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The effect of end groups of PEG on the crystallization behaviors of binary crystalline polymer blends PEG/PLLA

Wei-Chi Lai[a], Wen-Bin Liau[a,b,*], Tai-Tso Lin[a]

[a]Department of Materials Science and Engineering, National Taiwan University, 1 Roosevelt Rd. Sec.4,Taipei 106, Taiwan, ROC
[b]Institute of Polymer Science and Engineering, National Taiwan University, 1 Roosevelt Rd. Sec.4,Taipei 106, Taiwan, ROC

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Abstract

The effect of end groups (2OH, 1OH, $1CH_3$ and $2CH_3$) of poly(ethylene glycol) (PEG) on the miscibility and crystallization behaviors of binary crystalline blends of PEG/poly(L-lactic acid) (PLLA) were investigated by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). A single glass-transition temperature was observed in the DSC scanning trace of the blend with a weight ratio of 10/90. Besides, the equilibrium melting point of PLLA decreased with the increasing PEG. A negative Flory interaction parameter, χ_{12}, indicated that the PEG/PLLA blends were thermodynamically miscible. The spherulitic growth rate and isothermal crystallization rate of PEG or PLLA were influenced when the other component was added. This could cause by the change of glass transition temperature, T_g and equilibrium melting point, T_m^0. The end groups of PEG influenced the miscibility and crystallization behaviors of PEG/PLLA blends. PLLA blended with PEG whose two end groups were CH_3 exhibited the greatest melting point depression, the most negative Flory interaction parameter, the least fold surface free energy, the lowest isothermal crystallization rate and spherulitic growth rate, which meant better miscibility. On the other hand, PLLA blended with PEG whose two end groups were OH exhibited the least melting point depression, the least negative Flory interaction parameter, the greatest fold surface free energy, the greatest isothermal crystallization rate and spherulitic growth rate.

Keywords: Blends; Miscibility; Crystallization

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1. Introduction

Binary polymer blends can be classified into amorphous/amorphous, crystalline/amorphous, and crystalline/crystalline systems based on the crystallizability of the constituents. Most of them focused on the polymeric mixture containing two amorphous components [1–3]. On the other hand, polymer blends containing two crystalline components are more complicated and interesting since both components are able to crystallize. Furthermore, they may crystallize in different temperature regimes and within different periods of time. Thus, two crystalline polymer blends can provide various conditions to study the crystallization behavior and morphology in polymer blends. Recently, Liau et al. [4,5] and Qiu et al. [6–11] have done some work on the miscibility and crystallization in crystalline/crystalline polymer blends.

Both poly(ethylene glycol) (PEG) and poly(L-lactic acid) (PLLA) are very interesting and important crystalline polymers. PEG is soluble in water and many organic solvents. Meanwhile, PEG shows hydrophilicity and biocompatibility. PLLA is a biodegradable thermoplastic polyester and has attracted increasing attention due to their potential applications as biomedical and environment-friendly materials. In the present study, the binary blends of a biodegradable polymer, PLLA, with a biocompatible polymer, PEG, have been investigated. Younes and Cohn [12] have reported the miscibility and crystallization behavior of PEO/PLLA blends. According to them, melting point depression of PLLA occurred with increasing the PEO component, especially at higher content of PEO ($>80\%$ PEO). Nakafuka et al. [13,14] also has studied the PEO/PLLA polymer blend. It was found that the melting point of PLLA was depressed and different molecular weight of PEO

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* Corresponding author. Address: Department of Materials Science and Engineering, National Taiwan University, 1 Roosevelt Rd. Sec.4, Taipei 106, Taiwan, ROC. Tel.: +886-2-2362-6119; fax: +886-2-3363-4562.
E-mail address: wbliau@ntu.edu.tw (W.B. Liau).

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or PLLA did affect the miscibility and crystallization behavior of PEO/PLLA blends. However, Sheth and Kumar [15] have concluded DSC and DMA results that PEG/PLA blends range from miscible to partially miscible, depending on the composition. Nijenhuis et al. [16] has proposed the thermal and physical properties of high molecular weight PLLA and PEO blends. All blends containing up to 50 wt% PEO showed single glass transition temperature. Judging from the melting point depression of the blends, this system was miscible over the whole composition range in the melt. Yang et al. [17] has mentioned the PEG/PLLA blend systems were miscible in the melt and the crystallization behavior of PLLA could be influenced by the addition of PEG. From the above research, it was found the different molecular weight or blend compositions would make different miscibility and crystallization behavior of PEG/PLLA blends. In this work, the effect of end groups of PEG on the crystallization behaviors of PEG/PLLA blends was studied. Three kinds of PEG with different end groups were studied. They were PEG with two OH end groups (PEG-2OH), PEG with two CH_3 end groups (PEG-2CH_3), and PEG with one OH and one CH_3 end groups (PEG-1OH-1CH_3).

Besides, in some earlier reports they have considered primarily the effect of blending with PEG on the crystallization behavior of PLLA, and hence they mainly concern with a crystalline/amorphous blend system. When PEG/PLLA blends are cooled to the temperature below the melting point (< 60 °C) of PEG, both PEG and PLLA could crystallize, and the blend would turn into a crystalline/crystalline system whose behavior is more complicated than the crystalline/amorphous system. Since the investigation on crystalline/crystalline blends is quite limited, PEG/PLLA blends appear to be an interesting system for such a study. In this study, we will also discuss the different crystallization conditions of PEG/PLLA blends.

2. Experimental

2.1. Materials and preparing method of sample

The PLLA sample used in this study was obtained from Polysciences Co., and its weight-average molecular weight was 200,000.PEG(2OH), PEG(1OH-1CH_3) and PEG(2CH_3) obtained from Aldrich Co. had a weight-average molecular weight of 2000.

Preparation of PEG and PLLA blends was carried out by solution-casting method. The blending components were dissolved in chloroform yielding a 2% (0.4 g polymer blends/20 ml solvent) solution. The solution was subsequently poured onto a glass dish. A film was obtained after evaporating most chloroform solvent very slowly under ambient condition at room temperature. The film was then further dried in vacuum at 80 °C for 24 h. Also, TGA was used to check the residual solvent in the final films. The results showed no measurable residual solvent in the films.

2.2. Measurements

Thermal transitions of PEG/PLLA blends were measured with a TA instruments DSC 2010 differential scanning calorimetry (DSC). The samples were first heated up to 180 °C and held for 3 min, and then were cooled down to − 100 °C. At a heating rate of 10 °C/min, the samples were heated from − 100 to 200 °C, thus the glass transition temperature and enthalpy of melting would be observed.

The isothermal crystallization of PEG/PLLA blends was measured by TA DSC 2010 DSC. The samples were heated to 180 °C and held for 3 min on a Linkam THMS600 hot stage, and then quickly moved into the DSC cell, where the temperature was kept at crystallization temperature. After the crystallization peak completely showed up, isothermal crystallization of PEG/PLLA blends was observed.

The spherulitic growth of PEG/PLLA blends was observed by a Nikon HFX-DX polarizing optical microscope (POM). The samples were placed on cover glasses, heated to 180 °C and held for 3 min on a Linkam THMS600 hot stage. The samples were then quickly cooled to their crystallization temperature. Micrographs were taken at interval for measuring the spherulite radii at various time periods. The growth rate was calculated from the change of spherulite radius with time, dR/dt.

3. Results and discussion

3.1. Miscibility

Fig. 1(a)–(c) show DSC thermograms of PEG(2OH, 1OH-1CH_3 and 2CH_3)/PLLA blends. A single glass transition temperature (T_g) was identified in the figure for blends with a PEG composition of under 10 wt%. For higher compositions of PEG, the blend's T_g could not be observed. For blends with high PLLA composition, adding PEG to PLLA increased the crystallization rate of PLLA and the PLLA crystals form during quenching, resulting in the less amorphous part and the difficulty of T_g observation. Also, the increase of PEG resulted in the crystallization of PEG and the melting of PEG and the glass transition of blend might be overlapped. Thus, for the blends with high PLLA composition T_g could not be easily observed by DSC. On the other hand, for the blends with high PEG composition, the strong crystallizability and high crystallization rate of PEG during quenching resulted in the less amorphous part and the difficulty in the observation of T_g.

The miscibility of polymer blends is usually determined from the observation of a single T_g. However, in this system, only a 10/90 blend exhibits a single composition-dependent T_g. Other blends could not be determined for sure to be miscible in the melt. Consequently, other methods are presented to verify the miscibility. For blends containing a crystalline polymer, the melting point depression is also an indication of a miscible system. The equilibrium melting

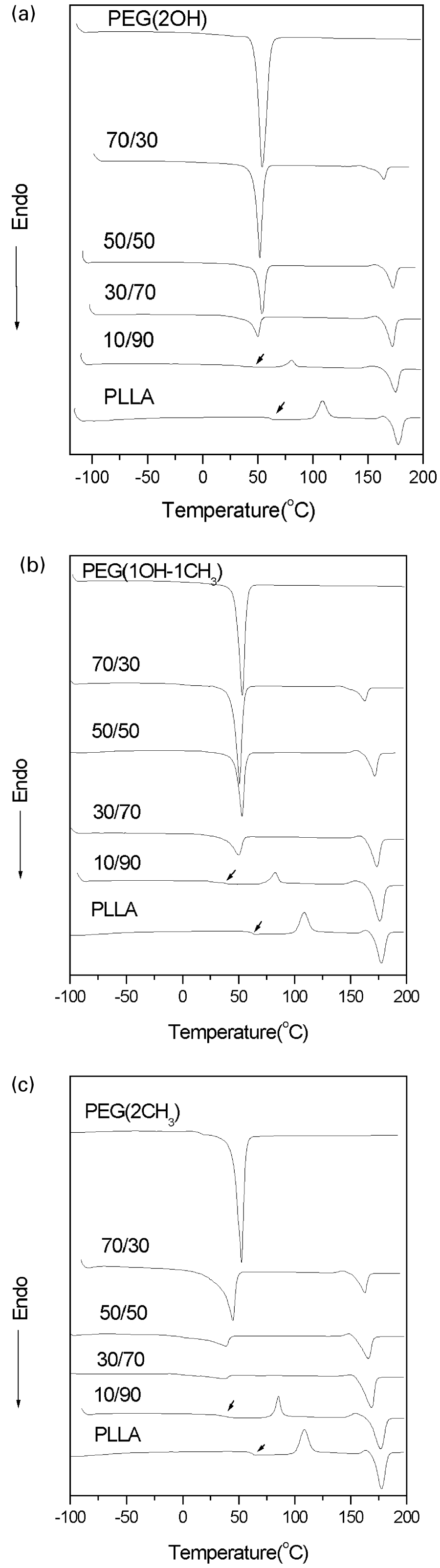

Fig. 1. (a). DSC traces from second run of PEG(2OH)/PLLA blends. Arrows indicate T_g. (b). DSC traces from second run of PEG(1OH-1CH$_3$)/PLLA blends. Arrows indicate T_g. (c). DSC traces from second run of PEG(2CH$_3$)/PLLA blends. Arrows indicate T_g.

point was determined by Hoffman–Weeks [18] analysis. The relevant equation was written in the following form:

$$T_m = \frac{1}{\gamma}T_c + \left(1 - \frac{1}{\gamma}\right)T_m^0 \qquad (1)$$

where T_m and T_m^0 are the experimental melting temperature and the equilibrium melting temperature of PLLA in the blend, respectively. γ is a proportional factor between the initial thickness of a chain-folded lamella, l_g^*, and the final lamellar thickness, l_c.

The equilibrium melting point of PLLA, T_m^0, was obtained from the extrapolation with the $T_m = T_c$ line. Fig. 2 plots T_m^0 as a function of the weight fraction of PEG(2OH,1OH-1CH$_3$ and 2CH$_3$)/PLLA blends. Regardless of end groups of PEG, the equilibrium melting point of PLLA declines as the PEG content increases. However, the reduction in the melting point of PLLA depends on end groups of PEG. The PEG(2CH$_3$) showed the greatest reduction in the melting-point and the PEG(2OH) showed the least reduction. The equilibrium melting point of PLLA is reasonable in comparison with the data reported by Nijenhuis [16] (196 °C) but is lower than that reported by Tsuji [19] (212 °C) and Kalb [20] (215 °C).

The melting point depression of a crystalline phase with non-crystalline polymeric diluent in a miscible blend was derived by Nishi and Wang [21]. The relevant equation can be written as:

$$\frac{1}{T_m^0} - \frac{1}{T_m^{0'}} = \frac{-RV_2}{\Delta H_f^0 V_1}\left[\frac{\ln \phi_2}{M_2} + \left(\frac{1}{M_2} - \frac{1}{M_1}\right)\phi_1\right] - \frac{RV_2}{\Delta H_f^0 V_1}(\chi_{12}\phi_1^2) \qquad (2)$$

where V is the molar volume of the polymer repeating unit, ψ is the volume fraction of the component in the blend, ΔH_f^0 is the perfect crystal heat of fusion of the crystallizable polymer, M is the degree of polymerization, R is the

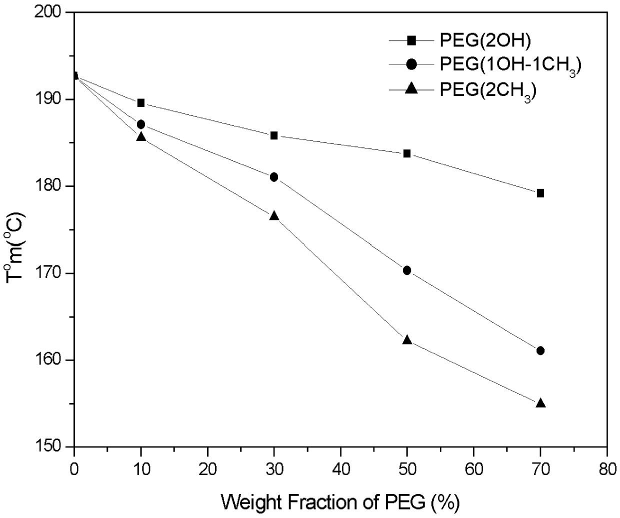

Fig. 2. T_m^0 as a function of weight fraction of PEG(2OH, 1OH-1CH$_3$ and 2CH$_3$)/PLLA blends.

universal gas constant, T_m^0 is the equilibrium melting point of pure crystalline polymer, $T_m^{0'}$ is the equilibrium melting point of a blend, and χ_{12} is the polymer/polymer interaction parameter. The subscripts 1 and 2 denote the amorphous and crystalline components, respectively. If the molecular weights of both components of blends are large enough, the entropy of mixing can be negligible and the melting point depression is dominated by an enthalpic term, then the equation reduces to:

$$\frac{1}{T_m^0} - \frac{1}{T_m^{0'}} = -\frac{RV_2}{\Delta H_f^0 V_1}(\chi_{12}\phi_1^2) \quad (3)$$

It is well known that experimental factors such as scanning rate, crystallization temperature range, and time of crystallization would affect the values obtained. However, the same experimental procedures were used for all blends. Therefore, the change of χ_{12} with different end groups still was meaningful. The following parameters were used [20,22–24]: $\Delta H_f^0 = 1.883$ kcal/mol, $V_1 = 24.16$ cm^3/mol, $V_2 = 44.65$ cm^3/mol, $\rho_1 = 1.22$ g/cm^3 and $\rho_2 = 1.27$ g/cm^3. Table 1 presents the χ_{12} values of different end groups of PEG for PEG/PLLA blends. Because the value of χ_{12} is negative, it confirms that the polymeric mixture is thermodynamically miscible in the melt. Besides, Nakafuku et al. [14] also has discussed the miscibility of PEO and PLLA was better as the molecular weight of PEO was smaller. In this system, the molecular weight of PEG is very small so it is believed they are miscible. Smaller χ_{12} values mean better miscibility. Thus, the PEG/PLLA blends with different end groups in order of decreasing miscibility are PEG(2CH$_3$)/PLLA, PEG(1OH-1CH$_3$)/PLLA and PEG(2OH)/PLLA.

Rozenberg et al. [25] examined the hydrogen bonding in PEG-200, PEG-400, PEG(1OH)-350 and PEG(2CH$_3$)-250 four systems using IR. They reported that, for the C–O–C group of PEG, the band at 1104 cm^{-1} will shift to 1127 cm^{-1}, due to the hydrogen bonding with the OH end group. Hydrogen bonding will decrease with increasing molecular weight and fewer OH groups. Although, the molecular weight of PEG is 2000 in this study, the OH end group is expected to form the hydrogen bonding. When PEG(2OH) is blended with PLLA, the hydrogen bonding is expected to form between PEGs themselves, such that the miscibility between PEG and PLLA decreases. Therefore, it is expected the miscibility decreases with more OH end groups.

Table 1
Interaction parameter of PEG/PLLA blends

Polymers	PEG(2OH)/ PLLA	PEG(1OH-1CH$_3$)/ PLLA	PEG(2CH$_3$)/ PLLA
X$_{12}$	−0.048	−0.144	−0.161

3.2. Crystallization behavior

For PEG/PLLA, four different crystallization situations could occur. First, PLLA crystallizes before the formation of PEG crystals. Second, PLLA crystallizes after the formation of PEG crystals. Third, PEG crystallizes before the formation of PLLA crystals. Last, PEG crystallizes following the formation of PLLA crystals. However, the crystallization temperature of PLLA is higher than the melting point of PEG and so the second situation is unable to study. Also, it was showed the crystallization of PLLA in blends could not be inhibited during such fast quenching from Fig. 1. Thus, the third situation is unable to study. Consequently, this study involves only two crystallization situations. One applies as the PLLA crystallization behavior is observed before PEG crystals are formed, and the other applies as PEG crystallization behavior is observed after PLLA crystals are formed.

DSC and POM instruments were used to elucidate the crystallization behavior of PEG/PLLA blends, including isothermal crystallization and spherulitic growth rate.

3.2.1. Isothermal crystallization

The kinetics of isothermal crystallization has been analyzed in terms of the Avrami equation [26–28] using the double logarithmic form:

$$\log[-\ln(1 - X_t)] = \log K_n + n \log t \quad (4)$$

where n is the Avrami exponent which is related to the geometry of the spherulitic growth and the mechanism of the nucleation. K_n is the overall kinetic rate constant. The time required to reach 50% crystallization is called half-time of crystallization and denoted as $t_{1/2}$.

First, the isothermal crystallization of PLLA was observed before PEG crystals were formed. Table 2 presents the values of n, K_n and $t_{1/2}$ in the Avrami equation for PEG(1OH-1CH$_3$)/PLLA blends isothermally crystallized at 124 °C. Only PLLA can crystallize at this temperature. The value of $t_{1/2}$ first increases and then decreases as the PEG content increases. The dilution of PEG, which depresses the equilibrium melting point (T_m^0), reduces the driving force of crystallization ($T_m^0 - T_c$), and blending with PEG lowers the system's glass transition temperature (T_g), increasing the segmental mobility of PLLA. These two factors are such competitive that the isothermal crystallization rate of PLLA first increases and then decreases with the increase of PLLA. Basically, if two polymers are immiscible, the values of n, K_n and $t_{1/2}$ in the Avrami equation should not be changed. However, in this system these values change with the composition, reconfirming that PEG/PLLA blends is a miscible system. For PEG(2OH)/PLLA and PEG(2CH$_3$)/PLLA blends, similar results are found, indicating that the isothermal crystallization rate of PLLA first increases and then decreases with the addition of PLLA.

With reference to the effect of different end groups of PEG on the isothermal crystallization of PLLA for

Table 2
The values of n, K_n, $t_{1/2}$ of PEG(1OH-1CH$_3$)/PLLA blends at 124 °C

Composition weight fraction, PEG(1OH-1CH$_3$)/PLLA	n	K_n	$t_{1/2}$ (s)
0/100	3.98	2.91×10^{-12}	694.8
10/90	3.58	6.24×10^{-11}	628.8
30/70	3.50	2.13×10^{-10}	498.0
50/50	3.24	6.57×10^{-10}	595.8

PEG/PLLA blends, Table 3 shows the values in the Avrami equation for PEG(2OH, 1OH-1CH$_3$ and 2CH$_3$)/PLLA 50/50 isothermally crystallized at 124 °C. The PEG(2OH)/PLLA blend system exhibits the fastest isothermal crystallization rate of PLLA, followed by the PEG(1OH-1CH$_3$)/PLLA blend system, and the PEG(2CH$_3$)/PLLA blend system exhibits the slowest isothermal crystallization rate of PLLA.

The glass transition temperature (T_g) and equilibrium melting point (T_m^0) are main factors that influence the crystallization rate of a polymer. In a PVAc/PEG[3]system, a single composition-dependent T_g of PEG(2CH$_3$) blended with PVAc has been reported to be higher by 2–5 °C than that of PEG(2OH) blended with PVAc. Furthermore, the difference between the T_g of these two end groups of PEG blended with PVAc did not change with the composition. Thus, they concluded that the end groups of PEG did not affect T_g of the polymer blend too much. In this study, the T_gs of different end groups of PEG blended with PLLA in a 10/90 ratio are very similar (Fig. 1). Hence, it is expected that T_m^0 is the dominant factor on the crystallization rate of PLLA. The experimental results on the equilibrium melting point depression of PLLA (Fig. 2) indicate that in decreasing order of T_m^0s of PLLA in blends are PEG(2OH)/PLLA, PEG(1OH-1CH$_3$)/PLLA and PEG(2CH$_3$)/PLLA. As the T_m^0 of PLLA is depressed, the degree of supercooling ($T_m^0 - T_c$) of PLLA is reduced. In general, the crystallization rate increases first and then decreases with the increasing supercooling. The crystallization temperature (124 °C) is close to the melting point of PLLA. In this region, the crystallization rate of PLLA increases with the increasing supercooling. From the POM observation also confirmed it. The PEG(2CH$_3$)/PLLA blend system has the lowest T_m^0 of PLLA, and therefore the slowest crystallization rate of PLLA.

Second, the isothermal crystallization of PEG is observed after PLLA crystals are formed. Consider PEG(1OH-1CH$_3$)/PLLA, for example. Samples were first heated to 180 °C, held for 3 min, and then cooled to 120 °C until the PLLA crystals formed completely. Then the sample was quickly quenched to 35 °C to observe the isothermal crystallization of PEG. Table 4 lists the values of n, K_n and $t_{1/2}$ in the Avrami equation isothermally crystallized at 35 °C after the formation of PLLA crystals for PEG(1OH-1CH$_3$)/PLLA blends. From Table 4, the crystallization rate of PEG declines as the amount of PLLA increases and potentially determines three causes: (1) blending with PLLA lowers the segmental mobility of PEG as T_g increases; (2) the dilution of PEG and the decline in the equilibrium melting point reduces the driving force of crystallization, and (3) the formation of PLLA crystal hinders the crystallization rate of PEG.

Table 3
The values of n, K_n, $t_{1/2}$ of PEG/PLLA 50/50 blends at 124 °C

Polymers	n	K_n	$t_{1/2}$ (s)
PEG(2OH)/PLLA 50/50	3.65	7.89×10^{-11}	501.0
PEG(1OH-1CH$_3$)/PLLA 50/50	3.24	6.57×10^{-10}	595.8
PEG(2CH$_3$)/PLLA 50/50	3.16	2.32×10^{-10}	929.4

3.2.2. Spherulite growth rate

PEG is oxidized easily at moderate temperature [29–34]. Therefore, all the measurement is under the nitrogen atmosphere. First, the spherulitic growth rate of PLLA is observed before PEG crystals are formed. The spherulites of PLLA are not suppressed when the crystallization temperature is less than 100 °C. Therefore, the experiment is carried out between 100 and 130 °C. The radial growth rate of PLLA spherulites is measured by observing the evolution of POM images over time. Fig. 3 plots the spherulitic growth rate, G, for various compositions as a function of T_c for PEG(1OH-1CH$_3$)/PLLA blends. For the blend compositions displayed in Fig. 3, only PLLA crystallizes and PEG acts as a non-crystallizable component at T_c. The variation of PLLA spherulite radius with time (not shown) is linear in all cases, which means that the crystallization environment at

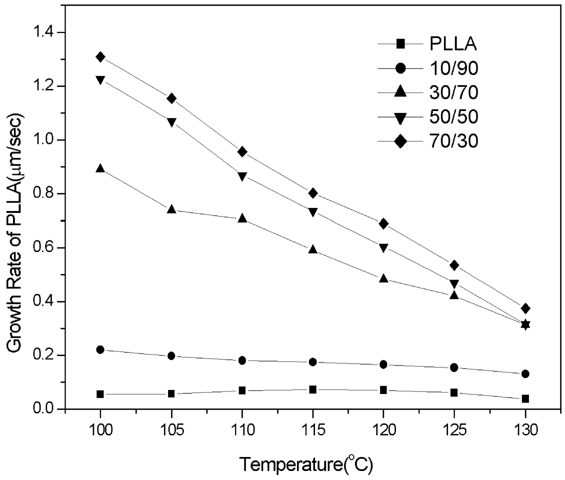

Fig. 3. The spherulitic growth rate G of PLLA versus crystallization temperature PEG(1OH-1CH$_3$)/PLLA blends.

Table 4
The Values of n, K_n, $t_{1/2}$ of PEG(1OH-1CH$_3$)/PLLA Blends at 35 °C After The Formation of PLLA Crystals

Composition weight fraction, PEG(1OH-1CH$_3$)/PLLA	n	K_n	$t_{1/2}$ (s)
100/0	3.53	2.59×10^{-7}	69.6
70/30	3.58	8.26×10^{-8}	90.6
50/50	3.65	2.72×10^{-8}	110.4
30/70	3.85	6.30×10^{-10}	111.6

the growth front is same during the crystallization process. This result suggests that PEG and un-crystallized PLLA could be trapped in the intra-spherulitic regions. Fig. 3 also shows that the spherulitic growth rate of PLLA is accelerated by increasing the amount of PEG. Although, the dilution of PLLA as well as depression in equilibrium melting point reduces the crystallization driving force, blending with PEG increases the segmental mobility of PLLA. Thus, the increased segmental mobility is assumed to be the major effect. Besides, for PEG(2OH)/PLLA and PEG(2CH$_3$)/PLLA blends, the spherulitic growth rate of PLLA also increases with PEG content. The trend does not like it showed in Table 2. However, the isothermal crystallization kinetics investigated by DSC may represent the bulk crystallization rate, which involves both the nucleation density and the spherulitic growth rate. This can be seen from the following observation.

Fig. 4 displays the spherulitic growth rate, G, as a function of T_c for PEG(2OH,1OH-1CH$_3$ and 2CH$_3$)/PLLA blends with 50/50 composition. The PLLAs in decreasing order of spherulitic growth rate are PEG(2OH)/PLLA, PEG(1OH-1CH$_3$)/PLLA and PEG(2CH$_3$)/PLLA, perhaps determined also by the competition between T_m^0 and T_g. Again, the end group of PEG blended with PLLA does not affect T_g much. Therefore, T_m^0 is the dominant factor. The PEG(2CH$_3$)/PLLA blend system has a greatly depressed equilibrium melting point and the least degree of supercooling of PLLA. From Fig. 4, the crystallization rate of PLLA falls on the decreasing side. Therefore, the spherulitic growth rate of PLLA is the slowest.

Besides, Fig. 5 shows the number of nuclei of PLLA versus the weight fraction of PEG in PEG(2OH, 1OH-1CH$_3$ and 2CH$_3$)/PLLA blends isothermally crystallized at 120 °C by POM. The number of nuclei of PLLA decreases with the increase of PEG regardless of end groups. Also, the number of nuclei of PLLA increases with more OH end groups when the content of PEG is same. From Figs. 4 and 5, it is expected that isothermal crystallization rate of PLLA first increases with PLLA and then decreases as more PLLA is added regardless of end groups. Furthermore, the PEG(2CH$_3$)/PLLA blend system has the fewest nuclei of PLLA and exhibits the slowest spherulitic growth rate of PLLA, such that the isothermal crystallization rate of PLLA is also the slowest.

The spherulitic growth rate of PEG was observed after the PLLA crystals are formed. However, the birefringence of PEG interferes with that of PLLA spherulites and thus was not clearly observed using POM.

3.2.3. Fold surface free energy

The kinetic theory of polymer crystallization developed by Hoffman et al. [35–37] has been used to analyze experimental crystallization data concerning the spherulite growth rate. According to this theory, the dependence of the growth rate G_m on the crystallization temperature T_c is

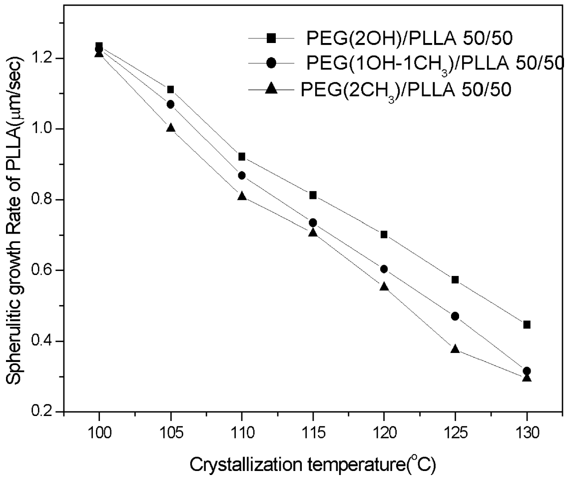

Fig. 4. The spherulitic growth rate G of PLLA in PEG/PLLA 50/50 with different end groups of PEG.

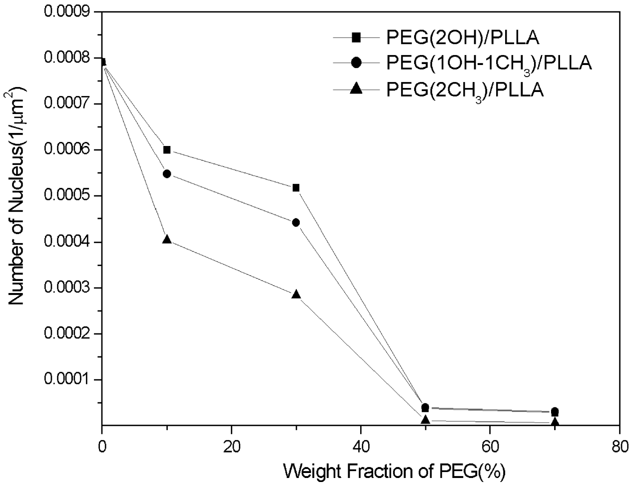

Fig. 5. Number of nuclei of PLLA in PEG/PLLA blends with different end groups of PEG isothermally crystallized at 120 °C.

described by the following equation:

$$G_{\mathrm{m}} = \phi_2 G_0 \mathrm{e}^{\frac{-\Delta E}{R(T_{\mathrm{c}}-T'_{\infty})}} \mathrm{e}^{\frac{-\Delta F^*_{\mathrm{m}}}{k_{\mathrm{B}} T_{\mathrm{c}}}}. \tag{5}$$

where G_0 is a pre-exponential factor, generally assumed to be constant or proportional to T_{c}, where, ΔE is the activation energy for the transport of the crystallizing units across the liquid–solid interface, ΔF^*_{m} is the free energy required to form a nucleus of critical size, $T'_{\infty} = T_{\mathrm{g}} - 30$, R is the gas constant, K_{B} is the Boltzmann, and ϕ_2 is the crystalline polymer volume fraction. According, to Flory [38] and Mandelkerm [39], ΔF^*_m in Eq. (5) can be expressed as:

$$\Delta F^*_{\mathrm{m}} = \frac{nb\sigma_{\mathrm{u}}\sigma_{\mathrm{e}}}{\Delta h_{\mathrm{u}} f\left(1 - \dfrac{T_{\mathrm{c}}}{T^0_{\mathrm{m}}} - \dfrac{RT_{\mathrm{c}}\chi_{12}}{\Delta h_{\mathrm{u}} f}\dfrac{V_{2\mathrm{u}}}{V_{1\mathrm{u}}}(1-\phi_2)^2\right)} \tag{6}$$

where Δh_{u} is the enthalpy of fusion per unit volume, T^0_{m} is the equilibrium melting point of the crystalline polymer in the blend, $V_{1\mathrm{u}}$ and $V_{2\mathrm{u}}$ are the molar volumes of component 1 (non-crystalline) and component 2 (crystalline), χ_{12} is the polymer/polymer interaction parameter, b is the layer thickness, σ_{u} and σ_{e} are lateral and fold surface free energies, n is a coefficient depends on the growth regime (Hoffman [37]): $n = 4$ in regime I and III, and $n = 2$ in regime II, and $f = 2T_{\mathrm{c}}/T^0_{\mathrm{m}} + T_{\mathrm{c}}$.

Taking Eqs. (6) into (5), the following expression is obtained:

$$G_{\mathrm{m}} = \phi_2 G_0 \mathrm{e}^{\frac{-\Delta E}{R(T_{\mathrm{c}}-T'_{\infty})}} \mathrm{e}^{\frac{-nb\sigma_{\mathrm{u}}\sigma_{\mathrm{e}}/k_{\mathrm{B}}T_{\mathrm{c}}}{\Delta h_{\mathrm{u}} f\left(1-\frac{T_{\mathrm{c}}}{T^0_{\mathrm{m}}}-\frac{RT_{\mathrm{c}}V_{2\mathrm{u}}}{\Delta h_{\mathrm{u}} f V_{1\mathrm{u}}}\chi_{12}(1-\phi_2)^2\right)}}. \tag{7}$$

Eq. (7) is using the double logarithmic form, and simplifying it:

$$\alpha = -\sigma_{\mathrm{u}}\sigma_{\mathrm{e}}\beta \tag{8}$$

$$\alpha = \ln G_{\mathrm{m}} - \ln \phi_2 - \ln G_0 + \frac{\Delta E}{R(T_{\mathrm{c}} - T'_{\infty})} \tag{9}$$

$$\beta = \frac{nb/k_{\mathrm{B}}T_{\mathrm{c}}}{\left[\Delta h_{\mathrm{u}} f\left(\dfrac{\Delta T}{T^0_{\mathrm{m}}}\right) - \dfrac{RT_{\mathrm{c}}V_{2\mathrm{u}}}{V_{1\mathrm{u}}}\chi_{12}(1-\phi_2)^2\right]} \tag{10}$$

The plot of $(\alpha + \ln G_0)$ against β will give the $\sigma_{\mathrm{u}}\sigma_{\mathrm{e}}$ in the slope. In this PEG/PLLA system, we assume the growth regime is regime II ($n = 2$). Table 5 gives the values of various parameters involved in Eqs. (9) and (10). T_{g} is estimated by Fox's equation. $T^0_{\mathrm{m}}, G_{\mathrm{m}}$ and χ_{12} are obtained from the above results. Fig. 6(a)–(c) display the L–H plot for PEG(2OH, 1OH-1CH$_3$ and 2CH$_3$)/PLLA blends. Table 6 lists the values of $\sigma_{\mathrm{u}}\sigma_{\mathrm{e}}$ products in PEG(2OH, 1OH-1CH$_3$ and 2CH$_3$)/PLLA blends. σ_{u} is intrinsic property, so it would not be changed by different blend composition. From Thomas–Stavely [40] equation: $\sigma_{\mathrm{u}} = \alpha b \Delta h^0_{\mathrm{f}}$, where α is a constant. For most polymers, $\alpha \sim 1; \alpha = 0.25$ as high melting point polyester. Thus, $\alpha = 0.25$ is used. b is the layer thickness. Δh^0_f is the enthalpy of 100% crystalline polymer. From Ref. [20] and [41], $b = 5.17 \times 10^{-10}$ m and $\Delta h^0_{\mathrm{f}} = 1.11 \times 10^8$ J/m^3. Therefore, we can get the lateral surface energy (σ_{u}) = 14.35 erg/cm^2.

Table 5
Parameters used for Lauritzen–Hoffman equation

Items	PEG	PLLA
ΔE (cal/mol)		4120
b (Å)		5.17
Δh_{u} (J/cm^3)		111
V_{u} (cm^3/mol)	24.16	44.65
ρ_{u} (g/cm^3)	1.22	1.27

From Table 6, the fold surface free energy of PLLA decreases with the increasing PEG content regardless of end groups. For the same composition, the PEG(2CH$_3$)/PLLA blend has the least fold surface free energy.

4. Conclusion

The results presented in this paper show that PEG and PLLA were miscible in the melt over the composition range investigated by DSC. As a miscible polymer blend, regardless of end groups, the crystallization of PLLA before the formation of PEG was influenced by two temperatures (T_{g} and T^0_{m}). However, the crystallization of PEG after the formation of PLLA crystals was more complicate. It was found the formation of PLLA crystals would also hinder the crystallization rate of PEG besides the temperature factors T_{g} and T^0_{m}.

The effect of end groups of PEG on the miscibility and crystallization behavior of PEG/PLLA blends was also investigated. The miscibility of PEO/PLLA blends in decreasing order were PEG(2CH$_3$)/PLLA, PEG(1OH-1CH$_3$)/PLLA and PEG(2OH)/PLLA. The equilibrium melting point, number of nuclei, and fold surface free energy of PLLA in blend increased with more OH end

Table 6
The values of $\sigma_{\mathrm{u}}\sigma_{\mathrm{e}}$ products in PEG/PLLA blends

Polymer blend	Blend composition	$\sigma_{\mathrm{u}}\sigma_{\mathrm{e}}$ (erg^2/cm^4)	σ_{e} (erg/cm^2)
PEG(2OH)/PLLA	0/100	7830	546
	10/90	5400	376
	30/70	3860	269
	50/50	2820	197
	70/30	2230	155
PEG(1OH)/PLLA	10/90	4950	345
	30/70	3620	252
	50/50	1940	135
	70/30	1090	76
PEG(2CH$_3$)/PLLA	10/90	4600	321
	30/70	2580	180
	50/50	1390	97
	70/30	844	59

groups. Thus, the spherulitic growth rate and isothermal crystallization rate of PLLA in decreasing order were PEG(2OH)/PLLA, PEG(1OH-1CH$_3$)/PLLA and PEG(2CH$_3$)/PLLA.

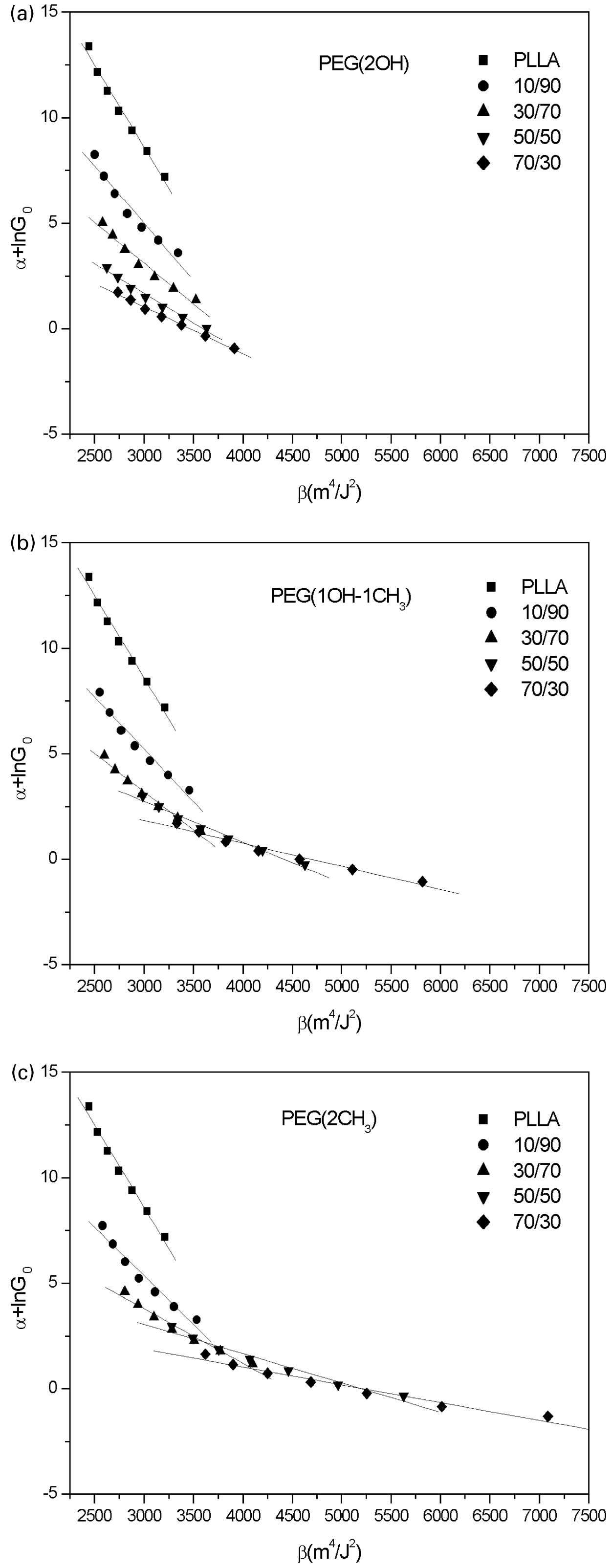

Fig. 6. (a) Growth rates analyzed using Lauritzen–Hoffman equation of PEG(2OH)/PLLA blends. (b) Growth rates analyzed using Lauritzen–Hoffman equation of PEG(1OH-1CH$_3$)/PLLA blends. (c). Growth rates analyzed using Lauritzen–Hoffman equation of PEG(2CH$_3$)/PLLA blends.

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