Enhanced crystallization of poly (lactic acid) through reactive aliphatic bisamide

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Abstract. The poor crystallization rate of poly (lactic acid) (PLA) is a major drawback in terms of controlling the properties of final products. To overcome this, a nucleating agent is normally applied. In this work, the aliphatic bisamide, N, N’-(1,3-propylene) bis (10-undecenamide) (PBU), having reactive functional groups is used as a crystallization promoter for PLA by adding PBU in various concentration (0.1-0.7 wt%) into PLA together with peroxide via reactive melt blending. The conventional ethylene bis-stearamide (EBS) is used for a comparison. The extruded samples are characterized for gel content and FT-IR spectroscopy. The crystallization behaviour and rate, and spherulites morphology are investigated by differential scanning calorimetry (DSC) and polarized optical microscopy (POM), respectively. It is found that the addition of PBU into PLA results in the dramatic increase in crystallinity and crystallization rate of PLA compared with neat PLA and PLA added EBS. The crystallinity increases to 24.9-28.3% higher than neat PLA under even cooling rate of 7°C/min. The addition of 0.7 wt% PBU shows the fastest crystallization rate with \( t_{1/2} \) value isothermally crystallized at 130°C of only 6 min. POM images indicate the increase in the nucleation density and very fine spherulites of PLA added PBU, promoting the fast crystallization.

1. Introduction

Many solutions have been established to reduce non-biodegradable plastic waste disposal and the consumption of non-renewable petroleum raw materials in order to cope with sustainability issues for balancing the use of resources and the growth of population. In terms of plastics, using renewable bio-derived raw materials and/or biodegradable plastics can best address the problem. Poly (lactic acid) (PLA) is one of the most fashionable biodegradable polymers which exhibits excellent performance in renewability, biocompatibility, transparency, processability, good mechanical, and barrier properties [1]. Unfortunately, semi-crystalline PLA exhibits very slow crystallization rate from melt, leaving its...
products (especially processed from injection molding) amorphous and hence poor barrier property and thermal resistance, which allow to be used for only some certain applications. To cope with this drawback, there are many methods to increase the crystallinity of PLA such as post-annealing [2], in-mold annealing, imposing shear flow [3], low crosslinking structure [4], or adding nucleation agents (NA). Many kinds of NA, both inorganic and organic nucleating agents, have been reported in the literatures and even in some marketed products. These include tale [5], nano-CaCO₃ [6], modified carbon black [7, 8], carbon nanotubes (CNTs) [9], organically modified layered silicate (OMLS) [10], multi-wall carbon nanotube (MWCNT) [9], zinc citrate complex (ZnCC) [1], bisurea compound [11], cellulose nanofibers [12], hydrazide compounds [13], N,N'-ethylene bis-stearamide (EBS) [14], and N,N'-ethylenebis(-12hydroxystearamide) (EBH) [14]. Among organic NA, aliphatic amides such as EBS and EBH have been extensively used as nucleating agents for PLA to form crystallisable products such as thermo-forming process [14]. Forming the crystalline with one-step processing is easily achievable through melt blending. The addition of bisamide with reactive moiety would in some extent help promoting the crystallization together with possibility of in situ grafting or crosslink to form nuclei in the crystallization process. The influence of reactive aliphatic amides, which has double bonds at chain ends, on the crystallization of the PLA has not yet been reported. Therefore, in this study, the effect of reactive aliphatic amide on crystallization behaviour and rate of PLA and also its spherulites morphology are investigated. The small amount of reactive PBU (0.1, 0.3, 0.5 and 0.7 wt%) is introduced into PLA with peroxide via reactive melt blending, and EBS is selected for a comparison.

2. Experimental

2.1. Materials
PLA resin (3052D grade) was purchased from NatureWork®, Thailand. The N, N'- (1, 3-propylene) bis (10-undecenamide) (PBU) (Tₘ = 118°C, Tₛ = 111°C) was synthesized from 10-undecenoyl chloride and 1, 3-diaminopropane based on the procedure described our previous work. N, N'-ethylene bis-stearamide (EBS) (Tₘ = 144°C, Tₛ = 139°C) was purchased from Sigma-Aldrich Co., Ltd, Thailand. Peroxide (Perkadox® 14-40B-pd) was purchased from AkzoNobel, Thailand.

2.2. Sample preparations
The different weight ratios of PLA blended with reactive PBU or EBS were prepared by using a twin-screw extruder (SHJ-25, China) with the screw speed of 80 rpm and the temperature profile of 100/110/130/160/180/185/190/200°C. Before mixing, PLA resins were dried at 65°C for 10 hr under vacuum. The blend samples were labelled as PLA/rPBUₓ, where r referred to reactive blends with peroxide 0.5 phr and x represented the weight ratio of PBU (0, 0.3, 0.5, 0.7 wt%). For a comparison, pure PLA and also PLA blended with EBS (1.0 wt%) samples were prepared by using the identical procedure, then labelled as neat PLA and PLA/EBS1.0, respectively.

2.3. Measurements
Differential scanning calorimetry (DSC) was carried out on a METTLER TOLEDO, DSC1 STAR instrument under a nitrogen atmosphere. To study the non-isothermal crystallization, the samples were first heated from 30 to 200°C at a rate of 7°C/min and held on for 3 min. the samples were then cooled down to 30°C and reheated to 200°C at rate of 7°C/min to study the melting behaviour of the samples. For the investigation of isothermal crystallization, the samples were initially heated up to 200°C at 10°C/min and kept for 3 min, then rapidly cooled (20°C /min) to 130°C and kept for a predetermined time. Spherulite morphologies of the samples were observed by OLYMPUS U-CMAD3 polarized optical microscopy (POM) equipped with digital camera and METTLER TOLEDO FP82HT hot stage. The samples were placed between two cover glasses and melted at 200°C for 3 min. Then they were quickly cooled to 130°C for isothermal crystallization. After the completion of crystallization, the spherulite morphologies were recorded. Gel content was measured by the weight remaining after dissolving the fine samples in chloroform using the following equation (1):
Gel content (%) = \( \left( \frac{W_g}{W_0} \right) \times 100 \) \hspace{1cm} (1)

where \( W_0 \) is the original weight (dry) of the PLA/rPBUx samples, \( W_g \) is the weight remaining (dry gel component) of the PLA/rPBUx samples after being dissolved in chloroform at 40°C for 16 hr. Fourier transform infrared (FT-IR) spectroscopy was performed at ambient temperature on a Vertex 70, German spectrometer. Before testing, pure PLA, PBU and dry gel component of PLA/rPBU0.7 samples were mixed with potassium bromide (KBr) into flakes for FTIR measurements. To investigate the chemical reaction of PLA and reactive PBU, the FT-IR spectra of the samples were recorded in the wavenumber range of 400 - 4000 cm\(^{-1}\).

### Table 1. Thermal transition data in non-isothermal crystallization at 7°C/min for several samples.

| Samples            | \( T_{cc} \) (°C) | \( \Delta H_{cc} \) (J/g) | \( T_m \) (°C) | \( \Delta H_m \) (J/g) | \( T_c \) (°C) | \( \Delta H_c \) (J/g) | \( X_c \) (%) |
|--------------------|-------------------|--------------------------|----------------|-----------------------|----------------|-----------------------|--------------|
| neat PLA           | 109.6             | 27.09                    | 147.8, 154.1   | 27.19                 | -              | -                     | 0.11         |
| PLA/rPBU0          | 108.7             | 28.80                    | 147.9, 149.3   | 29.00                 | -              | -                     | 0.21         |
| PLA/rPBU0.1        | 109.4             | 25.83                    | 148.3, 154.4   | 26.11                 | -              | -                     | 0.30         |
| PLA/rPBU0.3        | 98.2              | 3.25                     | 148.2, 152.8   | 29.63                 | 105.0          | 26.06                 | 28.3         |
| PLA/rPBU0.5        | 98.8              | 5.18                     | 148.2, 152.7   | 28.39                 | 103.0          | 24.28                 | 24.9         |
| PLA/EBS1.0         | 101               | 4.48                     | 148.9, 152.9   | 29.43                 | 104.3          | 24.28                 | 26.7         |

\( \Delta H_m \) and \%crystallinity \( (X_c) \) are shown in table 1. As seen in figure 1(a), in the cooling scan, no crystallization peak can be observed for neat PLA, PLA blended with only peroxide and even PLA added 0.1 wt% PBU. The cold crystallization peak appears at about 109°C for each sample in following heating scan (figure 1(b)). It indicates that they have low crystallization ability corresponding to their poor crystallinity, where the values are less than 1% as shown in table 1. With the addition of high amount of EBS (1.0 wt%), a small crystallization peak appears at 127.9°C in the cooling curve (figure 1(a)) and the \( X_c \) value increase to 5.34%. EBS can promote the crystallization of PLA due to the fact that the EBS crystallizes well at 118°C in the cooling process as known from its \( T_c \). For the addition of higher amount of reactive PBU (0.3, 0.5 and 0.7 wt%) into PLA with peroxide, a large crystallization peak appears remarkably at approximately at 104°C and their crystallization enthalpy significantly increases, resulting in the higher \( X_c \) values of 24.9-28.3%. In addition, as seen from figure 1(b), the cold crystallization of the PLA/rPBU0.3-0.7 samples almost disappears in the heating scan; it implies that the crystallization of the samples is completed during cooling step, which is very desirable for practical use. From figure 1(b), two melting peaks are observed in the DSC heating scan for all samples. However, with the increase of reactive PBU contents, it shows the broad double peaks. Similar results are observed when adding EBS. This finding has also been reported by other groups [1, 14, 15]. Tang et al. [14] demonstrated that the double peaks of PLA samples corresponded to the mechanism based on melting of the two crystals formed in the cold crystallization stage and recrystallization stage, which is consistent with the mechanism of melt-recrystallization.
3.2. Isothermal melt crystallization behaviors

The effect of reactive PBU compared with EBS on isothermal melts crystallization behaviours of PLA at 130°C are shown in figure 2(a). It is clearly seen that the crystallization rate of neat PLA is extremely slow, also by incorporating only peroxide without reactive PBU (PLA/rPBU0), which cannot crystallize within even 100 min. When 0.1 wt% reactive PBU is added, it shows a broad exothermal peak and PLA can crystallize within 60 min as well as the addition of 1.0 wt% EBS. With an increase of reactive PBU contents from 0.3 to 0.7 wt%, the sharper exothermal peak appears and PLA crystallizes much faster than the addition of 0.1 wt% PBU by 2-3 folds. For the initial crystallization of PLA/rPBU0.7 sample, its crystallization occurs almost immediately at the beginning of the isothermal crystallization at 130°C.

![Figure 1. DSC curves of (a) cooling and (b) second heating scans of various samples (7°C/min).](image1)

![Figure 2. (a) DSC exotherms and (b) Avrami plots of samples isothermally crystallized at 130°C.](image2)

The Avrami equation is the most common method to describe the isothermal crystallization process of polymers, and its logarithmic form can be expressed as equation (2).

\[
\ln[-\ln(1-X_t)] = \ln k + n \ln t
\] (2)

where \(X_t\) is the relative degree of crystallinity as a function of time, \(k\) is the crystallization rate constant, and \(n\) is the Avrami exponent, which is constant depending on the nature of nucleation and the dimension of crystal growth [1]. When \(\ln[-\ln(1-X_t)]\) is plotted against \(\ln t\) as shown in figure 2(b), the parameters \(n\) and \(k\) can be obtained from the slopes and intercepts of fitted lines, respectively. The value of crystallization half-time \((t_{1/2})\) is defined as the time required reaching 50% of the final crystallinity of the sample that can be determined from equation (3). \(n\), \(k\) and \(t_{1/2}\) values are listed in table 2.

\[
t_{1/2} = \left(\frac{\ln 2}{k}\right)^{1/n}
\] (3)

The \(n\) values ranging between 2 and 3 are found. This suggests that two growth mechanisms are present: two-dimensional at the beginning of the crystallization process, with the formation of two-dimensional lamellar shape-like crystals and three-dimensional during further growth with the formation of spherulites [16]. As shown from figure 2(a), it implies that the crystallization time of neat PLA and the addition of peroxide samples are taken more than 100 min while the addition of 0.1 wt%
PBU in reactive blending has crystallization half-time ($t_{1/2}$) 34.53 min. On the basis of the value of $k$ and $t_{1/2}$, the higher $k$ and lower $t_{1/2}$ values is assumed as the higher crystallization rate. It is evident that the crystallization ability of PLA increases following the increase of reactive PBU content 0.3 to 0.7 wt%, results in much lower $t_{1/2}$ values from 10.53 to 6.05 min. As the $t_{1/2}$ value of 6.05 for PLA/rPBU0.7 is about one-fifth of $t_{1/2}$ for PLA/EBS1.0, the reactive PBU is supposed to accelerate the crystallization rate of PLA/EBS blended by five times. It can be concluded that PLA/rPBU0.7 sample is the most effective accelerating the crystallization rate of polymers. Due to the possible presence of fixed-structures in PLA melt, they act as the heterogeneous nuclei so that heterogeneous nucleation and crystal growth is induced and starts more rapidly under supercooled state.

**Table 2.** Kinetic parameters of several samples isothermally crystallized at 130°C.

| Samples         | $n$  | $k$ (min$^{-1}$) | $t_{1/2}$ (min) |
|-----------------|------|-----------------|-----------------|
| PLA/rPBU0.1     | 2.4  | $1.7 \times 10^{-4}$ | 34.53           |
| PLA/rPBU0.3     | 3.0  | $5.9 \times 10^{-4}$ | 10.53           |
| PLA/rPBU0.5     | 3.3  | $3.9 \times 10^{-4}$ | 9.67            |
| PLA/rPBU0.7     | 2.3  | $1.1 \times 10^{-2}$ | 6.05            |
| PLA/EBS1.0      | 2.7  | $5.9 \times 10^{-5}$ | 32.23           |

3.3. Spherulite morphology

The spherulite images of neat PLA and its blends isothermally grown at 130°C are observed under a polarized optical microscope as depicted in figure 3. Normally, the rate of growth in the radial direction is constant until the spherulites meet [17]. However, each spherulite growth of neat PLA cannot meet to form the grain boundary in 10 hr due to the number of the nuclei of neat PLA is quite few and far away from each other, consequently obtaining large spherulites. The different size of the spherulite of neat PLA as shown in figure 3(a) indicates that the nucleation process is not formed at the same time following by an asynchronous crystallization. For the incorporation only peroxide into PLA (PLA/rPBU0), the spherulites are smaller and denser than the neat PLA as showed in figure 3(b), indicating that chains shortened by peroxide would increase its crystallization ability to some extent [4]. For adding small amount of PBU (0.1 wt%), it shows slight increase nuclei more than neat PLA; the spherulites can meet each other easier and then displays smaller crystals than neat PLA. With the further incorporation of PBU (0.3 to 0.7 wt%) as demonstrated in figure 3 (d-f), the spherulites appeared to be very fine throughout the recorded film area. The addition of the higher PBU could lead to higher degree of reactions, forming local crosslinks, which possibly act as nucleation sites to promote the crystallization process. Having a large number of nuclei, the crystallization will proceed very quickly to the limit of the space with small spherulites, thereby enhancing the overall rate of crystallization.

**Figure 3.** POM images of (a) neat PLA, (b) PLA/rPBU0, (c) PLA/rPBU0.1, (d) PLA/rPBU0.3, (e) PLA/rPBU0.5, (f) PLA/rPBU0.7 and (g) PLA/EBS1.0 isothermally crystallized at 130°C
This result is consistent with the DSC results in figure 2(a) and supported by the smaller $t_{1/2}$ values of their blends. Upon addition 1.0%wt of EBS, the spherulite size is also reduced compared with neat PLA but still bigger than the addition of reactive PBU (0.3 to 0.7 wt%). This indicated that PLA/EBS1.0 sample has less nucleated density than the reactive PBU blending samples even though EBS is added higher amounts.

3.4. Gel content and Infrared analysis
To elucidate the mechanism of reactive PBU, the gel contents and FT-IR of residual gels are measured. The gel content of the PLA/rPBU samples containing 0.5 phr of peroxide as a function of PBU content are shown in figure 4. It shows that the low gel content of the reactive blended samples starts at a very low concentration of PBU (0.3 wt%). The gel content increases from 0.5 to 16% (possible low cross-linking structure) with the increase of PBU contents from 0.3 to 0.7 wt%. After that the gel of PLA blended with 0.7 wt% PBU in the presence of peroxide is investigated using FT-IR spectroscopy technique, compared with PLA and PBU samples as shown in figure 5. Considering the gel spectrum, after the chemical reaction with PBU in the presence of peroxide, the peaks at 1757 cm$^{-1}$ and 1184 cm$^{-1}$ which belong to the C=O stretching and C–O–C stretching of PLA, respectively [4], and two new peaks can be observed at 3317 (N–H stretching of PBU) and 1637 cm$^{-1}$ (C=O of amide, PBU). However, the peaks at 3093 (=C–H stretching of PBU) and 917 cm$^{-1}$ (C=CH$^2$ bending of PBU) are disappear, which clearly confirms the chemical reaction between PLA and PBU.

Once the peroxide is added to the PLA/PBU melt blends, peroxide decomposed into the R$_1$O• and •OR$_1$O• radicals [4]. As the concentration of PLA is higher than PBU, then, the R$_1$O• or •OR$_1$O• radicals abstract hydrogen from PLA, which create the radicals at chiral centres in PLA chains [4]. After that, the double bonds in PBU are easily broken to produce radicals and then combine with the PLA radicals, and the chemical fixed-structure between PLA chains could take place as shown in scheme 1.

3.5. Proposed mechanism of reactive-induced crystallization
The reason for the effectiveness of reactive PBU over the EBS as induced crystallization for PLA remains unclear. With the incorporation of PBU, We propose that the nucleation of PLA is initiated by the fixed-structures between PLA chains so that the fixed-structures could have acted as nucleating centres, thereby inducing crystal growth. In addition, this reactive-induced crystallization process can aid the increased number of nuclei, thus leading to faster crystallization. These results were similarly reported by Y. Zhang et al. [4], With the addition of TAIC, the low crosslinking bundles are formed (not complete crosslinking network) and can act as precursor to promote the crystallization. During crystallization, the chains that surround the crosslinking bundles can be absorbed to stack in lamellas to forms spherulite [4]. It could imply that the fixed-structures can play the role as well as the low crosslinking bundles to induce the crystallization of PLA.
The fixed-structure by reactive-inducing

Scheme 1. A possible reaction of free radical reaction between PBU and PLA chains.

4. Conclusion
The local crosslinked structures could be achieved via the reactive melt blending of PLA with reactive bisamide (PBU) (for the small quantity of 0.3 to 0.7 wt%) incorporated with peroxide as an initiator. DSC results suggest that the fixed-structures created by partial local crosslinked structures can well promote and accelerate the crystallization of PLA while using peroxide alone does not affect the crystallization of PLA. With the incorporation of 0.3 to 0.7 wt% of reactive PBU, the crystallinity increases to 24.9-28.3%, which is higher than neat PLA and PLA added EBS almost by 260 and 6 times, respectively. The addition of 0.7 wt% PBU shows the fastest crystallization rate where the $t_{1/2}$ value isothermally crystallized at 130°C is only 6 min while the overall crystallization of neat PLA takes more than 100 min. The POM analysis confirms that a large number of nuclei are effectively involved on inducing the crystallization of PLA added PBU to be faster than PLA added EBS. Furthermore, the spherulites of the PLA/rPBU blends are smaller and denser compared to those of neat PLA and EBS. Thus, it can be summarized that the fixed-structures induced by reactive PBU can effectively induce crystallization of PLA as well.

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