MMT can improve plasticizer compatibility with PLA (Wang *et al.* 2009), the MMT content for this study was determined as 4 phr.

DSC Analysis

By means of the DSC method, the morphologic change of poly (lactic acid) mixed with different kinds of plasticizer and montmorillonite can be analyzed. The DSC curve provides the T_g and thus the thermal property of different samples. Figure 3 shows DSC curves of poly (lactic acid) and poly (lactic acid) composite materials. Table 1 shows T_g and crystallinity of poly (lactic acid) composite materials (Garlotta 2001).



a



b

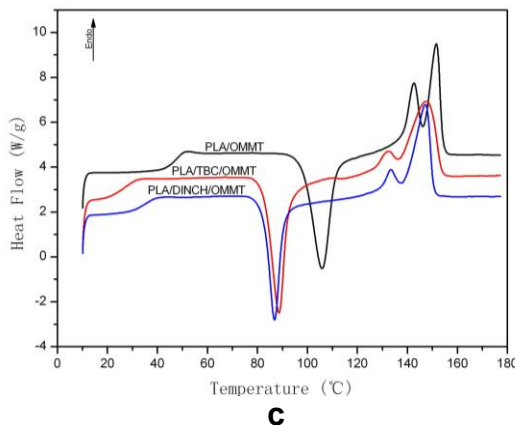


Fig. 3. DSC curves of PLA composites. (a) pure PLA and PLA/MMT, (b) PLA/TBC and PLA/DINCH, and (c) PLA/MMT, PLA/TBC/MMT and PLA/DINCH/MMT

Table 1. Thermal Performance and Crystallinity of Poly (lactic acid) Composites

Sample	T_g (°C)	T_c (°C)	T_m (°C)	ΔH_m (J/g)	X_c (%)
Pure PLA	59.5	113.1	146.8	16.8	17.9
PLA/MMT	48.2	98.3	137.8	33.3	35.5
PLA/DINCH	57.0	107.7	144.1	31.3	33.4
PLA/TBC/MMT	26.8	82.5	128.7	26.4	28.2
PLA/TBC	44.6	94.9	136.3	31.6	33.7
PLA/DINCH/MMT	36.2	82.7	129.4	29.7	31.7

From Fig. 3a it is apparent that the poly (lactic acid) cold crystallization peak is small; when adding MMT into poly (lactic acid), the cold crystallization temperature moves to a lower temperature and there is a strong cold crystallization peak. At the same time, the poly (lactic acid) glass transition temperature (T_g) drops from 59.5 °C to 48.2 °C, crystallization temperature (T_c) from 113.1 °C to 98.3 °C, and melting temperature (T_m) from 146.8 °C to 137.8 °C. These results show that the addition of MMT can promote cold crystallization of poly (lactic acid), increasing melting enthalpy and the crystallinity of poly (lactic acid).

From Fig. 3b it can be seen that, with the addition of plasticizer, the T_g , T_c , and T_m of poly (lactic acid) are all moving to a lower temperature; the plasticizer not only can improve the moving ability of poly (lactic acid) molecular chains (which causes T_g reduction) but also promote crystallization, and the influence of TBC on poly (lactic acid) composite is more apparent. Figure 3c shows the influence of TBC on T_g is greater than that of DINCH with the addition of MMT. However, there is little difference between them in terms of T_c and T_m .

According to the analysis of different composition of poly (lactic acid) composite, it can be concluded that the MMT, TBC, and DINCH can all increase the crystallinity and affect the thermal properties of poly (lactic acid) although their function mechanisms are different. The addition of MMT is to speed up the crystallization of poly (lactic acid) through the heterogeneous nucleation effect and improve the function of poly (lactic acid) crystallinity, while the main function of TBC is to improve the motility of poly (lactic acid) molecular chains by substantially reducing its T_g so that the crystallization rate and the crystalline of poly (lactic acid) increase. The function of DINCH is two-fold, which not only manifests the heterogeneous nucleation effect but also improves the moving

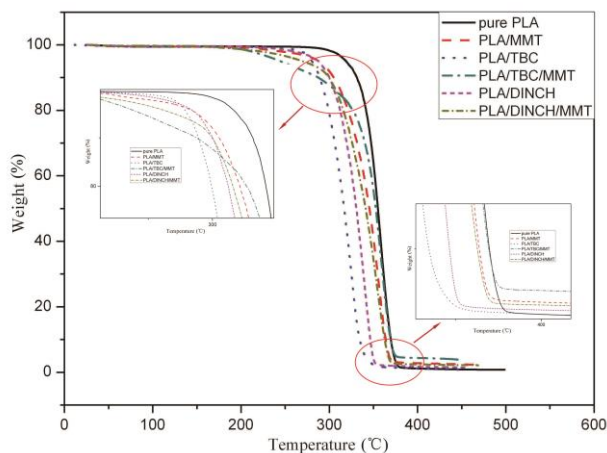
ability of polymolecular chains. In addition, the T_g of poly (lactic acid) is reduced in each case after the addition of MMT, TBC, or DINCH.

Thermogravimetric Analysis

The thermal decomposition parameters were studied for different composite materials through thermogravimetric analysis (TGA). Typical TGA thermograms of samples at a heating rate of 10 K/min and their corresponding derivative curves are shown in Fig. 4.

From Fig. 4 it can be seen that after adding MMT to PLA, the decomposition temperature of the modified PLA composites moved towards a lower temperature. This indicates that the thermal stability of poly (lactic acid) composite material decreased after adding the MMT. The TGA curves of PLA composites moved to the far left when DINCH or TBC was added. With the increase of temperature, the PLA/TBC composite was the first to reach the highest decomposition speed, and its T_{peak} was the lowest. Compared to the pure PLA, with the addition of DINCH or TBC, the thermal stability of PLA composites decreased. The reason could be that the organic modifiers decompose at relatively low temperatures and the decomposition products of the organic modifiers can catalyze the degradation of the PLA polymer matrix originating an earlier degradation. Thus, the thermal stability of the PLA composites in this work depended significantly on the thermal stability of the organic modifiers.

Figure 4c shows that the peak temperatures of PLA/MMT, PLA/TBC/MMT, and PLA/DINCH/MMT composites were almost the same, and the T_{peak} of PLA/TBC/MMT was a little higher than the other two samples. Therefore, the addition of montmorillonite can improve the thermal stability of PLA/TBC and PLA/DINCH, because the incorporation of nanoclays into a polymeric matrix can improve its thermal stability. This improvement is due to the dispersed silicate layers that hinder the diffusion of volatile decomposition products out of the materials, delaying the release of thermal degradation products in comparison to the pure PLA polymer. However, to achieve this improvement, an efficient dispersion of the clay layers into the polymeric matrix is needed.



a

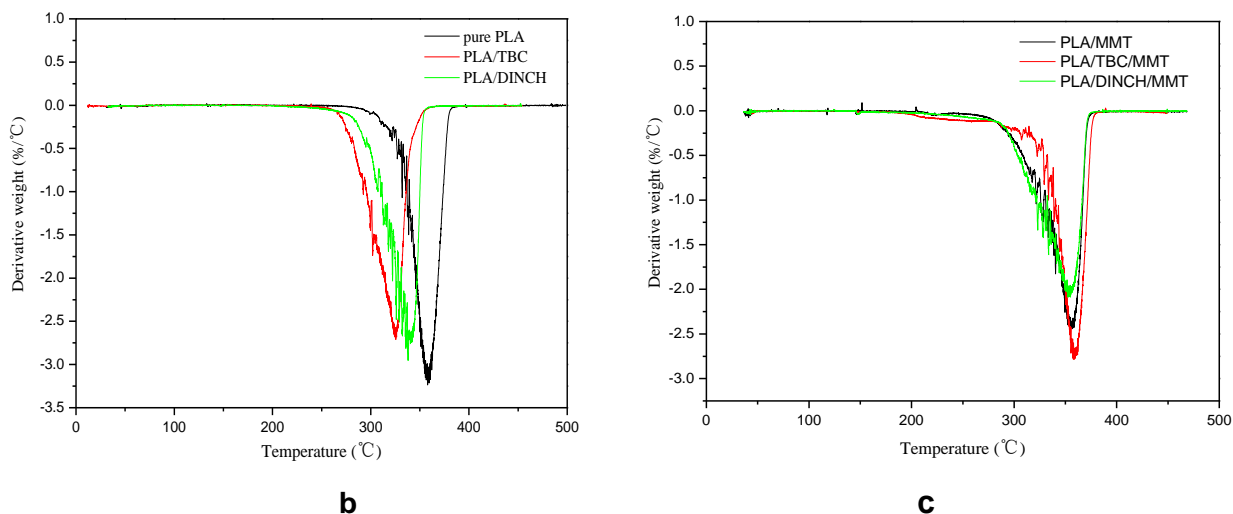


Fig. 4. TGA curves of PLA composites at a heating rate of 10 K/min. (a) TGA curves, (b) DTG curves of pure PLA, PLA/TBC, and PLA/DINCH, and (c) DTG curves of PLA/MMT, PLA/TBC/MMT, and PLA/DINCH/MMT

Kinetic Analysis

The activation energy of decomposition (E), reaction order (n), and pre-exponential factor (A) provide some important information for studying the kinetic mechanism. These kinetic parameters are determined based on the TGA analysis by using the Freeman-Carroll method or the Flynn-Walle-Ozawa method (Hu and Shi 2001). Generally, the polymeric materials' thermal decomposition process is a complex phenomenon that involves several mechanisms, so it is very difficult to define the degradation mechanism for a particular system. The TGA procedure of pure PLA was performed at a heating rate of 10, 15, 20, and 30 K/min, as shown in Fig. 5.

(1) Freeman-Carroll method (Hu and Shi 2001)

The Freeman-Carroll method was used in analyzing the data obtained from the TG curve, which was tested on one heating rate per sample. The thermal decomposition kinetics mechanism function is $f(\alpha) = (1 - \alpha)^n$; therefore, the conversion function can be expressed as:

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

where α is conversion, E is the activation energy of decomposition, A is the pre-exponential factor, R is the universal gas constant ($R=8.314 \text{ J}/(\text{K}\cdot\text{mol})$), β is the heating rate, and T is the absolute temperature. Thus the kinetic parameters can be determined from Eq. 2. Figure 6 shows the Freeman-Carroll curve of pure PLA. The activation energy of decomposition (E) and pre-exponential factor (A) obtained by Freeman-Carroll method for different composites are shown in Table 2. From Table 2, it can be seen that the activation energy of decomposition (E) and reaction order (n) of different PLA composites were almost same. This means that the addition of DINCH, TBC, and MMT did not affect the mechanism of degradation of PLA. Therefore, the differences could not be detected by kinetic analysis.

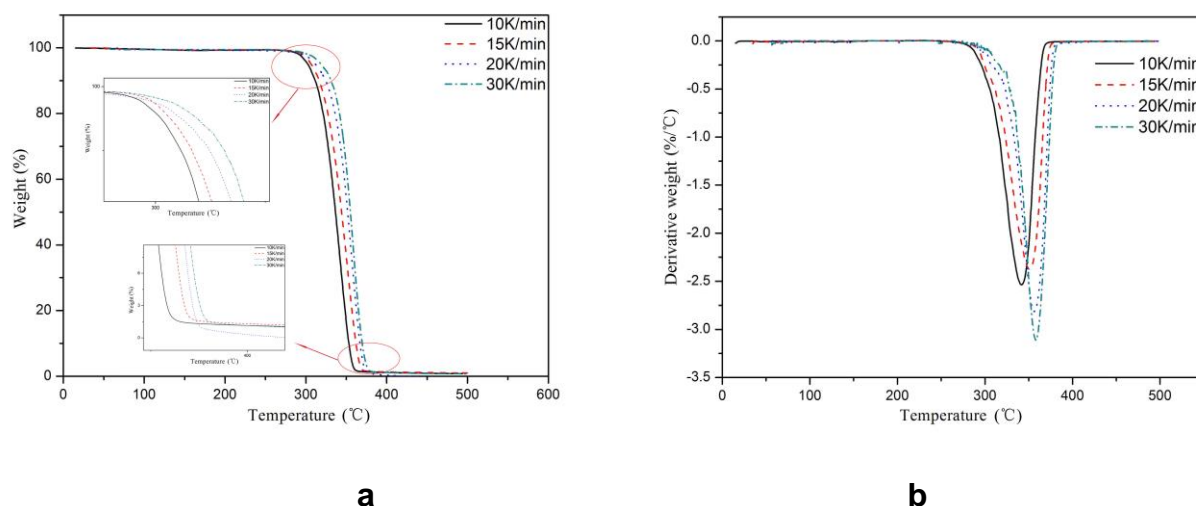


Fig. 5. TGA curves of pure PLA under different heating rates. (a) TG and (b) DTG

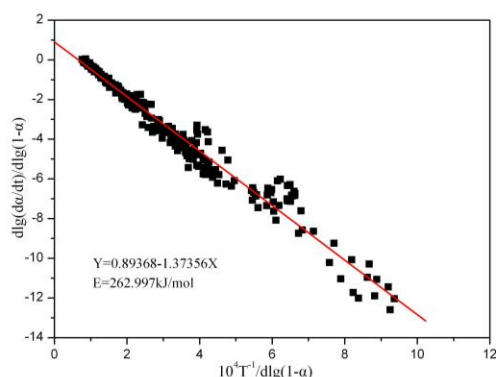


Fig. 6. Data analysis of TGA curves of pure PLA based on the Freeman-Carroll method

Table 2. Kinetics Parameters of PLA Composites by Freeman-Carroll Method

Sample	B (K/min)	E (kJ/mol)	reaction order (n)	lnA(s ⁻¹)
pure PLA	10	184.2	0.871	36.9
	15	188.6	0.872	37.6
	20	236.5	0.885	47.5
	30	263.0	0.894	52.3
PLA/MMT	10	176.7	0.843	30.1
PLA/TBC	10	190.3	0.872	40.7
PLA/TBC/MMT	10	178.2	0.859	36.2
PLA/DINCH	10	188.7	0.873	39.8
PLA/DINCH/MMT	10	180.2	0.863	36.8

(2) *Flynn-Walle-Ozawa method (Hu and Shi 2001)*

The Flynn-Walle-Ozawa method was used in analyzing the data obtained from four TG curves, which were based on tests at different heating rates of the samples. In this method the activation energy of decomposition (E) and pre-exponential factor (A) can be determined by applying Doyle's approximation for the integration and can be expressed as:

$$\lg \beta = \lg\left(\frac{AE}{RG(\alpha)}\right) - 2.315 - 0.4567 \frac{E}{RT_p} \quad (3)$$

In Eq. 3, T_p is the peak temperature on the DTG curve. The activation energy of decomposition (E) can be determined from the Eq. 3. From Fig. 5 one can get the T_p values of 342.4, 351.0, 356.3, and 357.4 °C at the corresponding heating rates of 10, 15, 20, and 30 K/min. Figure 7 shows the Flynn-Walle-Ozawa curve of pure PLA. So one can obtain the value of activation energy of decomposition (E) of pure poly (lactic acid) as 189.79 kJ/mol. The result also tells us that the activation energy of decomposition (E) calculated by the Flynn-Walle-Ozawa method are approximately the same as the result of 188.56 kJ/mol, which was calculated by the Freeman-Carroll method at a heating rate of 15 K/min. Also, the pre-exponential factor (A) can be determined as $\ln A = 35.61$.

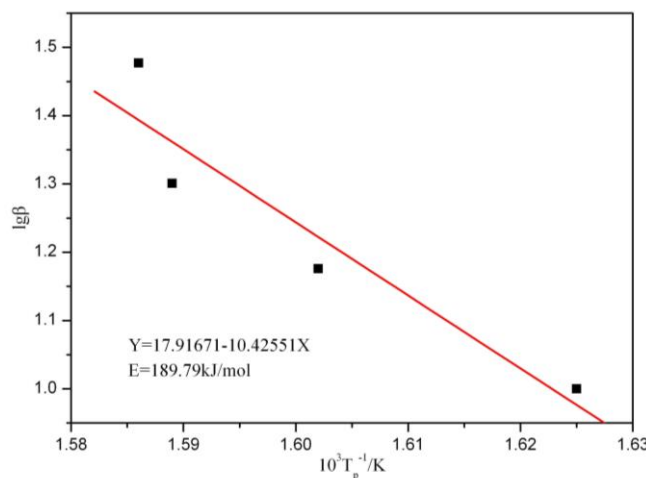


Fig. 7. Curve of $\lg\beta$ vs T_p^{-1} for pure PLA by Flynn-Walle-Ozawa method

CONCLUSIONS

1. According to the morphology analysis results, the agglomeration degree of MMT in the PLA composites increases with the rising of MMT content.
2. The addition of Hexamoll® DINCH, TBC, and MMT can efficiently decrease the T_g of PLA and improve the crystallinity of PLA polymer.
3. Compared to the pure PLA, with the addition of DINCH or TBC, the thermal stability of the PLA composites decreases. The thermal stability of the PLA composites in this work depends significantly on the thermal stability of the organic modifiers.
4. The addition of montmorillonite can improve the thermal stability of PLA/TBC and PLA/DINCH because the incorporation of nanoclays into a polymeric matrix can improve its thermal stability.
5. According to the Freeman-Carroll method, the activation energy of decomposition (E) and reaction order (n) of different PLA composites are almost same. This means that the addition of DINCH, TBC, and MMT does not affect the mechanism of degradation of PLA, and therefore the differences cannot be detected by kinetic analysis.

6. The kinetic parameters, including activation energy of decomposition (E), reaction order (n), and pre-exponential factor ($\ln A$) of PLA/DINCH/MMT composites are 180.2 kJ/mol, 0.863, and 36.8 respectively by using Freeman-Carroll method.

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