

Nonisothermal Crystallization Kinetics of Modified Bamboo Fiber/PCL Composites

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ABSTRACT: The nonisothermal crystallization kinetics of modified bamboo fiber/polycaprolactone (MBF/PCL) composites was investigated by differential scanning calorimetry (DSC) at different cooling rates. The results were studied by a direct fitting of the experimental data to various macrokinetic models, namely, Avrami, Ozawa, and Mo models. Both the Avrami analysis modified by Jeziorny and the method developed by Mo could describe the nonisothermal crystallization of the composites very well, but the Ozawa analysis

could not give an adequate description. Kinetic parameters such as the Avrami exponent (n), the kinetic crystallization rate constant (Z_c), the peak temperatures (T_{peak}) and the half-time of crystallization ($t_{1/2}$) etc. were determined at various scanning rates. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 2119–2125, 2010

Key words: PCL; bamboo fiber; nonisothermal crystallization kinetics; DSC

INTRODUCTION

Currently polycaprolactone (PCL) was the most widely used commercial polymer. Because the social demands for degradable and biocompatible polymers were rapidly increasing, especially in the packaging sector where it was highly encouraged by environmental management policies.¹ PCL was a type of synthetic, biodegradable polyester that was compatible with many types of polymers and it was one of the most promising biodegradable polymers currently available on the market.^{2,3} High costs and low melting temperature ($T_m \sim 60^\circ\text{C}$) were, however, the main limitations preventing the PCL widespread industrial use. To overcome these problems, PCL was usually mixed with other low cost biodegradable polymers.^{4,5}

Bamboo, one of the strongest natural structural composite materials, has many distinguishing features. Because of the high water-repellent properties, the high flexibility, the high strength, the low weight, the fast-growing, and the low purchasing

costs, bamboo became more and more popular as a building material with many opportunities.^{6,7} In this article, bamboo fiber were made from waste bamboo scrap. In this way, the environment was protected and the waste was avoided.

Modified bamboo fiber/polycaprolactone (MBF/PCL) composite as a wood polymer composite was few investigations currently. When proper coupling agents were used to improve fiber-matrix adhesion, bamboo fiber can also be used to reinforce the PCL. There were also economical and environmental reasons for replacing part of the PCL with bamboo fiber. For example, the MBF added into PCL was beneficial to reduce costs, avoid environmental pollution and increase stiffness of composites. The stiffness was an advantage in certain areas of practice. In addition, the melting temperature and onset temperature of crystallization of the MBF/PCL composites shifted to higher by adding MBF into PCL. It has a great significance in practice.

The crystallization behavior of polymer was a basic problem in polymer physics. Especially the filler in the polymer would affect the crystallization behavior of the polymer-based composites deeply.⁸ The crystallization behavior of polymer was usually studied by differential scanning calorimetry (DSC) method. The crystallization process can proceed under either isothermal conditions or nonisothermal conditions. Most frequently, the investigations were conducted under isothermal conditions because of

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the convenience of the theoretical treatment of the data. In fact, polymer and composite usually undergo a nonisothermal crystallization processing, especially in practical process. There were many articles on studying the crystallization kinetics of polycaprolactone or polycaprolactone composites.^{9–11} Investigation of crystallization behavior can serve as a guide for process and application. To be relevant to industrial processing, it was desirable to study the crystallization of MBF/PCL composites under nonisothermal conditions because the isothermal crystallization conditions were rarely met during the practical process.

EXPERIMENTAL

Materials

Bamboo fiber (BF) with the size of 74 μm was provided by Research Institute of comprehensive utilization of Biomaterials, Huazhong Agricultural University, China. Having been dried in 120°C for 24 h, the surface of BF was modified by silane coupling agent (SG-Si900) (BF/SG-Si900 100/2 by weight), which was purchased from Nanjing Shuguang Chemical, before using. Meanwhile, PCL ($M_n = 70,000$) pellets were acquired from Daicel Chemical Industries, Japan.

Preparation of MBF/PCL composites

The PCL and bamboo fiber modified with silane coupling agent were mixed by the Stirring Kneader (NH-20 Rugao Tong-da Machinery Manufacturing, China) at 80–85°C for 15–20 min. The acquired sheet was compressing molded at 100°C into 1 mm thick sheet under a pressure of 9 MPa for 15 min, and then kept at room temperature. The ratios of MBF/PCL particle were 0/100; 20/100; 40/100; 60/100; 80/100; 100/100 by weight, respectively.

Thermal measurements

The nonisothermal crystallization kinetics of MBF/PCL composites was carried out on a Nexus DSC 204F1 in nitrogen atmosphere. The temperature and melting enthalpy were calibrated with standard indium at each cooling rate in the measurement. The samples of 5–10 mg were encapsulated into aluminum pans and were heated first up to 100°C rapidly from 20°C and kept this temperature for 5 min to eliminate the thermal history of samples. Then the samples were cooled down to 0°C at four different cooling rates of 2.5, 5, 10, and 15°C/min, respectively.

RESULTS AND DISCUSSION

Theoretical background

The relative crystallinity (X_t) as a function of temperature was defined as the following equation:

$$X_t = \frac{\int_{T_0}^T (dH_c/dT)dT}{\int_0^\infty (dH_c/dT)dT} \quad (1)$$

where T_0 and T_8 were the onset and the end of crystallization temperature, respectively. dH_c/dT was the heat flow at temperature T .

The half-time of crystallization ($t_{1/2}$) was the time required for 50% crystallization. The smaller the value of $t_{1/2}$, the faster the crystallization rate.

The kinetic parameters of nonisothermal crystallization were determined, based on the simplified assumption that crystallization occurred under constant temperature. In this case, the Avrami equation can be used:^{12–14}

$$1 - X_t = \exp(-Z_t t^n) \quad (2)$$

where n was the Avrami crystallization exponent, which was a dimensionless constant and related with the nucleation and growth mechanisms. Z_t was a crystallization rate constant, and X_t was relative crystallinity of polymers at different temperatures or time, t was the time taken during the crystallization process. In our work, the relationship between time and temperature can be expressed as follows:

$$t = \frac{T_0 - T}{\phi} \quad (3)$$

where T was the temperature at crystallization time t , and ϕ was the cooling rate.

Using eq. (2) in double-logarithmic form

$$\ln[-\ln(1 - X_t)] = \ln Z_t - n \ln t \quad (4)$$

and plotting $\ln[-\ln(1 - X_t)]$ versus $\ln t$ for each cooling rate, a straight line was obtained. From the slope and intercept of the lines, we can determine the Avrami exponent n and the crystallization rate Z_t . Equation (2) was suitable for an isothermal crystallization system. Just like isothermal analysis, nonisothermal crystallization can also be analyzed by the Avrami equation, but considering the characterization of the process investigated, Jeziorny¹⁵ considered the effect of the cooling rate, Z_t was corrected by the cooling rate as follows:

$$\ln Z_c = \frac{\ln Z_t}{\phi} \quad (5)$$

where ϕ was the cooling rate, Z_c was the kinetic crystallization rate constant.

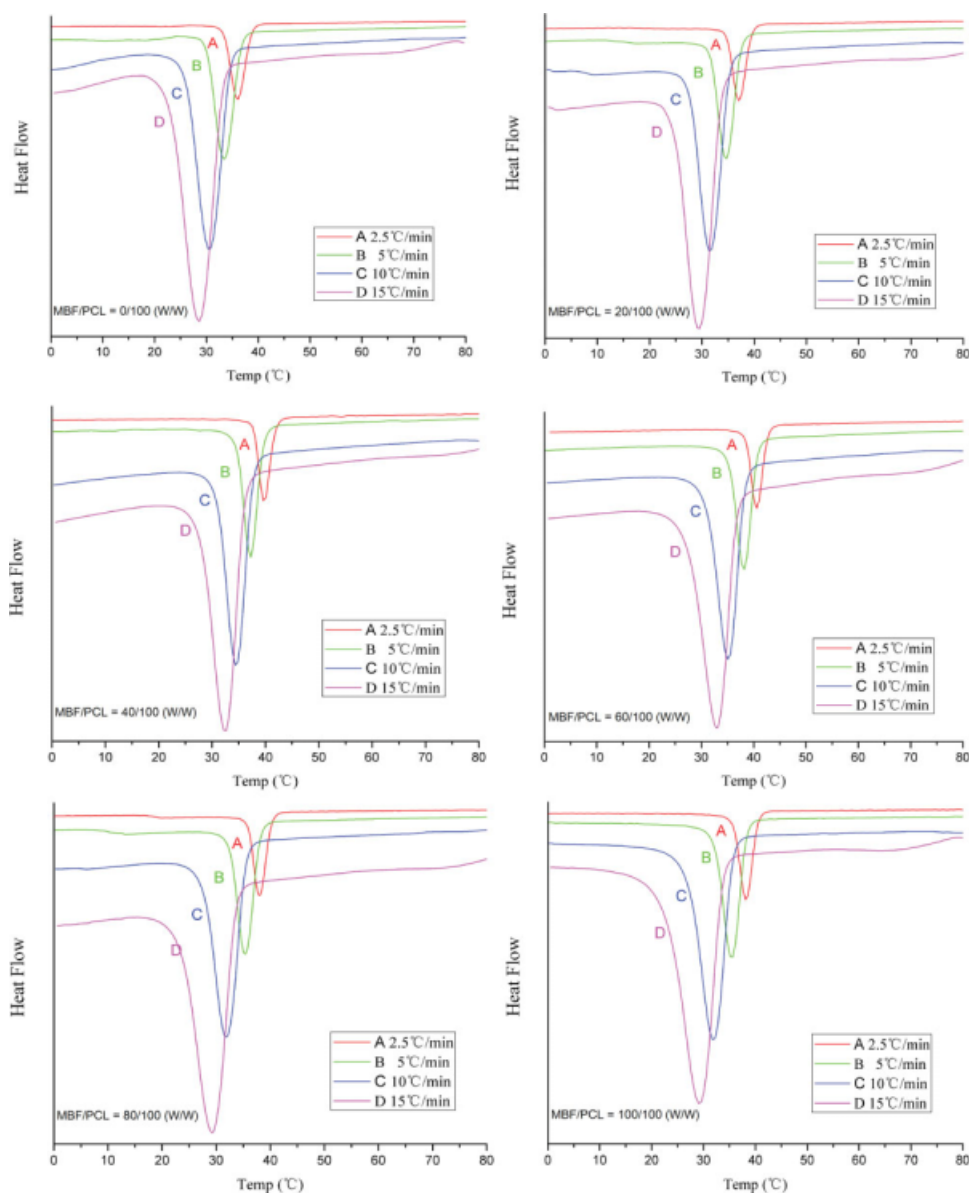


Figure 1 The DSC traces of samples nonisothermal crystallized at the specified cooling rate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Ozawa¹⁶ extended the Avrami equation based on derivation of Evans¹⁷ to describe the nonisothermal crystallization. The main difference compared to the Avrami model was that the time variable was replaced by a cooling rate ϕ . Assuming that the nonisothermal crystallization process may be composed of infinitesimally small isothermal crystallization steps, the following equation was derived:

$$1 - X_t = \exp[-K(T)/\phi^m] \quad (6)$$

or

$$\ln[-\ln(1 - X_t)] = \ln K(T) - m \ln \phi \quad (7)$$

where $K(T)$ was the crystallization rate constant, X_t was the relative crystallinity, ϕ was the cooling rate, and m was the Ozawa exponent depending on the crystal growth and nucleation mechanism. According to Ozawa's theory, the relative crystallinity, X_t , can be calculated from these equations. By drawing the plot of $\ln[-\ln(1 - X_t)]$ versus $\ln \phi$ at a given temperature, we should obtain a series of straight lines if the Ozawa analysis was valid, and the kinetic parameters m and $K(T)$ can be derived from the slope and the intercept, respectively.

A method modified by Mo was also employed to describe the nonisothermal crystallization, which combined the Avrami equation with the Ozawa equation. Its final form was given as follows:¹⁸

TABLE I
 T_{onset} , T_{peak} , $t_{1/2}$, n , Z_c at Different Cooling Rates

Samples	φ ($^{\circ}\text{C}/\text{min}$)	T_{onset} ($^{\circ}\text{C}$)	T_{peak} ($^{\circ}\text{C}$)	ΔH (J/g)	$t_{1/2}$ (min)	n	Z_c
MBF/PCL (0/100 W/W)	2.5	38.8	36.0	199.7	33.31	2.70	0.60
	5	36.6	33.4	207.8	21.04	2.49	2.42
	10	34.2	30.6	213.1	14.68	2.48	8.74
	15	32.7	28.5	212.2	12.48	2.07	10.55
MBF/PCL (20/100 W/W)	2.5	39.5	37.1	141.2	32.88	2.33	0.91
	5	37.5	34.6	144.4	20.79	2.46	3.00
	10	35.1	31.5	151.7	14.55	2.11	6.53
	15	34.3	29.4	153.1	12.41	2.47	11.68
MBF/PCL (40/100 W/W)	2.5	41.8	39.8	118.9	31.8	2.31	1.27
	5	39.5	37.2	114.6	20.28	2.14	3.40
	10	38.1	34.5	125.5	14.26	2.46	11.51
	15	35.8	32.4	125.1	12.23	2.24	20.72
MBF/PCL (60/100 W/W)	2.5	42.7	40.6	99.53	31.47	2.25	1.17
	5	40.5	38.1	102.4	20.1	2.01	2.90
	10	38.1	35.2	107.2	14.22	2.13	8.28
	15	35.9	32.9	118.3	12.23	2.18	17.24
MBF/PCL (80/100 W/W)	2.5	40.2	38	88.13	32.48	2.13	0.93
	5	38.0	35.3	91.03	20.64	2.15	2.91
	10	35.0	31.8	93.49	14.55	1.81	4.21
	15	33.0	29.3	93.1	12.47	2.34	16.84
MBF/PCL (100/100 W/W)	2.5	40.5	38.2	64.84	32.43	2.42	0.96
	5	38.4	35.4	66.49	20.62	2.24	2.15
	10	35.2	31.9	69.41	14.55	2.26	8.04
	15	33.0	29.2	69.45	12.48	2.25	12.45

$$\ln\varphi = \ln F(T) - \alpha \ln t \quad (8)$$

where the parameter $F(T) = [K(T)/Z_t]^{1/m}$, $F(T)$ refers to the value of cooling rate chosen at unit crystallization time when the system amounted to a certain degree of crystallinity. The smaller the value of $F(T)$ was, the higher the crystallization rate became. Therefore, $F(T)$ has a definite physical and practical meaning. α refers to the ratio of the Avrami exponent n to the Ozawa exponent m ($\alpha = n/m$). Plotting $\ln\varphi$ versus $\ln t$ yields a linear relationship between $\ln\varphi$ and $\ln t$. The data of kinetic parameter $F(T)$ and α can be estimated from the intercept and slope.

Nonisothermal crystallization behavior of PCL and MBF/ PCL composites

Nonisothermal crystallization exotherms of the pure PCL and MBF/ PCL composites at four cooling rates of 2.5, 5, 10, and 15 $^{\circ}\text{C}/\text{min}$ were shown in Figure 1. Some kinetic parameters can be derived from the DSC curves. They were the peak temperature (T_{peak}), the relative degree of crystallinity X_t , crystallization enthalpy ΔH_c , onset crystallization temperature (T_{onset}), which was the temperature at the crossing point of the tangents of the baseline and the high temperature side of the exotherm, and half crystallization time $t_{1/2}$, which were listed in Table I.

The effect of the different cooling rates was following: The decreased onset temperatures (T_{onset}) and half crystallization time ($t_{1/2}$) of both pure PCL

and MBF/PCL composites were observed when cooling rate increased. The faster the cooling rate, the lower the temperature at which the crystallization occurs. At slower cooling rate, there was sufficient time to activate nuclei at higher temperature. On the contrary, at faster cooling rates, there was not enough time on the activation of nuclei, so it occurred at lower temperature. The T_{onset} ($^{\circ}\text{C}$) of MBF/PCL composites shift to higher. It showed that the crystallization of composites occurred easier with the bamboo fiber increased. T_{peak} ($^{\circ}\text{C}$) and $t_{1/2}$ also proved this conclusion. The crystallization enthalpy ΔH_c increased as the cooling rate increases, but shifted to lower values when the MBF loading in the composites increases. It means that the crystallization of MBF/PCL composites became more imperfect than the pure PCL. The relative degree of crystallinity X_t was a function of temperature which was plotted in Figure 2. It can be seen that all these curves have the same reversed "S" shape. However, because of shorter crystallization time at a faster cooling rate, the values of X_t were lower than those at a slower cooling rate at the same crystallization temperatures.

NONISOTHERMAL CRYSTALLIZATION KINETICS OF MBF/ PCL COMPOSITES

Avrami method

Plots of $\ln[-\ln(1-X_t)]$ versus $\ln t$ for the nonisothermal crystallization of the pure PCL and the MBF/

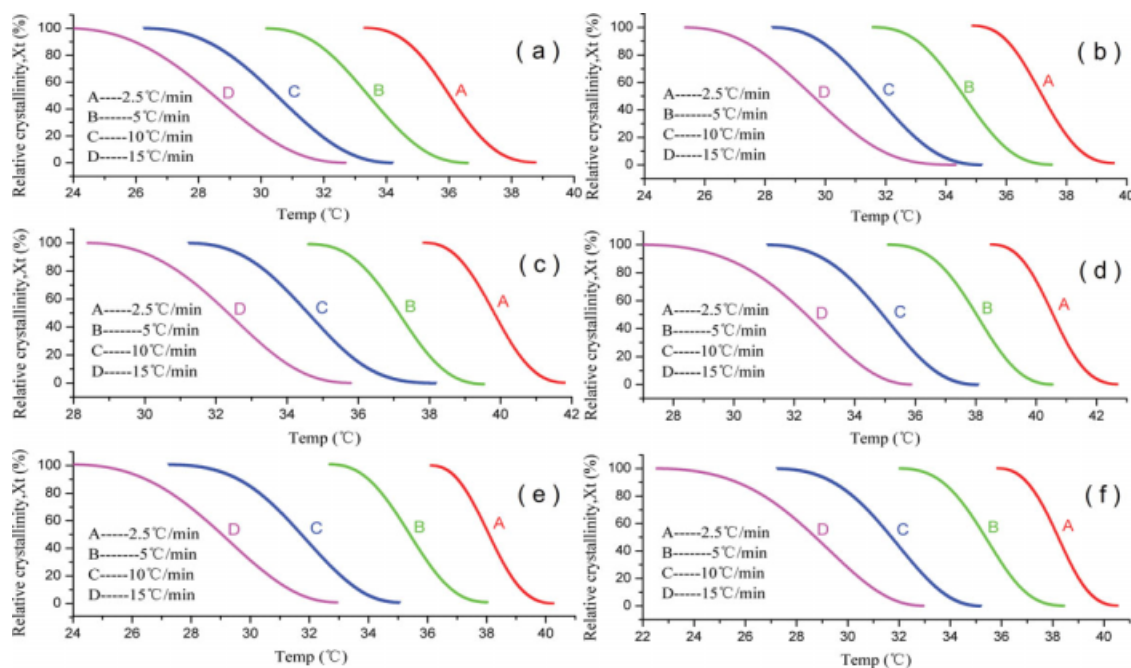


Figure 2 Plots of X_t versus T for the nonisothermal crystallization of the samples at the specified temperature: (a) MBF: PCL = 0 : 100; (b) MBF: PCL = 20 : 100; (c) MBF: PCL = 40 : 100; (d) MBF: PCL = 60 : 100; (e) MBF: PCL = 80 : 100; (f) MBF: PCL = 100 : 100. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

PCL composites (20/100, 60/100, and 100/100 W/W) at four cooling rates of 2.5, 5, 10, and 15 °C/min were shown in Figure 3. A good linear relationship was shown. Two adjustable parameters, Z_t and n , can be obtained by a linear regression. The Z_t and n parameters do not have the same physical meaning as in the isothermal crystallization, because the temperature varies constantly in nonisothermal crystal-

lization. This affects the rates of both nuclei formation and spherulite growth ascribed to their temperature dependence. Therefore Z_t must be calibrated to Z_c by Jeziorny method. The value of Z_c increases sharply with increasing the cooling rates for the pure PCL and the MBF/PCL composites. This showed that the faster cooling rate, the faster crystallization rate. The results were listed in Table

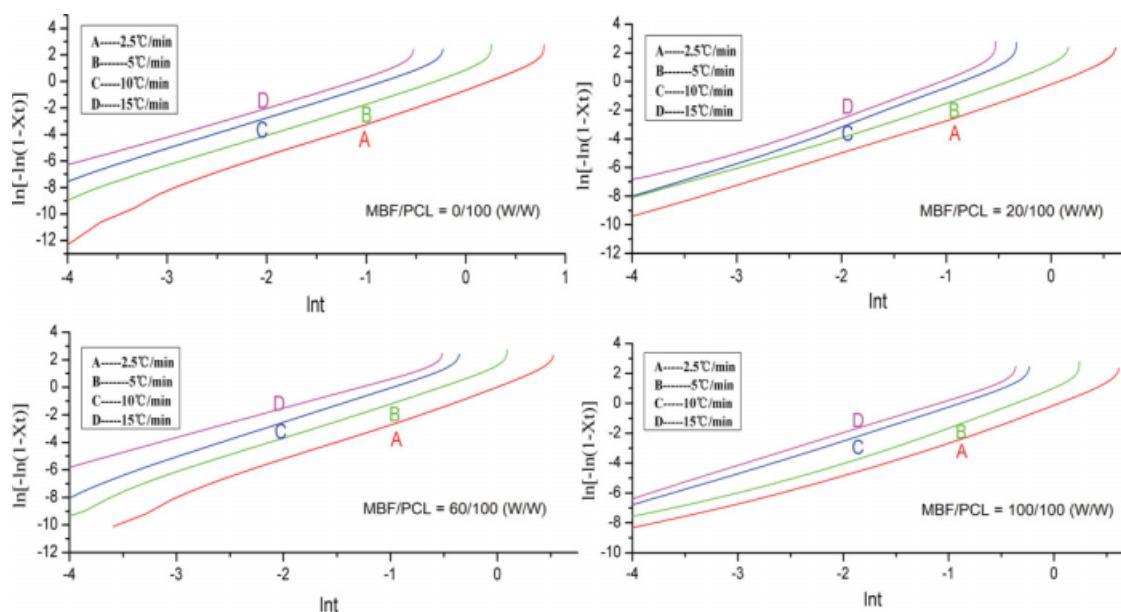


Figure 3 Plots of $\ln[-\ln(1-X_t)]$ versus $\ln t$ for the nonisothermal crystallization of the MBF/PCL composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

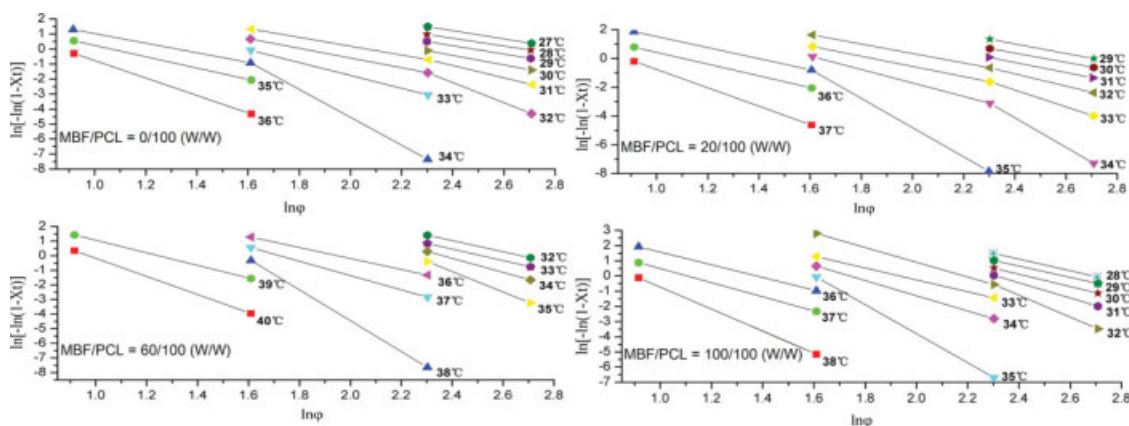


Figure 4 Plots of $\ln[-\ln(1-X_t)]$ versus $\ln\phi$ for crystallization of the MBF/PCL composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

I. As seen from Table I, the Z_c values of the MBF/PCL composites were bigger than that of the pure PCL at the same cooling rate, indicating that the crystallization rates of the MBF/PCL composites were faster than that of the pure PCL. In other words, the MBF act as a nucleating agent for the PCL matrix. The range of the value of n was 2–3 suggested that the nonisothermal crystallization of the pure PCL and the MBF/PCL composites correspond to a three-dimensional growth with homogeneous nucleation.

The Ozawa method

Plots of $\ln[-\ln(1-X_t)]$ versus $\ln\phi$ for crystallization of the pure PCL and the MBF/PCL composites (20/100, 60/100, and 100/100 W/W) at different temperatures were shown in Figure 4. The parameters of m and $K(T)$ can be determined from the slope and intercept, respectively. The nonlinear dependence of $\ln[-\ln(1-X_t)]$ upon $\ln\phi$ showed that the Ozawa equation was not suitable to describe the nonisothermal

thermal crystallization in the MBF/PCL composites. The curvature (in Fig. 4) presented an accurate analysis of the nonisothermal crystallization data. For PCL and its composites, the crystallization was complicated due to an additional slow process, referred to as secondary crystallization, which was considered to involve improvement of the crystalline order. The secondary crystallization effect for PCL may be the reason that the Ozawa equation was not fulfilled.

The Mo method

Plots of the $\ln\phi$ versus $\ln t$ for the nonisothermal crystallization of the pure PCL and the MBF/PCL composites (20/100, 60/100, and 100/100) at various relative crystallinity were shown in Figure 5, from which the values of α and $F(T)$ can be obtained by the slopes and the intercepts of these lines, respectively (Table II). It can be seen from Table II that the values of $F(T)$ systematically increased with an increase in the relative degree of crystallinity, which

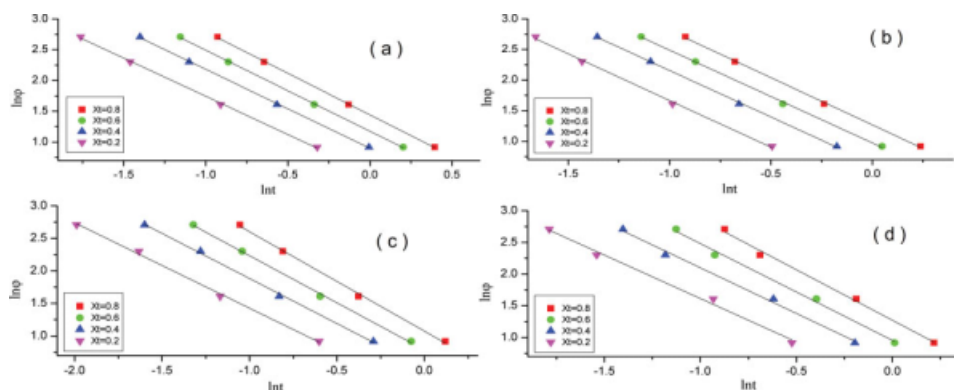


Figure 5 Plots of the $\ln\phi$ versus $\ln t$ for the nonisothermal crystallization of the composites: (a) MBF: PCL = 0 : 100; (b) MBF: PCL = 20 : 100; (c) MBF: PCL = 60 : 100; (d) MBF: PCL = 100 : 100. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Nonisothermal Crystallization Kinetic Parameters Based on the Mo Method

Samples	X_t	$F(T)$	α	Samples	X_t	$F(T)$	α
MBF/PCL (0/100 W/W)	0.2	0.50	1.24	MBF/PCL (60/100 W/W)	0.2	0.11	1.31
	0.4	0.90	1.28		0.4	0.50	1.39
	0.6	1.18	1.32		0.6	0.79	1.44
	0.8	1.44	1.35		0.8	1.07	1.53
MBF/PCL (20/100 W/W)	0.2	0.14	1.53	MBF/PCL (80/100 W/W)	0.2	0.07	1.41
	0.4	0.64	1.52		0.4	0.49	1.49
	0.6	0.97	1.52		0.6	0.80	1.56
	0.8	1.27	1.54		0.8	1.11	1.63
MBF/PCL (40/100 W/W)	0.2	0.01	1.43	MBF/PCL (100/100 W/W)	0.2	0.25	1.37
	0.4	0.42	1.48		0.4	0.66	1.44
	0.6	0.74	1.49		0.6	0.96	1.52
	0.8	1.03	1.54		0.8	1.27	1.60

makes sense according to the meaning of $F(T)$. It means that a higher cooling rate should be used within the unit crystallization time at a given degree of crystallinity, indicating the difficulty of polymer crystallization. By comparing the values of $F(T)$ of different samples, we have found that the values of pure PCL were higher than that of MBF/PCL composites, meaning that the crystallization rate of MBF/PCL composites was faster than that of virgin PCL. This was in accordance with the result obtained from the Avrami approach. α values remain almost close as the degree of crystallinity increased for each blends, indicating that the ratio of crystallization between 2.5°C/min and 15°C/min remains constant whatever the relative crystallinity.

CONCLUSIONS

In this study, a systematic study of the nonisothermal crystallization kinetics of the pure PCL and the MBF/PCL composites has been performed by DSC. The nonisothermal crystallization kinetics of each sample were analyzed according to three various kinetic models, namely, the Avrami method, the Ozawa method and the Mo method. The Avrami equation modified by Jeziorny's method and the Mo method were successful for describing the nonisothermal crystallization process of the neat PCL and the MBF/PCL composites. Meanwhile, the Ozawa equation fails to provide an adequate description of the nonisothermal crystallization.

T_{onset} (°C) and T_{peak} (°C) showed that with the addition of bamboo fiber increased, the crystallization occurred at a higher temperature. In the Avrami method, the parameters Z_c and $t_{1/2}$ suggested that the crystallization rates of all samples increased with the increasing cooling rate. The changes of the n

value illustrated that the crystallization mechanism of the pure PCL and the MBF/PCL composites was different. $t_{1/2}$ showed that the crystallization rates of the MBF/PCL composites were faster than that of the pure MBF at given cooling rates. These were consistent with the results obtained from the Mo method.

References

- Flemming, H. C. *Polym Degrad Stab* 1998, 59, 309.
- Hung, S. J.; Edelman, P. G. *Degradable Polymers: Principles and Application*; Scott, G., Gilead, D., Eds.; Chapman and Hall: London, 1995; pp 8–24.
- Li, S.; Vert, M. *Degradable Polymers: Principles and Application*; Scott, G., Gilead, D., Eds.; Chapman and Hall: London, 1995; pp 3–76.
- De Kesel, C.; Vander Wauven, C.; David, C. *Polym Degrad Stab* 1997, 55, 107.
- Nakayama, A.; Kawasaki, N.; Maeda, Y.; Arvanitoyannis, I.; Ariba, S.; Yamamoto, N. *J Appl Polym Sci* 1997, 66, 741.
- Li, S. H.; Zeng, Q. Y.; Fu, S. Y.; Zhou, B. L. *Mater Sci Eng* 1995, 3, 125.
- Van Der Lugt, P.; Van Den Dobbelen, A. A. J. F.; Janssen, J. J. A. 2006, 20, 648.
- Kundu, P. P.; Biswas, J.; Kim, H.; Choe, S. *Eur Polym J* 2003, 39, 1585.
- Leandro, N.; Luduena, V. A.; Alvarez, A. V. *Mater Sci Eng A* 2007, 460–461, 121.
- Matzinos, P.; Tserki, V.; Gianikouris, C.; Pavlidou, E.; Panayiotou, C. *Eur Polym J* 2002, 38, 1713.
- Luigi, V.; Giuliana, G.; Andrea, S.; Vittoria, V. *Carbohydr Polym* 2009, 75, 172.
- Avrami, M. *J Chem Phys* 1939, 7, 1103.
- Avrami, M. *J Chem Phys* 1940, 8, 212.
- Avrami, M. *J Chem Phys* 1941, 9, 177.
- Jeziorny, A. *Polymer* 1978, 19, 1142.
- Ozawa, T. *Polymer* 1971, 12, 150.
- Evans, U. R. *Trans Faraday Soc* 1945, 41, 365.
- Liu, T. X.; Mo, Z. S.; Wang, S.; Zhang, H. F. *Polym Eng Sci* 1997, 37, 568.