Research Article

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Nonisothermal Cold Crystallization Kinetics of Poly(lactic acid)/Bacterial Poly(hydroxyoctanoate) (PHO)/Talc

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Abstract: The effects of bacterial poly(hydroxyoctanoate) (PHO) and talc on the nonisothermal cold crystallization behaviours of poly(lactic acid) (PLA) were analysed with differential scanning calorimetry (DSC), and the thermal stability of the samples was observed with thermal gravimetric analysis (TGA). The modified Avrami’s model was used to describe the nonisothermal cold crystallization kinetics of neat PLA and its blends. The activation energies E for nonisothermal cold crystallization were calculated by the isoconversional method of Kissinger-Akahira-Sunose (KAS). The DSC results showed that the PLA/PHO blends were immiscible in the whole studied range, and as the PHO and talc content increased, the crystallization rate of PLA accelerated, and the crystallinity of PLA in the PLA samples increased. The values of the Avrami exponent indicated that the nonisothermal cold crystallization of the neat PLA and its blends exhibited heterogeneous, three-dimensional spherulitic growth. The E values were strongly dependent on PHO and talc. The TGA results showed that the presence of PHO and talc slightly influenced the thermal stability of PLA.

Keywords: PLA, PHO, talc, DSC, TGA, isoconversional method of Kissinger-Akahira-Sunose (KAS), modified Avrami, Activation Energy

1 Introduction

All aspects of human life have been influenced by petrochemical-derived plastic products. However, these plastics are nondegradable and have a high carbon footprint, thereby imposing environmental issues. Therefore, because of their biodegradability, relatively small carbon footprint, and easy processability, bioplastics have gained considerable attention as industrial products. Poly(lactic acid) (PLA) has been considered an outstanding candidate among all bioplastics, which will serve as a replacement for conventional polymers.

PLA is a linear aliphatic polyester that results from renewable resources, such as sugar cane and maize [1]. PLA is a semicrystalline polymer with a glass transition temperature (T_g) of approximately 60°C and a melting temperature of approximately 170°C [2]. PLA is now one of the most natural biodegradable polymers because it has many advantages, including biodegradation, easy processing, high mechanical capabilities, gas permeability and transparency [3]. These advantages make PLA applicable not only in tissue engineering, medical, pharmaceutical and drug transportation systems but also in agricultural and food packaging applications [4].

Regrettably, because of its high T_g, the implementation of PLA is restricted in its amorphous shape, whereas only the crystalline structure can provide helpful mechanical characteristics at temperatures above the T_g. The slow crystallization rate of PLA is also attributed to poor processability, such as complicated remoulding [2]. Therefore, to expand the applicability of PLA, focus should be placed on the crystallization improvement of PLA.

In general, two strategies are regarded for promoting PLA crystallization. One strategy involves mixing PLA with traditional synthetic polymers or with other biodegradable polymers. At present, PLA has been mixed with many kinds of polymers with very distinct features, biodegradable or...
nonbiodegradable, amorphous or semicrystalline, such as poly(ethylene glycol) (PEG) [2], poly(ethylene-co-vinyl acetate) (EVA) [1, 5], poly(hydroxy ester ether) (PHEE) [6], starch [7], poly(vinyl alcohol) (PVA) [8], poly(butylene terephthalate) (PBT) [9], poly(β-hydroxybutyrate) (PHB) [10] and chemically modified polyhydroxyoctanoate (mPHO) [11]. Poly(3-hydroxyalkanoates) (PHAs) are microbially derived and renewable biodegradable polymers [12]. PHAs are classified into two groups: short chain length (SCL) of 3–5 carbon atoms and medium chain length (MCL) of 6–14 carbon atoms. Hybrid structures, combining SCL and MCL moieties in the polymer, are also reported [12]. MCL PHA, such as poly(3-hydroxyoctanoate) (PHO), has a low melting temperature (43.3 to 66.5 ± 0.2°C) [13], crystallinity (37.5%) [14] and glass transition temperature (-1.0 ± 0.2°C) [13], and exhibits elastomeric properties [12], [15] and a contact angle of 77.3° [13]. A large number of researchers have mixed PLA with an elastomer or another polymer to improve the flexibility, elasticity, and ductility. However, a few papers on PLA/elastomer blends have studied the crystallization kinetics. Considering these points, PHO was chosen as the favoured candidate for the present work.

Another strategy able to improve the properties of PLA includes adding a nucleation agent to enhance crystallization on the surface of additive particles by thick heterogeneous nucleation. Several effective nucleating agents have been examined in the literature, including modified carbon black composite [16], clay nanocomposites [17], silica nanoparticles (SiO2) [18], graphene oxide [19], CaCO3 [3, 20, 21], TiO2 [21], BaSO4 [21], dilithium hexahydrophthalate [22] and ethylenebishydroxyesteramide (EBH) [23]. Talc, in practice, acts as an efficient nucleation agent according to the literature review [2, 3, 31, 10, 24–30].

This work aimed to prepare and characterize blends of PLA with PHO and talc. Since most handling strategies actually occur under nonisothermal conditions, the consideration of crystallization kinetics could be a key to understanding the connection between processing and properties; hence, the nonisothermal cold crystallization behaviour and kinetics of PLA blends were investigated using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The experimental data were analysed based on the modified Avrami’s method. Kissinger-Akahira-Sunose (KAS) was used as an isoconversion method to evaluate the activation energies of the processes.

## 2 Experimental Methods

### 2.1 Materials and Sample Preparation

The PLA, consisting of 98% L-lactic acid and 2% D-lactic acid, was given by Prof. Dr. Haenggi, Biomer Company (Krailling, Germany) with a commercial grade known as Biomer L9000, an average molecular weight (Mw) of 200 kDa and a polydispersity index of 1.98. The PLA was received in the form of white pellets and was used without further drying. PHO containing ~96 mol% of 3-hydroxyoctanoate, ~2.8 mol% of 3-hydroxyhexanoate, and 0.9 mol%, 3-hydroxydecanoate was produced from Pseudomonas putida GPoil under nitrogen-limited conditions. Bacterial cells were grown on a fed-batch fermentation system using sodium octanoate, octanoic acid and ammonium solution as sources for carbon and nitrogen as described by Elbahloul and Steinbüchel [32]. PHO was extracted by acetone and precipitated using a mixture of methanol and ethanol (70%, v/v). The material was purified through repeatedly dissolution-precipitation cycles, then shaped into long thin strips and allowed to dry at room temperature for further investigations. Chloroform with 99.9% purity was provided from Sigma Aldrich, Germany. The casting film technique was used to prepare mixtures of PLA with different contents of PHO and talc. For each transparent sheet, approximately 2.0 g of the total sample was mixed and dissolved in 50 ml of chloroform by stirring at 40°C for 45 min to guarantee full component dissolution. Afterwards, the solution was kept at room temperature for 120 min and then cast onto a glass Petri dish at room temperature until films were formed homogeneously by slowly evaporating the solvent. The details of the blends are listed in Table 1.

### 2.2 Differential Scanning Calorimetry (DSC)

To study the thermal behaviour of the PLA formulations, a DSC-Q2000 (TA instruments) was used. A pure indium standard was used to calibrate the temperature and energy scale. The sample weight varied between 6.0 and 8.0 mg. All the runs were carried out in a nitrogen atmosphere. To study the miscibility, the samples were first heated from -90°C to 200°C to eliminate their thermal history and increase thermal contact at a heating rate of 20°C/min; then, the samples were cooled to -90°C at a rate of 20°C/min and then reheated to 200°C at a rate of 20°C/min (2nd heating rate). The glass transition temperature (Tg) was taken from the 2nd heating run as the midpoint of the
specific heat capacity. For nonisothermal crystallization from the glass to record cold crystallization, the samples were first melted at 200°C for 1 min to remove the thermal history and then cooled to 0°C at a rate of 60°C/min to ensure that the samples reached the amorphous state. Consequently, heating scans at rates of 1, 2, 3, 4, 5, and 7°C/min were performed in the temperature range from 0 to 200°C. The cold crystallization temperature ($T_{cc}$) and its enthalpy ($\Delta H_{cc}$) were determined from the exothermal processes in the DSC scans at all heating runs. The degree of crystallinity ($X_{cc}$%) of the samples was calculated with the following equation:

$$X_{cc} \% = 100 \times \frac{\Delta H_{cc}}{w. \Delta H_m}$$

where $w$ is the mass fraction of PLA and $\Delta H_m$ is the enthalpy of fusion of 100% crystalline PLA, which has a value of 93.6 J/g [33].

The kinetic analysis in this study was conducted using advanced thermokinetics software from Advanced Kinetics and Technology Solutions, Switzerland (AKTS-Thermokinetics ver. 4.02) [34]. Calculations with the AKTS software increase the accuracy of the estimated kinetic parameters because the software simultaneously optimizes the baseline of the data curves. The software applies the isoconversional method for kinetic analysis.

### 2.3 Thermal Gravimetric Analysis (TGA)

TGA measurements were performed using a TA Instruments SDT-Q600. The sample mass of approximately 2–5 mg was ramped from ambient temperature to 700°C in an alumina crucible at a heating rate of 10°C/min. The experiments were carried out in a nitrogen atmosphere with a purge of 20 ml/min to avoid thermoxidative degradation.

Ethical approval: The conducted research is not related to either human or animal use.

### 3 Results and Discussion

#### 3.1 Nonisothermal Cold Crystallization Behaviour of the Samples

Figure 1 shows DSC thermograms for the PLA, PLA/PHO and PLA/PHO/talc samples, which were cooled from 200°C with a cooling rate of 20°C/min and then subjected to second heating at 20°C/min. Figure 1(a) shows that no exothermic crystallization peak was observed for the PLA/PHO and PLA/PHO/talc samples. The outlined results indicated that the PLA samples are completely amorphous with a cooling rate of 20°C/min, and the presence of PHO and talc could not significantly improve the PLA crystallization rate when the PLA melt was cooled at 20°C/min. The glass transition temperatures ($T_g$) and the heat capacities ($\Delta C_p$) were detected from the second heating to investigate the miscibility of PHO with PLA in the presence and absence of talc. The DSC curves in Figure 1 show that all of the blends have two glass transitions, one for PHO at approximately -40°C and the other for PLA at approximately 60°C, suggesting that the blends are not thermodynamically miscible. The reason for this immiscibility, as mentioned before [11], is attributed to a viscosity mismatch between PLA and PHO. The DSC curves for PLA/PHO/talc have two glass transition temperatures, where their values are close to that of pure components of blends, emphasizing the immiscibility of the blend. Moreover, their heat capacities are lower than those of pure components and/or PLA/PHO (70:30). A similar trend has been reported in the literature [2, 3, 10, 21–26]. Moreover, during the subsequent heating DSC scanning, each PLA sample exhibits a strong exothermic peak in the DSC thermogram obtained for subsequent heating at 20°C/min. These exothermic peaks in the amorphous solid state are ascribed to the cold crystallization of PLA. The crystallization peaks of PLA/PHO blends are close to those of neat PLA, indicating the immiscibility of PLA/PHO blends in the whole studied composition. However, after the addition of talc into the PLA/PHO blend, sharp crystallization peaks appear and their maximum temperature values are lower than those of neat PLA. The crystallization peaks of PLA/PHO/talc samples with talc contents of 1, 3, and 5 mass% were detected at 135, 127, and 131°C, respectively. These results suggest that talc acts as an efficient nucleating agent for PLA in PLA/PHO

### Table 1: PLA and its blends.

| Sample name | PLA: PHO: talc |
|-------------|----------------|
| PLA         | 100:0:0        |
| PLA90/PHO10 | 90:10:0        |
| PLA70/PHO30 | 70:30:0        |
| PLA70/PHO29/talc1 | 70:29:1 |
| PLA70/PHO27/talc3 | 70:27:3 |
| PLA70/PHO25/talc5 | 70:25:5 |
Nonisothermal Cold Crystallization Kinetics of Poly(lactic acid)/Bacterial Poly(hydroxyoctanoate) (PHO)/Talc blends. The degree of crystallinity of the PLA, PLA/PHO and PLA/PHO/talc samples was calculated according to Eq. (1). Moreover, the degree of crystallinity was 4% for neat PLA, 9% for PLA/PHO (70:30) and 29% for PLA/PHO/talc (70:27:3). The obtained results indicate that talc and PHO enhance the crystallization process of PLA. Neat PLA exhibits a broad weak endothermic peak at 166°C, and the temperature of the maximum melting endothermic peak does not change with the addition of PHO. However, with the incorporation of talc, the endothermic peak became sharper and stronger, and the temperature of the maximum melting endothermic peak of PLA in PLA/PHO/talc gradually decreased, indicating that the presence of talc provides efficient nucleation.

Figure 2(a-c) shows typical DSC curves measured for neat PLA and its blends at different heating rates, \( \Phi \). The cold crystallization temperature \( T_{cc} \), cold crystallization enthalpy \( \Delta H_{cc} \) and crystallinity degree \( X_{cc} \) % are listed in Table 2. The results in Table 2 show that the crystallization behaviours of neat PLA and its blends depend on the heating rate, \( \Phi \), and the type and concentration of additives. Generally, \( T_{cc} \) values for all samples shift to higher temperatures as the heating rate increases, and the peak height simultaneously increases. A similar phenomenon has been reported in the literature. The \( T_{cc} \) values for PLA/PHO were slightly higher than the corresponding values of the pure PLA at the same heating rate. The slight shift in cold crystallization temperature upon the incorporation of PHO (approximately 3°C lower). This result may indicate that the blend components separate first before the crystallization process of PLA begins. However, \( T_{cc} \) values shift to lower values than those for neat PLA and PLA/PHO blends with the addition of talc. Note that when the talc loading increases to 5 mass%, the \( T_{cc} \) shifts to a higher value than that of blend PLA/PHO with 3 mass% talc but the \( T_{cc} \) is still lower than that of the neat PLA. These results suggest that 3 mass% talc is an efficient concentration for enhancing the crystallization rate of PLA/PHO blends. Table 2 also clearly shows that the \( \Delta H_{cc} \) values increase as the heating rate increases. Moreover, the PLA/PHO blends have higher value of normalized crystallinity than that of neat PLA. A similar trend was observed by other authors for PLA blends [35–37], and this phenomenon reflects the melting process of crystals with different degrees of perfection. Note that the value of the maximum melting peak did not change significantly (approximately ± 3°C) in response to increasing heating rate or the incorporation of PHO and talc (approximately ± 3°C).
3.2 Nonisothermal Cold Crystallization Kinetics

The relative degree of crystallinity \( \alpha(T) \) as a function of crystallization temperature \( T \) can be formulated as follows [38]:

\[
\alpha(T) = \frac{\int_{T_0}^{T} (dH_{cc} / dT)dT}{\int_{T_0}^{T_{\infty}} (dH_{cc} / dT)dT} \tag{2}
\]

where \( T_0 \) and \( T_{\infty} \) represent the crystallization onset and end temperatures, respectively, and \( dH_{cc} \) is the enthalpy of cold crystallization released during an infinitesimal temperature range \( dT \). The relationship between the relative degree of crystallinity \( \alpha(T) \) and the crystallization temperature \( T \) at different heating rates is shown in Figure 3. The data of \( \alpha(T) \) can be converted into \( \alpha(t) \) by using the following relationship:

\[
t = (T_0 - T) / \Phi \tag{3}
\]

where \( T \) is the temperature at crystallization time \( t \). Figure 3 illustrates the change in \( \alpha(t) \) with respect to time at different heating rates for all samples. At any heating rate, \( \alpha(t) \) increases exponentially as time elapses and finally levels off. The time required to finish the crystallization decreased as the heating rate increased. It was more direct to compare the time needed to reach 50% of the final crystallinity (i.e., the half-time crystallization \( t_{1/2} \) of the samples) when referring to the nonisothermal cold crystallization rate. The values of \( t_{1/2} \) for the samples are listed in Table 3 at various heating rates. Generally, the \( t_{1/2} \) values of the PLA samples decreased with increasing heating rate, indicating that the nonisothermal crystallization rate of PLA in the PLA samples was enhanced at higher heating rates. Moreover, at the same heating rate, neat PLA presented a larger \( t_{1/2} \) value than its blends. Additionally, with the incorporation of PHO and/or talc, the \( t_{1/2} \) value decreased. As mentioned in the literature [3, 30, 31], increasing the talc loading can provide nucleating sites for PLA and significantly reduce the activation energy of nucleation, resulting in a rapid crystallization rate. Moreover, the decrease in the \( t_{1/2} \) value upon the addition of PHO resulted from a decrease in the viscosity of PLA in PLA/PHO, as mentioned in the literature [11].
The modified Avrami model [39] was reported in the literature [1, 2, 10, 16-18, 22, 40] to describe the nonisothermal crystallization kinetics of PLA samples. In this model, the relative degree of crystallinity $\alpha(t)$ is correlated to the crystallization time $t$ as follows:

$$\alpha(t) = 1 - \exp(kt^n) \quad \text{OR} \quad \ln[-\ln(1-\alpha(t))] = \ln k_c - n \ln t$$

Jeziorny [41] indicated that the $k_c$ values should be effectively corrected with the heating rate ($\Phi$) as follows:

$$\ln(k_c) = \ln(k_{c}) - \Phi$$

This correction is needed because the calculated values of the nonisothermal crystallization rate constant ($k_c$) and the Avrami exponent ($n$) do not have the same physical meanings as they do in isothermal crystallization because the temperature changes immediately in nonisothermal crystallization [2]. Plots of $\ln[-\ln(1-\alpha(t))]$ versus $\ln t$ are shown in Figure 4. The nonisothermal crystallization rate constant ($k_c$) and Avrami exponent ($n$) are shown in Table 3. The Avrami exponent, $n$, generally ranges from 1-4, for which the smaller values (1-2) are associated with two-dimensional growth with rapid and irregular nucleation and the larger values (3-4) are associated with three-dimensional spherulite growth with only irregular nucleation or a combination of regular and irregular nucleation [29]. From the obtained results, the $n$ values decrease with increasing heating rate but are not affected by the addition of PHO or talc; herein, the $n$ values fall in the range of 3.7-2.4. This finding means that the neat PLA and its samples exhibit heterogeneous, three-dimensional spherulitic growth. Similar results have also been reported by Li et al. [2] and Saad et al. [35]. The values of $k_c$ increased with increasing heating rate, and the $k_c$ values were smaller for pure PLA than for the rest of the samples. These values increase with increases in the PHO and talc content; however, the $k_c$ values of the PLA/PHO/talc samples were not significantly different from those of the PLA/PHO samples. This phenomenon may occur because the addition of PHO into PLA enhances the transportation ability of polymer chains and makes the molecular chains more flexible [42]. Talc, on the other hand, decreases the transport capacity of polymer chains and avoids the rearrangement of PLA molecular segments [3, 16, 23, 24] so that both PHO and talc enhance the rate of crystallization with a different role.

### Table 2: Characteristic data of nonisothermal cold crystallization for neat PLA and its samples.

| Name of PLA Sample | $\Phi$ (°C/min) | $T_c$ (°C) | $T_{cc}$ (°C) | $\Delta H_{cc}$ (J/g) | $X_{cc}$ (%) |
|--------------------|----------------|-----------|--------------|----------------------|--------------|
| **PLA: PHO**       |                |           |              |                      |              |
| 100:0              | 1              | 57        | 91           | 27.11                | 29           |
|                    | 2              | 57        | 96           | 27.75                | 30           |
|                    | 3              | 57        | 100          | 28.93                | 31           |
|                    | 4              | 57        | 106          | 32.04                | 34           |
|                    | 5              | 57        | 110          | 33.99                | 36           |
|                    | 7              | 57        | 116          | 34.62                | 37           |
| 90:10              | 1              | 57        | 95           | 29.75                | 35           |
|                    | 2              | 57        | 101          | 31.15                | 37           |
|                    | 3              | 58        | 105          | 32.40                | 38           |
|                    | 4              | 58        | 109          | 37.27                | 44           |
|                    | 5              | 59        | 112          | 38.79                | 46           |
|                    | 7              | 58        | 119          | 41.77                | 50           |
| 70:30              | 1              | 57        | 91           | 23.37                | 36           |
|                    | 2              | 58        | 98           | 24.70                | 38           |
|                    | 3              | 58        | 103          | 26.88                | 41           |
|                    | 4              | 57        | 107          | 28.09                | 43           |
|                    | 5              | 57        | 110          | 29.79                | 45           |
|                    | 7              | 56        | 117          | 32.38                | 49           |
| **PLA: PHO: talc** |                |           |              |                      |              |
| 70:29:1            | 1              | 55        | 90           | 26.31                | 40           |
|                    | 2              | 54        | 96           | 28.02                | 43           |
|                    | 3              | 54        | 99           | 29.41                | 45           |
|                    | 4              | 54        | 101          | 30.52                | 47           |
|                    | 5              | 54        | 103          | 31.94                | 49           |
|                    | 7              | 54        | 107          | 32.93                | 50           |
| 70:27:3            | 1              | 56        | 86           | 21.23                | 32           |
|                    | 2              | 56        | 92           | 22.31                | 34           |
|                    | 3              | 56        | 95           | 23.64                | 36           |
|                    | 4              | 56        | 98           | 24.90                | 38           |
|                    | 5              | 56        | 100          | 27.25                | 42           |
|                    | 7              | 57        | 105          | 27.89                | 43           |
| 70:25:5            | 1              | 57        | 87           | 21.83                | 33           |
|                    | 2              | 57        | 94           | 23.03                | 35           |
|                    | 3              | 57        | 99           | 23.69                | 36           |
|                    | 4              | 57        | 103          | 24.05                | 37           |
|                    | 5              | 57        | 106          | 26.22                | 40           |
|                    | 7              | 57        | 111          | 27.71                | 42           |

### 3.3 Activation Energy of Crystallization

The most commonly used method for calculating the activation energy of nonisothermal crystallization is the KAS method. This model implies that during the process of transformation, the activation energy, $E$, should differ during the transformation. The Kissinger approach has been used in several recent studies [1, 10, 17, 35, 40].
The kinetic model equation combined with the Arrhenius method to the temperature function of the reaction rate constant can usually be defined as follows [43, 44]:

\[
\frac{da}{dt} = A \exp\left(-\frac{E}{RT}\right)f(\alpha),
\]

where \( t \) is the time, \( T \) is the temperature, \( \alpha \) is the relative degree of crystallinity, \( A \) (s\(^{-1}\)) is the pre-exponential (frequency) factor, \( E \) (kJ mol\(^{-1}\)) is the activation energy, \( R \) is the universal gas constant, and \( f(\alpha) \) is the reaction model.

**Eq. (6)** may be rewritten under nonisothermal conditions with a constant heating rate of \( \Phi = dT/dt \) as follows:

\[
\frac{da}{dT} = \frac{1}{\Phi} \frac{da}{dt} = \frac{A}{\Phi} \exp\left(-\frac{E}{RT}\right)f(\alpha),
\]

**Figure 3:** \( \alpha(T) \) and \( \alpha(t) \) as a function of temperature and time, respectively, at different heating rates and compositions.
It is possible to obtain results using the KAS method [45–47] from Eq. (7). Logarithm application and rearrangement yields the following expression:

\[
\ln \left( \frac{\Phi_i}{I_{\alpha_i}} \right) = C_x(\alpha) - \frac{E_a}{RT_{\alpha_i}},
\]

where \( C_x(\alpha) = \int \frac{df(\alpha)}{da} \frac{AR}{E_a} \).

A corresponding \( T_{\alpha_i} \) and heating rate \( \Phi_i \) are used to plot \( \ln \left( \frac{\Phi_i}{I_{\alpha_i}} \right) \) against \( 1/T_{\alpha_i} \) for each relative degree of crystallinity, \( \alpha \). Then, \( E_a \) is determined from the regression slope. The precision and variants of the KAS method were evaluated in the literature [48].

The analysis of the activation energy for crystallization, \( E_a(T) \), starts by applying the isoconversional methods stated in Eq. (8) for all heating rates applied to the overall data of crystallization to obtain the dependence of \( E_a(T) \) on \( \alpha \). By replacing \( \alpha \) with the respective temperature, the dependence of \( E_a \) on the temperature can be determined [44]. Figure 5 shows the dependence of \( E_a \) on the relative degree of crystallinity, \( \alpha \). The resulting \( T \) versus \( a \) dependence is also shown in Figure 5. Figure 5(a) shows that the activation energy of crystallization, \( E_a \), changes significantly with respect to \( \alpha \). The results show that the activation energy for all PLA samples are positive and continuously decrease with increasing \( \alpha \). A similar trend has been reported for PLA blends and composites. The values of \( E \) are also affected by the ratio of the additive. The PLA/PHO/talc always exhibits higher \( E_a \) values than the neat PLA and other PLA samples. A similar trend has been reported for PLA with an efficient nucleating agent, such as talc [2], SiO\(_2\) [18] and dilithium hexahydrophthalate [22].

For the immiscible blend PLA/PHO, the incorporation of PHO has a slight influence on the \( E_a \) of PLA, as shown in Table 4. Figure 5(b) shows the change in crystallization temperature with respect to \( \alpha(T) \), wherein, as expected, the crystallization temperatures shift to higher values as the degree of crystallinity increases. As discussed in the previous section, PHO incorporation slightly shifts the crystallization temperature to a higher value than that of neat PLA, whereas the incorporation of talc leads to a significant shift in the crystallization temperature to a lower value than that of PLA/PHO. The crystallization temperature is also affected by the presence of PHO and talc in the samples. The dependence of \( E_a(T) \) on the crystallization temperature, as estimated from Eq. (8), is presented in Figure 6. Generally, the values of \( E_a \) are positive and decrease with increasing temperature, indicating that the crystallization rate increases as the temperature increases. Figure 6 shows that the effective activation energy exhibited higher positive values at lower temperatures, which is consistent with the results of a previous report. The addition of talc to PLA/PHO encouraged the formation of more nuclei at lower crystallization temperatures, as shown in Figure 6 and Table 4.
3.4 Thermal gravimetric analysis

Thermal degradation is an essential concern when processing PLA. TGA provides thermogravimetry (TG) and derivative thermogravimetry (DTG) curves. The thermal degradation of neat PLA, PLA/PHO and PLA/PHO/talc, where the weight loss due to the volatilization of the degradation products was monitored as a function of temperature, is shown in Figure 7. The onset (at 10% weight loss) \(T_i\), maximum \(T_d\) and end of degradation \(T_f\) temperatures are evaluated and tabulated in Table 5. Figure 7 shows that neat PHO exhibits a single stage of degradation, and the products of PHO degradation have been reported to be a mixture of trans-2-octenoic and trans-2-hexenoic acids [12]. The \(T_i\), \(T_d\) and \(T_f\) for neat PHO, as shown in Table 5, are 271, 283 and 294°C, respectively. Moreover, it has been reported that neat PLA was also degraded by one step, which is due to the intramolecular transesterification reaction [1] (above 300°C). The onset degradation temperature for PLA is
335°C, and the maximum degradation rate is achieved at 353°C. For PLA/PHO blends, two degradation steps are detected. The first degradation stage is related to PHO degradation, and the second stage located at higher temperatures is attributed to PLA degradation. From Figure 7(b), the DTG results show that PHO has a slight influence on the maximum degradation temperature ($T_d$) of PLA. Similarly, PLA has a slight effect on the maximum degradation temperature ($T_d$) of PHO. These results revealed a lack of chemical interactions and immiscibility between PLA and PHO. Because talc particles began to lose weight at temperatures higher than 800°C [49, 50], the weight loss of PLA/PHO/talc blends between 200 and 400°C was attributed mainly to the degradation of PHO and PLA. It was expected that the thermal degradation temperatures for PLA/PHO in the presence of talc are slightly shifted to lower values. It is well known that the addition of fillers to a polymer matrix causes a decrease in the permeability/diffusivity of oxygen and volatile degradation products, providing polymer composites improved thermal degradation. The results in Figure 7(c,d) show that talc has a slight influence (approximately 3°C) on the thermal stability of the PLA phase in the PLA/PHO blend.

4 Conclusions

In this paper, we examined the nonisothermal cold crystallization behaviours and kinetics and the thermal degradation of neat PLA and PLA samples mixed with PHO and talc. The nonisothermal cold crystallization data were investigated by the modified Avrami’s method, and the activation energies of crystallization were calculated.
Figure 7: TG & DTG thermograms for PLA, PHO and their blends.

Table 5: TGA analysis of PHO, PLA and their blends.

| Sample         | PHO Phase | PLA Phase | PHO Phase | PLA Phase |
|----------------|-----------|-----------|------------|------------|
|                | T \(_i\) (°C) | T \(_d\) (°C) | T \(_f\) (°C) | T \(_i\) (°C) | T \(_d\) (°C) | T \(_f\) (°C) |
| PLA:PHO        |           |           |            |            |            |            |
| 0:100          | 271       | 283       | 294        | --         | --         | --         |
| 100:0          | --        | --        | --         | 335        | 353        | 370        |
| 90:10          | 270       | 283       | 293        | 337        | 356        | 370        |
| 70:30          | 263       | 280       | 285        | 340        | 357        | 370        |
| PLA: PHO: talc |           |           |            |            |            |            |
| 70:29:1        | 262       | 280       | 286        | 340        | 356        | 371        |
| 70:27:3        | 264       | 280       | 285        | 337        | 354        | 366        |
| 70:25:5        | 246       | 271       | 278        | 338        | 353        | 370        |
by the isoconversional method of KAS. The following conclusions can be drawn from the experimental results:

The blends of PLA/PHO were immiscible in the whole studied range. The cold crystallization peak ($T_c$) shifted slightly to a higher temperature with increasing PHO content ($2^\circ$C). However, introducing talc to PLA/PHO decreased the $T_c$ values. The crystallization rate of PLA in samples was enhanced with increasing PHO and talc content in the structure; consequently, the normalized crystallinity of PLA in PLA samples was increased. The values of the Avrami exponent revealed that the nonisothermal cold crystallization of the neat PLA and its blends exhibited heterogeneous, three-dimensional spherulitic growth. The DSC results indicated that a talc content of 3 mass% was an efficient nucleating agent for PLA/PHO. The E values decreased with increasing PHO in the blends, whereas increasing the talc content shifted E to higher values. TGA observations showed that the thermal stability of PLA was slightly influenced by the introduction of PHO and talc.

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