

The Effect of Ionic Interaction on the Miscibility and Crystallization Behaviors of Poly(ethylene glycol)/Poly(L-lactic acid) Blends

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ABSTRACT: The effect of end groups (2NH₂) of poly(ethylene glycol) (PEG) on the miscibility and crystallization behaviors of binary crystalline blends of PEG/poly(L-lactic acid) (PLLA) were investigated. The results of conductivity meter and dielectric analyzer (DEA) implied the existence of ions, which could be explained by the amine groups of PEG gaining the protons from the carboxylic acid groups of PLLA. The miscibility of PEG(2NH₂)/PLLA blends was the best because of the ionic interaction as compared with PEG(2OH, 1OH-1CH₃, and 2CH₃)/PLLA blends. Since the ionic interaction formed only at the chain ends of PEG(2NH₂) and PLLA,

unlike hydrogen bonds forming at various sites along the chains in the other PEG/PLLA blend systems, the folding of PLLA blended with PEG(2NH₂) was affected in a different manner. Thus the fold surface free energy played an important role on the crystallization rate of PLLA for the PEG(2NH₂)/PLLA blend system. PLLA had the least fold surface free energy and the fast crystallization rate in the PEG(2NH₂)/PLLA blend system, among all the PEG/PLLA systems studied. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3616–3623, 2008

Key words: blends; miscibility; crystallization

INTRODUCTION

In recent decades, many polymer blends have been well studied and documented by scientific and industrial research. One of the major concerns is the miscibility and crystallization behaviors of polymer blends. Binary polymer blends can be classified into amorphous/amorphous, crystalline/amorphous, and crystalline/crystalline systems based on the crystallizability of the components. Most of them focused on the polymeric mixture containing two amorphous components.^{1–3} In contrast, polymer blends containing two crystalline components are less frequently discussed.

Both poly(ethylene glycol) (PEG) and poly(L-lactic acid) (PLLA) are very attractive and significant crystalline polymers. PEG is soluble in water and in many organic solvents. Meanwhile, PEG shows hydrophilicity and biocompatibility. PLLA is a biodegradable thermoplastic polyester and has been paid a lot of attentions because of their potential

applications as biomedical and environment-friendly materials. Up to now, the binary blends of a biodegradable polymer, PLLA, with a biocompatible polymer, PEG, have been investigated.^{4–13} From our previous studies,¹⁴ the effect of end groups of PEG(2OH, 1OH-1CH₃, and 2CH₃) on the miscibility and crystallization behavior of PEG/PLLA blends were investigated. The miscibility of PEG/PLLA blends in decreasing order were PEG(2CH₃)/PLLA, PEG(1OH-1CH₃)/PLLA, and PEG(2OH)/PLLA. The equilibrium melting point and fold surface free energy of PLLA in blend increased with more OH end groups. Thus, the spherulitic growth rate and isothermal crystallization rate of PLLA in decreasing order were PEG(2OH)/PLLA, PEG(1OH-1CH₃)/PLLA, and PEG(2CH₃)/PLLA.

In this work, the effect of PEG with two amine end groups (PEG-2NH₂) on the miscibility and crystallization behaviors of PEG/PLLA blends will be discussed and compared with our previous results.¹⁴ Hydrogen bonds or polar forces between components of polymer blends generally are beneficial for the formation of miscible systems, such as poly(vinylidene fluoride)/poly(1,4-butylene adipate) (PVDF/PBA), poly(ethylene oxide)/poly(methyl methacrylate) (PEO/PMMA), poly(ethylene oxide)/poly(vinyl phenol) (PEO/PVPh), poly(vinylidene fluoride)/

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poly(pivalolactone) (PVDF/PPVL), and so on.^{15–21} However, if there is ionic interaction between two polymers, the miscibility and crystallization behaviors of the polymer blends may be affected. In particular, if the ionic interaction forms at the chain end of PEG and PLLA, the chain folding conformation may be changed during crystallization. In addition, the existence of ions could also affect the properties of the polymer blends. Since there are many biomolecules having amine groups in the human body, studying the PEG(2NH₂)/PLLA blend system might provide useful information for the applications of PLLA.

EXPERIMENTAL

Materials and sample preparation

The PLLA sample used in this study was purchased from Polysciences Co., and its weight-average-molecular weight was 200,000. PEG(2OH), PEG(1OH-1CH₃), PEG(2CH₃), and PEG(2NH₂) obtained from Aldrich Co. had a weight-average-molecular weight of 2000. The sample information provided by these companies confirmed that the end groups of PEG(2OH), PEG(1OH-1CH₃), PEG(2CH₃), and PEG(2NH₂) were the same as indicated, and those of PLLA were COOH.

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.

Measurements

The conductivity values of PEG/PLLA samples in solution (chloroform) were measured by a Radiometer CDM 230 conductivity meter. The samples were placed in a circulating shaker water bath at (30 ± 0.01)°C, and the solution concentration (C_M) was 0.001M.

The dielectric properties of PEG/PLLA samples were characterized using a TA instruments DEA 2970 dielectric analyzer (DEA) equipped with a liquid nitrogen cooling system. Film samples were prepared by the solution-casting method. The dielectric behaviors of samples were measured at different frequencies (100,000, 50,000, 10,000, 1000, 100, 10, 1,

TABLE I
Conductivity Values for PEG and PEG/PLLA 50/50 Blends in CHCl₃ (CHCl₃: 0.21 μS/cm)

Samples	Conductivity (μS/cm)
PEG(2OH)	0.21
PEG(1OH-1CH ₃)	0.21
PEG(2CH ₃)	0.21
PEG(2NH ₂)	0.21
PEG(2OH)/PLLA 50/50	0.21
PEG(1OH-1CH ₃)/PLLA 50/50	0.21
PEG(2CH ₃)/PLLA 50/50	0.21
PEG(2NH ₂)/PLLA 50/50	0.28

and 0.3 Hz) at a heating rate of 3°C/min in the temperature range –120 to 60°C.

The isothermal crystallization and equilibrium melting point (T_m^0) of PEG/PLLA blends were measured with a TA instruments DSC 2010 differential scanning calorimetry (DSC). A sealed aluminum pan containing 5–10 mg sample was heated to 180°C and held for 3 min (to erase the previous thermal history) on a Linkam THMS600 hot stage. Then it was quickly moved into the DSC cell, which was kept at the crystallization temperature (T_c). The isothermal crystallization was allowed to proceed until the exothermic peak was complete. Subsequently, the sample was heated to 200°C at a heating rate of 10°C/min to determine the melting point (T_m). The equilibrium melting point, T_m^0 , was obtained from the extrapolation with the $T_m - T_c$ plot to the $T_m = T_c$ line.

The spherulitic growth (G) 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 THMS 600 hot stage. The samples were then quickly cooled to their crystallization temperature (T_c). 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 .

RESULTS AND DISCUSSION

Conductivity and dielectric properties

Table I lists the conductivity values in solution of PEG(2OH, 1OH-1CH₃, 2CH₃, and 2NH₂) samples and PEG(2OH, 1OH-1CH₃, 2CH₃, and 2NH₂)/PLLA 50/50 blends. For the PEG samples of different end groups, it was found the conductivity values were all 0.21 μS/cm, the same as that of the solvent (chloroform). However, for the blends with PLLA, the conductivity value of the PEG(2NH₂)/PLLA blend increased to 0.28 μS/cm. This enhancement may be attributed to the existence of ions.

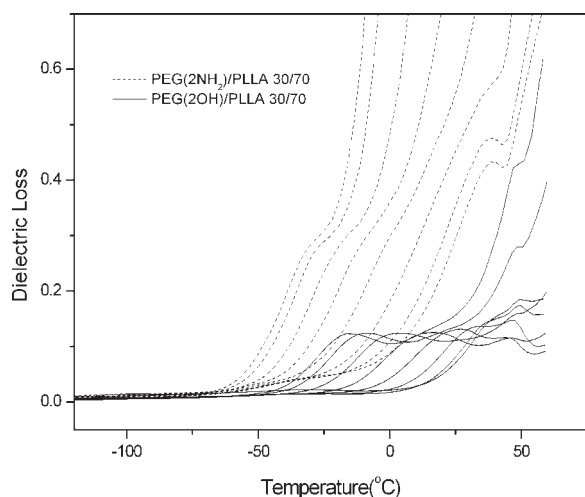


Figure 1 Variation of the dielectric loss with the temperature for PEG(2OH)/PLLA 30/70 and PEG(2NH₂)/PLLA 30/70 blend.

From the above experiment, we believe that ions appear in the solution of PEG(2NH₂) and PLLA. However, samples used in other experiments of this study were prepared by solution-casting; the samples were thin films, not solutions. Therefore, a DEA was used to elucidate the dielectric/conductive properties of thin films of PEG/PLLA blends. Figure 1 shows the variation of the dielectric loss with temperature of PEG(2OH)/PLLA 30/70 and PEG(2NH₂)/PLLA 30/70 blends at frequencies ranging from 0.3 Hz to 10 kHz. Note that the mechanical properties of PEG were poor due to the low-molecular weight, and blend samples with higher compositions of PEG were thus not suitable for the DEA experiment. As a result, PEG(2OH)/PLLA 30/70 and PEG(2NH₂)/PLLA 30/70 blends were chosen. In Figure 1, the dielectric loss of the PEG(2NH₂)/PLLA 30/70 blend sharply increased after the glass transition temperature, while the increase was less marked and began much later in the PEG(2OH)/PLLA blend. Three reasons might have caused this phenomenon. First, if the glass transition temperature of PEG(2NH₂)/PLLA blend was lower, the increase in the dielectric loss would happen earlier than that of the PEG(2OH)/PLLA blend. However, from the Table II, both samples had very similar glass transition temperatures. Thus, this effect was not the main factor. Second, the interfacial polarization could also raise the dielectric loss.^{22–24} Nevertheless, the interfacial polarization should be excluded because both systems were miscible (discussed later). Third, the sharp increase in the dielectric loss suggests that the ionic conduction term in the classic Debye equation was significant for the PEG(2NH₂)/PLLA blend, which might result from the ionic species in the system. As mentioned earlier, the conductivity measurements showed that ions

appeared in the solution of PEG(2NH₂) and PLLA. Since the two blend films had similar glass transition temperatures and no interfacial polarization, the sharp increase in the dielectric loss of the PEG(2NH₂)/PLLA blend system was most likely due to the existence of ions in the blend system, which could be explained by the amine groups (–NH₂) of PEG receiving the protons from the carboxylic acid groups (–COOH) of PLLA. Therefore, there would be ionic interaction between the chain ends of PEG (2NH₂) and PLLA as well. In this study, the molecular weight of PLLA and PEG(2NH₂) were 200,000 and 2000. The number of PEG chains was much larger than that of PLLA, and thus all the end groups (–COOH) of PLLA should be able to interact with the end groups (–NH₂) of PEG, ensuring the homogeneity of the chain ends of PLLA. In addition, the lower molecular weight of PEG should manifest the effect of end groups on the miscibility and crystallization behaviors.

The following discussions will focus on the effect of ionic interaction on the miscibility and crystallization behaviors of PEG/PLLA blends and compare current and previous results.¹⁴

Miscibility

The miscibility of polymer blends is usually determined by the observation of a single glass transition temperature (T_g). However, from our previous results¹⁴ only a 10/90 blend exhibits a single composition-dependent T_g for PEG/PLLA blends. Other blends could not be determined for sure to be miscible in the melt. Furthermore, for blends containing a crystalline polymer, the melting point depression is also an indication of a miscible system.²⁵ The equilibrium melting point was determined by Hoffman-Weeks²⁶ analysis. The equation was written in the following form:

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

where T_m and T_m^0 are the experimental melting temperature and equilibrium melting temperature of PLLA in the blend, respectively, T_c is the

TABLE II
The Values of T_g at Different Frequency for PEG/PLLA 30/70 Blends

Composition weight fraction	10,000 Hz	50,000 Hz	100,000 Hz
PEG(2OH)/PLLA 30/70	29.31	33.17	36.52
PEG(2NH ₂)/PLLA 30/70	28.89	34.88	36.32

Unit: °C.

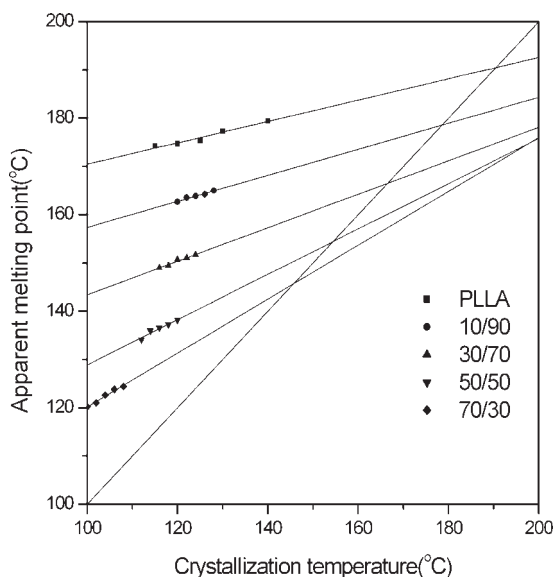


Figure 2 Hoffman-Weeks plots of PEG(2NH₂)/PLLA blends.

crystallization temperature, and γ is the proportional factor between the initial thickness of a chain-folded lamella, l_g^* , and final lamellar thickness, l_c .

The equilibrium melting point, T_m^0 , was obtained from the extrapolation with the $T_m - T_c$ plot to the $T_m = T_c$ line. Figure 2 displays the Hoffman-Weeks plots of PEG (2NH₂)/PLLA blends, where experimental data were obtained by isothermal crystallization. Figure 3 shows the equilibrium melting point (T_m^0) as a function of weight fraction for PEG (2NH₂)/PLLA blends, and the other data for PEG (2OH, 1OH-1CH₃, and 2CH₃)/PLLA blends was obtained from Ref 14. It was found that the equilibrium melting point of PLLA decreased with increasing PEG content, regardless of the end groups of PEG. Nonetheless, the amount of reduction in the melting-point of PLLA depended on the end groups of PEG. The PEG(2NH₂)/PLLA blend system showed the greatest reduction in the melting-point of PLLA, while the PEG(2OH)/PLLA blend system showed the least reduction. The equilibrium melting point of PLLA from our experiment is reasonable in comparison with the data reported by Nijenhuis⁶ (196°C) but is lower than that reported by Tsuji²⁷ (212°C) and Kalb²⁸ (215°C).

The melting point depression of a crystalline phase with noncrystalline polymeric diluent in a miscible blend was derived by Nishi and Wang.²⁵ The relevant equation can be written as:

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

where V is the molar volume of the polymer repeating unit, ϕ 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 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, so the change of χ_{12} with different end groups was still meaningful. Figure 4 was plotted to obtain χ_{12} from eq. (3). The following parameters were used²⁸⁻³¹: $\Delta H_f^0 = 1.883$ kcal/mol, $V_1 = 24.16$ cm³/mol, $V_2 = 44.65$ cm³/mol, $\rho_1 = 1.22$ g/cm³ and $\rho_2 = 1.27$ g/cm³. Table III shows the χ_{12} values of PEG of different end groups for PEG/PLLA blends. The negative value of χ_{12} confirms that the polymeric mixture was thermodynamically miscible in the melt. Moreover, smaller χ_{12} values mean better miscibility. Thus, the PEG/PLLA blends in the order of decreasing miscibility were PEG(2NH₂)/PLLA, PEG(2CH₃)/PLLA, PEG(1OH-1CH₃)/PLLA, and PEG(2OH)/PLLA.

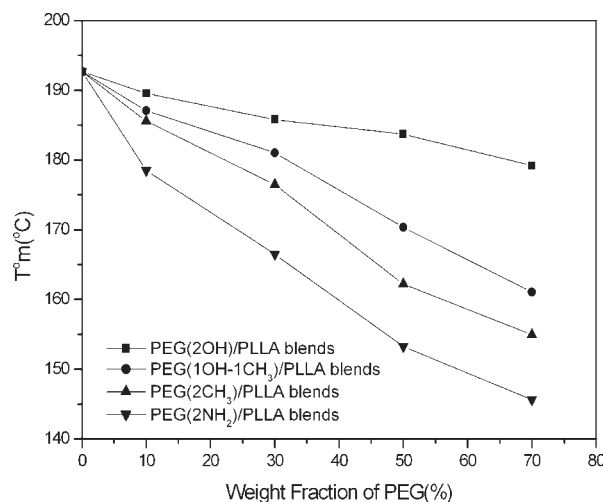


Figure 3 Equilibrium melting point (T_m^0) as a function of weight fraction of PEG(2OH, 1OH-1CH₃, 2CH₃, and 2NH₂)/PLLA blends.

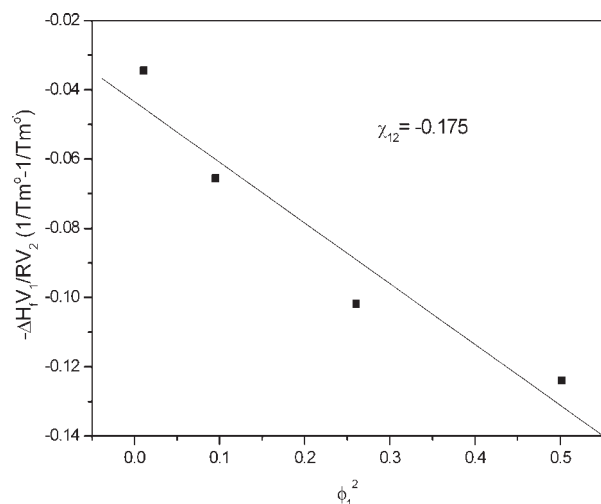


Figure 4 Relative plot of melting point depression and volume fraction of PEG(2NH₂)/PLLA blends according to Nishi-Wang equation.

As PEG(2OH) was blended with PLLA, the hydrogen bonding was expected to form between PEGs themselves, so the miscibility between PEG and PLLA decreased. Therefore, it was expected the miscibility decreases with more OH end groups.¹⁴ For the PEG(2NH₂)/PLLA blend system, the end groups (2NH₂) of PEGs should also form the hydrogen bonding by themselves, and the degree of miscibility of PEG(2NH₂)/PLLA blends could be reduced. However, from Table III, the degree of miscibility of PEG(2NH₂)/PLLA blends was the greatest. This could be explained by the existence of ions in the PEG(2NH₂)/PLLA blends. The resulting ionic interaction forces should be far greater than the hydrogen bonds or polar forces between polymer blends, so the degree of miscibility of PEG(2NH₂)/PLLA blends was the best.

Crystallization behaviors

Isothermal crystallization

The kinetics of isothermal crystallization has been analyzed in terms of the Avrami equation^{32–34} using the double logarithmic form:

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

TABLE III
Interaction Parameter (χ_{12}) of PEG/PLLA Blends

Samples	χ_{12}
PEG(2OH)/PLLA ^a	-0.048
PEG(1OH-1CH ₃)/PLLA ^a	-0.144
PEG(2CH ₃)/PLLA ^a	-0.161
PEG(2NH ₂)/PLLA	-0.175

^a The data was obtained from Ref. 14.

TABLE IV
The Values of n , K_n , and $t_{1/2}$ of PLLA for PEG(2NH₂)/PLLA Blends at 120°C

PEG(2NH ₂)/PLLA	n	k_n	$t_{1/2}$ (s)
0/100	3.46	5.66×10^{-4}	648.0
10/90	3.83	5.91×10^{-3}	290.4
30/70	3.75	1.59×10^{-3}	374.4
50/50	3.54	9.66×10^{-4}	415.2

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 $t_{1/2}$.

Table IV presents the values of n , K_n , and $t_{1/2}$ in the Avrami equation for PEG(2NH₂)/PLLA blends isothermally crystallized at 120°C. Only PLLA can crystallize at this temperature. The value of $t_{1/2}$ first increased and then decreased with the increase of PEG contents. The addition of PEG, which causes depression in the equilibrium melting point (T_m^0), reduced the driving force of crystallization ($T_m^0 - T_c$). In contrast, PEG would lower the system's glass transition temperature (T_g), which increased the segmental mobility of PLLA. These two factors are competitive, so the isothermal crystallization rate of PLLA first increased and then decreased as the PEG content increased. For PEG(2OH)/PLLA, PEG(1OH-1CH₃)/PLLA, and PEG(2CH₃)/PLLA blends, similar results were found.¹⁴

Table V lists the values in the Avrami equation ($t_{1/2}$) for PEG(2OH, 1OH-1CH₃, 2CH₃, and 2NH₂)/PLLA 10/90 isothermally crystallized at 120°C. PLLA in the PEG(2NH₂)/PLLA blend system exhibited the fastest isothermal crystallization rate, followed by that in the PEG(2OH)/PLLA, PEG(1OH-1CH₃)/PLLA, and PEG(2CH₃)/PLLA blend systems.

The glass transition temperature (T_g) and equilibrium melting point (T_m^0) are general factors to influence the crystallization rate of a polymer.³⁵ In this study, the T_g s of different end groups of PEG blended with PLLA should be very similar.¹⁴ Therefore, it was expected that T_m^0 was the dominant factor affecting the crystallization rate of PLLA. The experimental results of the equilibrium melting point depression of PLLA (Fig. 3) indicated that T_m^0 of

TABLE V
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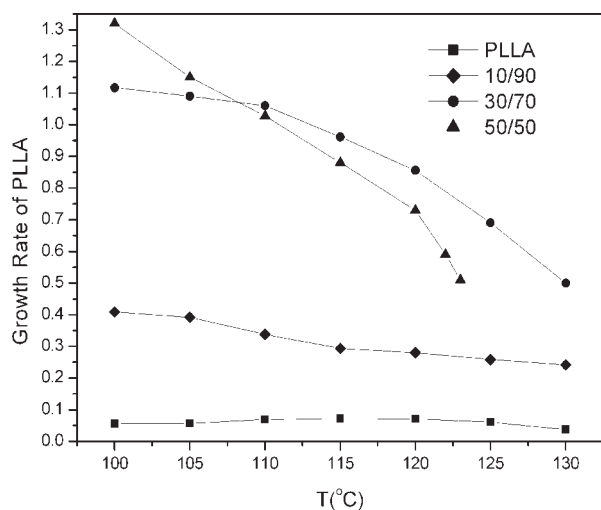


Figure 5 The spherulitic growth rate G of PLLA versus crystallization temperature PEG(2NH₂)/PLLA blends.

PLLA in the blends in decreasing order were PEG(2OH)/PLLA, PEG(1OH-1CH₃)/PLLA, PEG(2CH₃)/PLLA, and PEG(2NH₂)/PLLA. When the T_m^0 of PLLA was depressed, the degree of supercooling ($T_m^0 - T_c$) of PLLA was reduced. In general, the crystallization rate increases first and then decreases with increasing supercooling. However, because the chosen crystallization temperature (120°C) was close to the melting point of PLLA, the crystallization rate of PLLA would increase with increasing supercooling in this region. Therefore, the isothermal crystallization rate of PLLA in the decreasing order should be PEG(2OH)/PLLA, PEG(1OH-1CH₃)/PLLA, PEG(2CH₃)/PLLA, and PEG(2NH₂)/PLLA. Yet the crystallization rate of PLLA in the PEG(2NH₂)/PLLA blend system was the fastest and not coincident with the degree of supercooling. The reason will be discussed in the next section.

Spherulitic growth rate

The spherulitic growth rate (G) of PLLA was measured by observing the evolution of POM images over time. Figure 5 displays the spherulitic growth rate of PLLA for various compositions as a function of T_c for PEG(2NH₂)/PLLA blends. Only PLLA can crystallize at these temperatures, and PEG cannot. The variation of PLLA spherulite radius with time was linear in all cases, which meant that the concentration of PLLA at the growth front was constant during the crystallization process. This result suggested that PEG and uncrystallized PLLA could be trapped in the intraspherulitic regions. From these curves in Figure 5, it emerged that the addition of PEG mostly caused the increase in the spherulitic growth rate. The growth rate was also affected by

two effects: (i) The dilution of PLLA as well as depression in equilibrium melting point reduced the crystallization driving force. (ii) The segmental mobility of PLLA was increased when PLLA was blended with PEG. Thus, the increased segmental mobility was obviously the major effect. However, the spherulitic growth rate of PLLA of the composition 30/70 was higher than that of the composition 50/50 as the temperature was above the 110°C. Since the equilibrium melting point of PLLA in PEG(2NH₂)/PLLA 50/50 was only 153.24°C (Fig. 3), effect (i) could be a dominant factor when the crystallization temperature was higher and close to the equilibrium melting point. Thus, the spherulitic growth rate of PLLA would be reduced. In contrast, for PEG(2OH)/PLLA, PEG(1OH-1CH₃)/PLLA, and PEG(2CH₃)/PLLA blends, all the spherulitic growth rate of PLLA increased with PEG content.¹⁴ As for the blends of PEG weight fraction higher than 50%, the spherulite of PLLA was hard to measure because of the dilution of PLLA. Furthermore, the trend in Figure 5 does not coincide with that showed in Table IV. This was due to the fact that isothermal crystallization kinetics investigated by DSC represents the bulk crystallization rate, which involves both the nucleation density and the spherulitic growth rate.¹⁴

Figure 6 plots the effect of end groups of PEG on spherulitic growth rate, G , as a function of T_c for PEG(2OH, 1OH-1CH₃, 2CH₃ and 2NH₂)/PLLA blends with 50/50 composition. The spherulitic growth rate of PLLA in PEG/PLLA blends in the decreasing order were PEG(2NH₂)/PLLA, PEG(2OH)/PLLA, PEG(1OH-1CH₃)/PLLA, and PEG(2CH₃)/PLLA. The results were coincident with the isothermal crystallization rate observed by DSC. This could also be explained by T_m^0 and T_g . Because

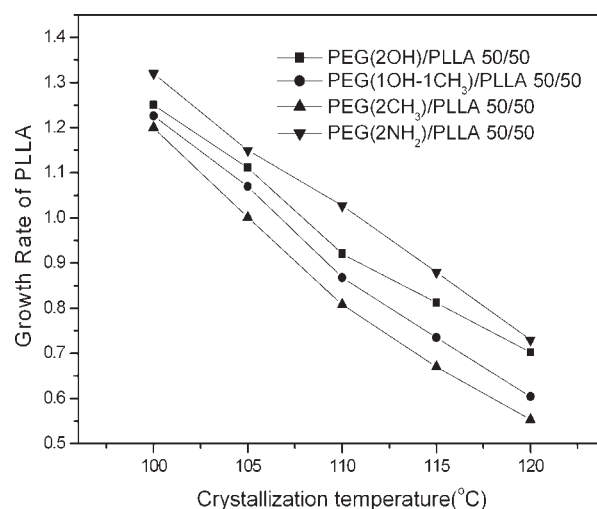


Figure 6 The spherulitic growth rate G of PLLA versus crystallization temperature for PEG(2OH, 1OH-1CH₃, 2CH₃, and 2NH₂)/PLLA 50/50 blends.

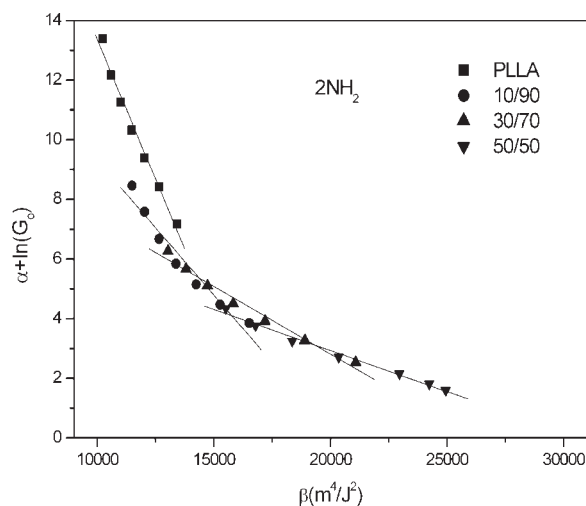


Figure 7 Growth rates analyzed using Lauritzen-Hoffman equation of PEG(2NH₂)/PLLA blends.

the end groups of PEG blended with PLLA did not affect T_g , T_m^0 was the dominant factor. In the PEG(2CH₃)/PLLA blend system, PLLA had a greatly depressed equilibrium melting point and the least degree of supercooling, so the spherulitic growth rate of PLLA was the slowest. Again, the fastest spherulitic growth rate of the PEG(2NH₂)/PLLA blend system could not be explained by the above rationale.

The kinetic theory of polymer crystallization developed by Hoffman et al.^{36–38} has been used to analyze experimental crystallization data regarding the spherulitic growth rate. According to this theory, the crystallization rate of a polymer is influenced by the fold surface free energy besides T_m^0 and T_g . The final results can be described by the following equation (the detailed equations were listed in Ref. 14):

$$G_m = \phi_2 G_0 e^{\frac{-\Delta E}{R(T_c - T_\infty)}} e^{\frac{\Delta h_{uf}}{RT_c}} \left(1 - \frac{T_c}{T_m^0} \frac{RT_c V_{2u}}{\Delta h_{uf} V_{1u}} \chi_{12} (1 - \phi_2)^2 \right)^{\frac{-nb\sigma_u \sigma_e / k_B T_c}{}} \quad (5)$$

Simplifying the double-logarithmic form of eq. (5) yields

$$\alpha = -\sigma_u \sigma_e \beta \quad (6)$$

where

$$\alpha = \ln G_m - \ln \phi_2 - \ln G_0 + \frac{\Delta E}{R(T_c - T_\infty)} \quad (7)$$

and

$$\beta = \frac{nb/k_B T_c}{\left[\Delta h_{uf} \left(\frac{\Delta T}{T_m^0} \right) - \frac{RT_c V_{2u}}{V_{1u}} \chi_{12} (1 - \phi_2)^2 \right]} \quad (8)$$

The plot of $(\alpha + \ln G_0)$ against β will give the $\sigma_u \sigma_e$ in the slope. The values of various parameters

involved in eqs. (6)–(8) were obtained in Ref 14. Figure 7 displays the L-H plot for PEG(2NH₂)/PLLA blend. Table VI shows the fold surface free energy of PLLA in PEG(2OH,1OH-1CH₃, 2CH₃, and 2NH₂)/PLLA blends. For the same composition, the PEG(2NH₂)/PLLA blend system had the least fold surface free energy. The fold surface free energy, instead of T_m^0 or T_g , may be a dominant factor affecting the crystallization rate of PLLA in the PEG(2NH₂)/PLLA blend system. It was assumed that the ionic interaction formed only at the chain ends of PEG(NH₂) and PLLA. In comparison, hydrogen bonds could form at various sites along the chains in the other PEG/PLLA blend systems. The folding of PLLA blended with PEG(2NH₂) could be different. As a result, the fold surface free energy played an important role on the crystallization rate of PLLA for the PEG(2NH₂)/PLLA blend system. The lower fold surface free energy of PLLA meant more flexible chains and faster crystallization rate of PLLA. Hence PLLA in the PEG(2NH₂)/PLLA blend system had the fastest crystallization rate.

CONCLUSIONS

For PEG(2NH₂)/PLLA blends, the conductivity and dielectric data implied the existence of ions. It was due to the amine groups of PEG gaining the protons from the carboxylic acid groups of PLLA. From the DSC results, the equilibrium melting point depression of PLLA and a negative interaction parameter indicated that PEG(2NH₂) and PLLA were miscible in the whole range of composition. The miscibility should be contributed by the ionic interaction. The isothermal crystallization rate and spherulitic growth

TABLE VI
The Values of $\sigma_u \sigma_e$ Products for PEG/PLLA Blends

Samples	Composition	$\sigma_u \sigma_e$ (erg ² /cm ⁴)	σ_e (erg/cm ²)
PEG(2OH)/PLLA ^a	0/100	7830	546
10/90	10/90	5400	376
30/70	30/70	3860	269
50/50	50/50	2820	197
PEG(1OH-1CH ₃)/PLLA ^a			
10/90	10/90	4950	345
30/70	30/70	3620	252
50/50	50/50	1940	135
PEG(2CH ₃)/PLLA ^a			
10/90	10/90	4600	321
30/70	30/70	2580	180
50/50	50/50	1390	97
PEG(2NH ₂)/PLLA			
10/90	10/90	3880	270
30/70	30/70	1760	123
50/50	50/50	1050	73

Remarks: The lateral surface energy (σ_u) = 14.35 erg/cm².¹⁴
^a The data was obtained from Ref. 14.

rate of PLLA in PEG(2NH₂)/PLLA blends were affected by two temperatures (T_g and T_m^0).

The miscibility and crystallization behaviors of PEG(2NH₂)/PLLA blends were different from those of PEG(2OH,1OH-1CH₃, and 2CH₃)/PLLA blends. The PEG(2NH₂)/PLLA blend system has the best miscibility because of the ionic interaction. In all the PEG/PLLA blend systems studied, the ionic interaction occurred only in the PEG(2NH₂)/PLLA blend system. In addition, the ionic interaction formed at the chain ends of PEG(NH₂) and PLLA, while the hydrogen bonds would form at various sites along the chains of PEG(2OH, 1OH-1CH₃, or 2CH₃) and PLLA. The ionic interaction influenced the isothermal crystallization rate and spherulitic growth rate of PLLA. PLLA in the PEG(2NH₂)/PLLA blend system had the lowest fold surface free energy, and therefore the crystallization rate was the fastest.

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