Isothermal Crystallization Behaviour and Mechanical Properties of Poly(L-lactic Acid)/Talc/Ethylene *bis*-Stearamide Composites

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Talc is very effective on the enhancement of crystallization of poly(L-lactic acid) (PLLA) and can retain fine mechanical properties with addition of ethylene *bis*-stearamide (EBS), thus, PLLA/talc/EBS composites were prepared to improve the crystallization rate and retain fine mechanical properties of material. Compared to the neat PLLA at 110 ºC, upon the addition of 10 % talc and 3 % EBS, the induction period of poly(L-lactic acid) decreased from 4.0-0.4 min and half time of overall crystallization decreased from 10-1.8 min at 101 ºC. The Avrami theory was used to describe the kinetic of isothermal crystallization of PLLA/talc/EBS composites. PLLA/talc/EBS composites not only take a heterogeneous nucleation process followed by a three-dimensional crystal growth but also have other complicated nucleation mechanism. Scanning electron microscopy showed that addition of talc enhanced compatibility between poly(L-lactic acid) and ethylene *bis*-stearamide. The mechanical results showed that addition of high content of talc significantly weakened the mechanical properties of biodegradable poly(L-lactic acid). However, Adding ethylene *bis*-stearamide to poly(L-lactic acid)/talc composites can retain fine mechanical properties of biodegradable poly(L-lactic acid).

Key Words: PLLA, Isothermal crystallization, Mechanical properties, Composites.

INTRODUCTION

With the increasing public attention to environmental problems, the research of biodegradable polymers has gained considerable momentum in recent years[1-5]. Usually, poly(L-lactic acid) (PLLA) is produced from renewable resources such as corn, potato, *etc.*[6], with lower energy consumption, biopolymer and non-toxic to the environment[7]. However, PLLA has some disadvantages that restrict its practical applications, including brittle properties and low crystallization rate. In many applications, slow crystallization rate and poor heat resistance are sometimes too weak for practical use compared to the conventional thermoplastic. Thus, it is necessary to improve the crystallization rate and heat resistance of PLLA.

Usually, the most viable method to increase the overall crystallization rate is the blending with nucleating agent. Cai *et al.*[8] studied the isothermal crystallization behaviour of blends of PLLA with a small amount of N,N'-*bis*(benzoyl) suberic acid dihydrazide (NA). With incorporation of N,N'-*bis*(benzoyl) suberic acid dihydrazide, the crystallization peak became sharper and shift to higher temperature as the degree of super-cooling decreased at a cooling rate of 1 ºC/min from melt. Upon the addition of 0.8 % N,N'-*bis*(benzoyl) suberic acid dihydrazide, the crystallization half-time of PLLA/NA decreased

from 26.5-1.4 min at 115 ºC. Talc was widely used nucleating agent. It was shown that talc nucleates the crystallization of polymers through an epitaxial mechanism[9]. Kolstad studied the crystallization behaviour and the morphology of poly(L-lactide-co-meso-lactide) and poly(L-lactide-co-meso-lactide)/talc composites[10]. His work has shown that strong increase in nucleation density with addition of talc was found in poly(L-lactide-co-meso-lactide). Tianyi's work showed that the crystallization half-time can be reduced by more than one order of magnitude when 1 % talc is added[11]. The overall crystallization rate of PLLA increase with increasing content of talc. However, PLLA/talc composites with high content of talc become brittle. Angela *et al.*[12] reported that ethylene *bis*-stearamide (EBS) can improved mechanical performance of poly(L-lactic acid).

In this paper, in order to increase the overall crystallization rate and retain fine mechanical properties of PLLA, PLLA/talc/EBS composites were prepared by counter-rotating mixture and hot-press forming process. The isothermal crystallization behaviour of PLLA/talc/EBS composites was investigated by depolarized light intensity technique and the Avrami theory was used to describe the kinetic of isothermal crystallization of PLLA/talc/EBS composites. Upon addition of talc, the compatibility between PLLA and EBS was investigated by scanning

electron microscopy and the mechanical properties of PLLA/talc/EBS composites were examined.

EXPERIMENTAL

Poly(L-lactic acid) (PLLA) (Mw = 1.95×10^5) was purchased from Nature Works LLC, USA. Talc was obtained from YueJiang Chem, Shanghai, China. Ethylene *bis*-stearamide (EBS) was purchased from Chengdu Kelong Chemical Reagents Company, Sichuan, China.

Preparation of composites: PLLA, EBS and talc were dried over night at 60 ℃ under vacuum to remove residual water. Blending of PLLA, talc and EBS was performed on a counter-rotating mixer with a rotation speed of 32 rpm for 5 min, then at 64 rpm for 5 min. The processing temperature was set at 180 ℃ but it increased to 185 ℃ upon mixing. Products were hot pressed at 180 ℃ under 20 MPa for 3 min to prepare sheets. The sheets were then cooled down by being compressed at room temperature under 20 MPa for 10 min.

Characterization: The overall isothermal crystallization behaviour of PLLA was investigated by GJY-III optical depolarizer (DongHua University, Shanghai, China) in the region from 99-115 ℃.

Tensile properties were carried out on an tensile machine (YX-25(D), China) at a crosshead speed of 10 mm/min. The measurement of impact strength was performed on impact testing machine (JJ-20, China).

Freeze-fracture surfaces of neat PLLA and composites were observed by scanning electron microscope (S4800, Hitachi, Ltd. Japan).

RESULTS AND DISCUSSION

Overall isothermal crystallization behaviour: Traditionally, isothermal crystallization behaviour can be investigated by using depolarized-light intensity[13] technique as the transmitted light intensity (I) increases with the increasing of crystallinity and finally levels off when crystallization completes. In our research, we used the relative light intensity (I_r) defined by the following equation as an index of crystallinity:

$$I_r\ (\%) = 100 \times \frac{(I_t - I_0)}{(I_\infty - I_0)} \tag{1}$$

where I_t and I_0 are the I values at t_c = t and 0, respectively, I_∞ is the I value when crystallization completes. Fig. 1 shows the effect of the composition and the crystallization temperature (T_c) against the induction period t_i and the half time of overall PLLA crystallization $t_{1/2}$. With the increasing of crystallization temperature, t_i become shorter due to the enhancement of the macromolecule segment active ability. However, it is hard for PLLA to form the spherulite if the T_c is too high, because the excessive macromolecule segment activity restricts the formation of spherulite and the t_i become longer. On the other hand, t_i also change with the different composition of composites and t_i decrease from 4 min to minimum value 0.4 min, with 10 % talc and 3 % EBS at 101 ℃, Compared to the neat PLLA at 110 ℃ (optimal crystallization temperature). Furthermore, t_i of PLLA/10 %talc composites is faster than that of PLLA/3 % EBS composites, which show talc is more effective on the enhancement of crystallization of PLLA. It is clear that $t_{1/2}$

have same trend with t_i. As shown in Fig. 1, the $t_{1/2}$ of PLLA/talc/EBS composites samples crystallizing at 101 ℃ is the minimum value 1.8 min.
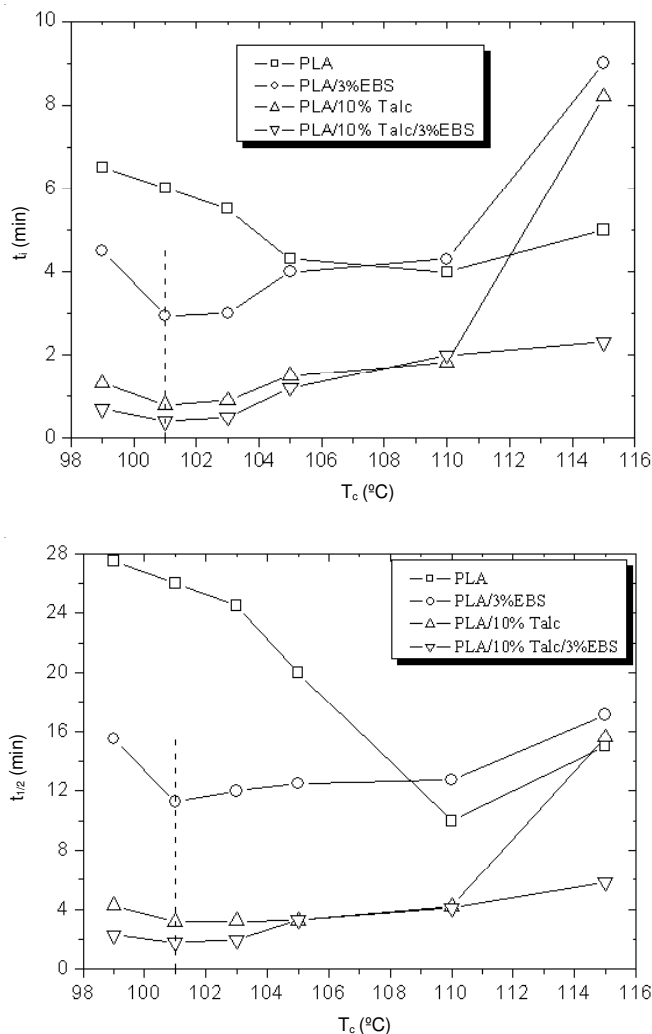

Fig. 1. t_i and $t_{1/2}$ for composites with different composition plotted as a function of T_c

The polymer isothermal crystallization process can be described by the following Avrami equation[14]:

$$1 - \frac{X_c}{100} = \exp(-kt^n) \tag{2}$$

where k is the crystallization rate constant (min^{-1}) and n value is the Avrami exponent. $X_c(t)$ represents the percentage of relative crystallization after time t. Eqn. 2 can be transformed to eqn.

$$\log\left[-\ln\left(1 - \frac{X_t}{100}\right)\right] = \log k + n \log t \tag{3}$$

In this study, we used I_r as X_c in eqn. 3. Fig. 2 shows the Avrami plots of PLLA/3 % EBS, PLLA/10 % talc and PLLA/10 % talc/3 % EBS composites. Obtained the kinetic parameters n and k values of neat PLLA, PLLA/3 % EBS, PLLA/10 % talc and PLLA/10 % talc/3 % EBS are listed in Table-1. It is generally agreed that Avrami exponent n depends on the nucleation and growth mechanisms of spherulites. For the spherulite three-dimensional growth, n is 4 in homogeneous
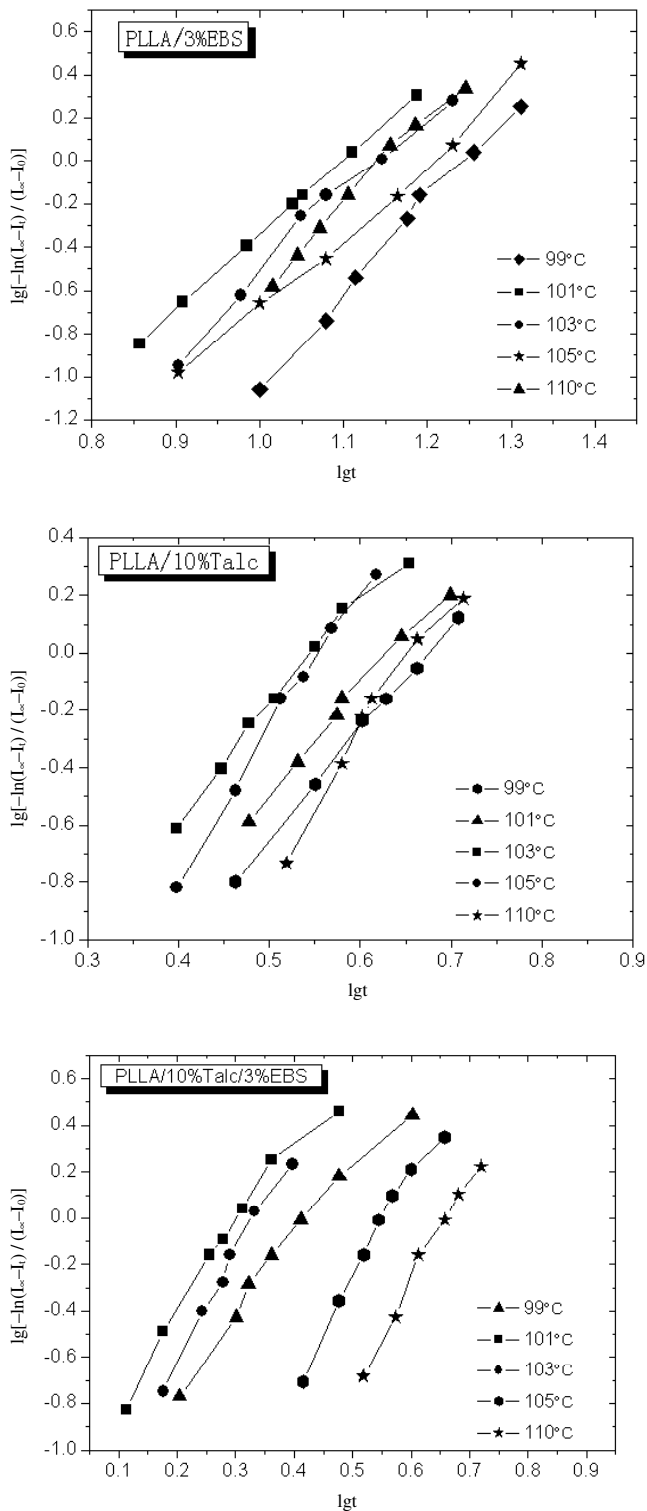
Fig. 2. Avrami plots for PLLA/3 % EBS, PLLA/10 % talc and PLLA/10 % talc/3 % EBS composites at different temperature

TABLE-1
ISOTHERMAL CRYSTALLIZATION
PARAMETERS OF SAMPLES

Sample	T_c (ºC)	n	log K
Poly(L-lactic acid) (PLLA)	99	4.2	-6.1135
	101	3.7	-5.6595
	103	3.9	-5.5237
	105	3.6	-5.7258
	110	4.1	-5.2848
PLLA/3 % EBS	99	4.3	-5.3359
	101	3.4	-3.8004
	103	3.7	-4.2655
	105	3.4	-4.0339
	110	4.1	-4.6768
PLLA/10 % Talc	99	3.7	-2.5191
	101	3.6	-2.2898
	103	3.7	-2.0394
	105	5.0	-2.7981
	110	4.8	-3.1491
PLLA/10%Talc/3%EBS	99	3.0	-1.3149
	101	3.5	-1.1260
	103	4.5	-1.5053
	105	4.4	-2.4835
	110	4.6	-3.0372

For PLLA/EBS, PLLA/talc, PLLA/talc/EBS smaple, the n values range between 3 and 5 as the increasing T_c, representing that PLLA/talc/EBS composites not only take a heterogeneous nucleation process followed by a three-dimensional crystal growth but also have other complicated nucleation mechanism[8]. The k values have a similar trend with the $t_{1/2}$ values and have the largest values in the case of PLLA/10 % talc/3 % EBS at 101 ºC.

Fig. 3 shows the SEM images of the freeze-fracture surfaces of neat PLLA and composites with different composition. Neat PLLA shows a smooth freeze-fracture surface in Fig. 3A. Fig. 3B shows PLLA/EBS composites which have non-uniform particles with large diameter. These particles might be EBS particles in PLLA matrix because as the less content dispersed phase EBS is immiscible with PLLA. Fig. 3C shows PLLA/talc composites also has small particles. Although phase-separated particles also can be seen in PLLA/talc/EBS composites (Fig. 3D), the size of them has slightly decreased. From the results listed above, it is quite interesting that talc plays a role as compatibilizer. This phenomenon may mainly be due to the intercalation of polymer molecules in talc which
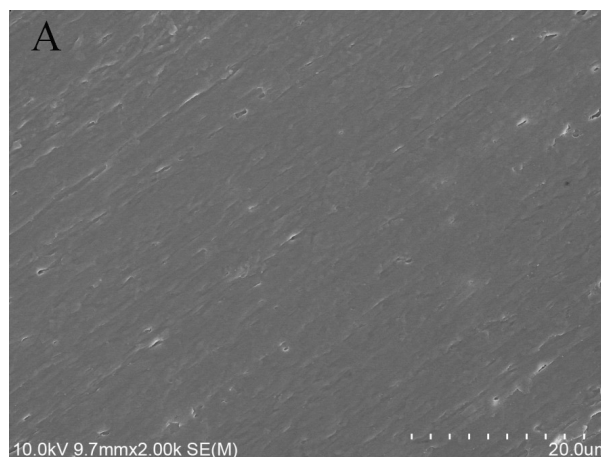
nucleation system and 3 in heterogeneous nucleation system. n should be integer but always are decimal fraction[15]. It might be due to the presence of crystalline branching and/or two stage crystal growth during the crystallization process and/or mixed growth and nucleation mechanism[16]. From Table-1 we can see that most of n are non-integral values between 3.0 and 5.0. The n values of pure PLLA are around 4 in Table-1 shows that pure PLLA follow the homogeneous nucleation mechanisms.

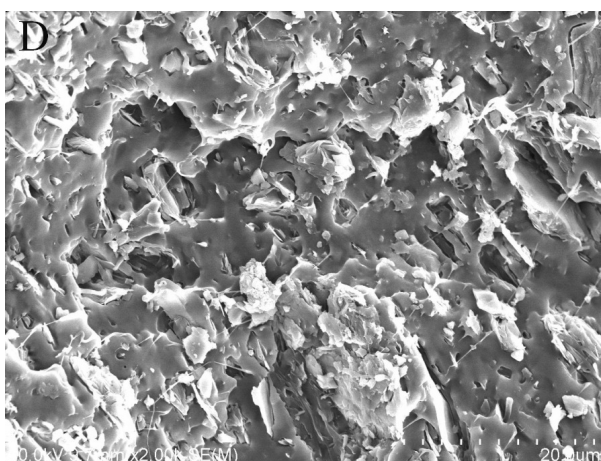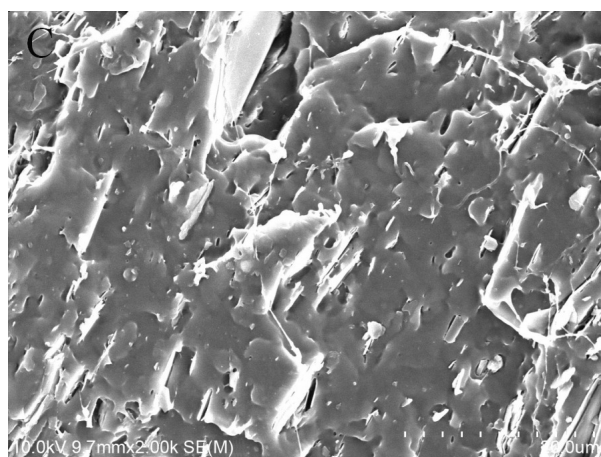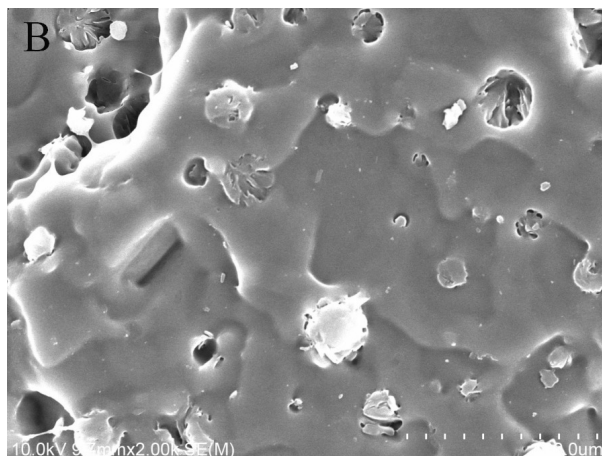|	TABLE-2			
	MECHANICAL PROPERTIES OF POLY(L-LACTIC ACID) (PLLA) AND ITS COMPOSITES			
Sample	Impact strength (KJ/m^2)	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)
PLLA	14.5 ± 1.7	47.6 ± 2.4	3125 ± 40.5	5.2 ± 0.63
PLLA/3 % EBS	18.9 ± 1.9	56.1 ± 1.5	2782.4 ± 72.6	6.99 ± 1.5
PLLA/10 % Talc	11.6 ± 2.3	58.7 ± 1.6	1336.8 ± 59.7	2.31 ± 0.33
PLLA/10 % Talc/3 % EBS	17.2 ± 2.5	49.5 ± 0.6	2422.7 ± 54.1	5.45 ± 0.8

increases the viscosity ratio and results in the retardation of coalescence of the dispersed phase-separated particles and the enhanced compatibility.

The static mechanical properties of neat poly(L-lactic acid) and its composites were investigated by the tensile and impact test. As seen in Table-2, PLLA/10 % talc composites has maximum value 58.7 MPa of tensile strength, However, the tensile modulus is minimum, Although PLLA/3 % EBS composites are nearly the same with the mechanical properties of neat poly(L-lactic acid), crystallization rate is slow. As seen in Table- 2, PLLA/10 % talc/3 % EBS composites not only increase crystallization rate, but also retain fine mechanical properties of material.

ACKNOWLEDGEMENTS

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Fig. 3. SEM images of the freeze-fracture surfaces of neat poly(L-lactic acid) (PLLA) and its composities