

NONISOTHERMAL CRYSTALLIZATION AND MORPHOLOGY OF POLY(BUTYLENE SUCCINATE)/LAYERED DOUBLE HYDROXIDE NANOCOMPOSITES*

Mei-qiu Zhan^a, Guang-yi Chen^b, Zhi-yong Wei^{b**}, Yu-mei Shi^b and Wan-xi Zhang^{a, b}

^a School of Material Science and Engineering, Jilin University, Changchun 130022, China

^b School of Automotive Engineering, Dalian University of Technology, Dalian 116024, China

Abstract Biodegradable poly(butylene succinate) (PBS) and layered double hydroxide (LDH) nanocomposites were prepared *via* melt blending in a twin-screw extruder. The morphology and dispersion of LDH nanoparticles within PBS matrix were characterized by transmission electron microscopy (TEM), which showed that LDH nanoparticles were found to be well distributed at the nanometer level. The nonisothermal crystallization behavior of nanocomposites was extensively studied using differential scanning calorimetry (DSC) technique at various cooling rates. The crystallization rate of PBS was accelerated by the addition of LDH due to its heterogeneous nucleation effect; however, the crystallization mechanism and crystal structure of PBS remained almost unchanged. In kinetics analysis of nonisothermal crystallization, the Ozawa approach failed to describe the crystallization behavior of PBS/LDH nanocomposites, whereas both the modified Avrami model and the Mo method well represented the crystallization behavior of nanocomposites. The effective activation energy was estimated as a function of the relative degree of crystallinity using the isoconversional analysis. The subsequent melting behavior of PBS and PBS/LDH nanocomposites was observed to be dependent on the cooling rate. The POM showed that the small and less perfect crystals were formed in nanocomposites.

Keywords: Poly(butylene succinate); Layered double hydroxide; Nonisothermal crystallization.

INTRODUCTION

Poly(butylene succinate) (PBS) is one of the most promising materials for the production of high-performance, environmentally friendly, biodegradable materials^[1]. PBS is chemically synthesized by the polycondensation of 1,4-butanediol with succinic acid. It has particularly attracted increasing commercial interest because of its many interesting properties, including biodegradability, melt processability and thermal and chemical resistance. However, its softness and low gas-barrier properties have restricted further application of PBS. Polymer nanocomposites have attracted enormous interest from the materials community because they theoretically promise substantial improvement of properties at very low filler loadings^[2–4]. For example, Okamoto and coworkers^[5–7] prepared PBS/layered silicate nanocomposites by melt compounding. The obtained PBS/layered silicate nanocomposites exhibited a concurrent improvement of materials properties when compared with pure PBS. Yoon and coworkers^[8, 9] synthesized and characterized PBS/epoxy group functionalized organoclay nanocomposites and studied their nonisothermal crystallization kinetics. PBS/functional multiwalled carbon

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** Corresponding author: Zhi-yong Wei (魏志勇), E-mail: zywei@dlut.edu.cn.

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nanotube nanocomposites were prepared by melt compounding^[10–12]. It was found that the presence of functional multiwalled carbon nanotubes in the nanocomposites had a significant heterogeneous nucleation effect on the crystallization and morphology of PBS.

However, the most extensive research work has been focused on cationic clays, such as the montmorillonite systems, whereas the layered double hydroxide (LDH) systems have rarely been reported in the literature^[13]. LDHs, known as anionic clays or hydrotalcite clays, can be expressed as the following general chemical formula: $[M_{1-x}^{2+}L_x^{3+}(\text{OH})_2]^{x+}A^{n-x/n}\cdot m\text{H}_2\text{O}$, where M^{2+} and L^{3+} are divalent and trivalent metal cations, such as Mg^{2+} and Al^{3+} , respectively, and A is an anion. In contrast to layered clays, LDH particles, being composed of metal hydroxide layers, display a positive surface charge, which is counterbalanced by anions located in the domains between adjacent layers. The typical metal hydroxide-like chemistry and conventional clay-like layered crystalline structure make LDH potential flame retardant^[14] and suitable for the fabrication of polymer nanocomposites.

Recently, the synthesis and properties of polymer/LDH nanocomposites have caused great interest either in theoretical aspects or practical applications, because they exhibit improved physical and performance properties in comparison to the pristine polymers and conventional composites^[15–19]. Not only some nonbiodegradable polymer/LDH nanocomposites have been prepared (e.g., PMMA^[15], polystyrene^[16], polyethylene^[17], polypropylene^[18], polyamide 6^[19] and other polymer matrices), but also a series of studies on biodegradable polymer/LDH nanocomposites have been reported so far, such as poly(ϵ -caprolactone)^[20, 21], poly(3-hydroxybutyrate)^[22], poly[(3-hydroxybutyrate)-*co*-(3-hydroxy valerate)]^[23], poly(L-Lactide)^[24–26] or poly(*p*-dioxanone)^[27]. To our best knowledge, there are rare papers reported the use of LDH as filler for PBS nanocomposite systems and the interfacial attrition between PBS and LDH^[28]. However, there was no literature on LDH induced nonisothermal crystallization and melting behavior of PBS.

The study of the nonisothermal crystallization behavior of nanocomposites is of technological importance because most composites and polymer blends are practically processed under nonisothermal conditions^[29]. PBS is a semicrystalline polymer, and the final properties, such as thermal properties, impact resistance, stress-strain behavior, and biodegradable properties, of PBS-based nanocomposites in applications are critically dependent on the level of crystallinity, which, in turn, depends on the processing conditions.

In this article, PBS/LDH nanocomposites were prepared by melt compounding at various LDH contents, and kinetics analysis of nonisothermal crystallization was performed with the Ozawa, Avrami, and Mo methods from differential scanning calorimetry (DSC) measurements. The effective activation energy barrier of nonisothermal crystallization was explained by an isoconversional approach. Melting behavior after nonisothermal crystallization process was also discussed. The crystalline structure and spherulitic morphology were investigated by wide angle X-ray diffraction (WAXD) and optical polarizing microscopy (POM), respectively.

EXPERIMENTAL

Materials

A commercial grade of poly(butylene succinate) (PBS) was purchased from Anqing Hexing Chemical Co., Ltd (Anhui, China) with melt flow index of 20–30 g/10min (190°C/2.16 kg) as reported by the manufacturer. It was dried in an airflow oven prior to use. A Mg/Al layer double hydroxide (LDH) with the formula $\text{Mg}_{0.66}\text{Al}_{0.34}(\text{OH})_2(\text{CO}_3)_{0.17}\cdot 0.67\text{H}_2\text{O}$, was kindly supplied by Dalian Fumeida New Materials Co., Ltd (China).

Preparation of PBS/LDH Nanocomposites

The PBS/LDH nanocomposites were prepared by melt mixing on a GIANT SHJ-20 (Nanjing, China) twin screw corotating extruder with L/D 32–40 (D21.7 mm). The weight fraction of LDH dispersed in PBS was 0.25 wt%, 0.5 wt%, 1 wt%, 3 wt% and 5 wt%. For brevity, the resultant composites were denoted as PBS/LDH0.25, PBS/LDH0.5, PBS/LDH1, PBS/LDH3 and PBS/LDH5, respectively. In addition, a pure PBS sample was prepared with the identical operating process for comparison.

Characterization

A field emission transmission electron microscope (Tecnai G2 F20, USA) was utilized to observe the morphology and dispersion of PBS/LDH nanocomposite and operated under an accelerating voltage of 200 kV. The nanocomposite specimen for TEM observations was prepared by ultramicrotoming under cryogenic conditions using a Leica ultramicrotome (Leica EM FC 6, Germany) with a diamond knife.

Thermal analysis was performed on a DSC1 (Mettler-Toledo, Switzerland) differential scanning calorimeter. The instrument was calibrated using high purity indium and zinc standards. For nonisothermal crystallization, the samples were first heated to 130°C at 40 K/min, held at 130°C for 5 min to erase thermal history and cooled to 30°C at four preset cooling rates of 5, 10, 15, and 20 K/min, respectively. Then, the samples were subsequently heated to 130°C at 10 K/min. The heat flows during both crystallization and melting processes were recorded for the later data analysis.

Wide-angle X-ray diffraction (WAXD) patterns of the samples were performed on a Dmax-Ultima+ X-ray diffractometer (Rigaku, Japan) with Ni-filtered Cu/K- α radiation ($\lambda = 0.15418$ nm). The operating target voltage was 40 kV and the tube current was 100 mA. The scanning speed was 1.2 (°)/min from 5° to 30°.

The crystalline morphologies of PBS and PBS/LDH nanocomposites were observed with a Leica 4500P polarized optical microscope (Leica, Germany) with a Linkam THMS 600 hot stage. Thin films of PBS and PBS/LDH nanocomposites were sandwiched between two thin glass slides and heated to 130°C for 5 min to erase its thermal history. They were subsequently cooled to room temperature at a cooling rate of 10 K/min, and then the spherulitic morphology that formed during the nonisothermal crystallization process was observed with POM.

RESULTS AND DISCUSSION

Dispersion of LDH in PBS Matrix

It is well known that the dispersion and morphology of nanofillers in the polymer matrix are the key factors influencing the physical properties of the polymer matrix. A homogeneous dispersion of LDH together with strong interfacial interactions between the polymer matrix and LDH nanoparticles can effectively improve the thermal and mechanical performances of the composites. Accordingly, the nanocomposites were examined with TEM to investigate the morphology and the dispersion of the LDH nanoparticles in the PBS matrix. Figure 1 presents a TEM image of 1 wt% PBS/LDH composites. The TEM image of the sample showed that the distribution of the LDH nanoparticles is rather homogeneous. Of course, a number of aggregates of LDH nanoparticles were observed. In nanocomposites containing 1 wt% LDH, the aggregate size is up to 200 nm. The size of these aggregates depends on the LDH content and increases as the content of LDH increases due to the powerful interaction of the surface hydroxyl groups^[2].

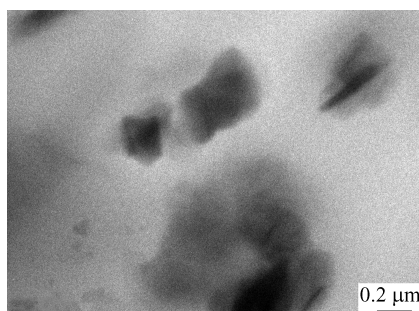


Fig. 1 TEM image of PBS/LDH1 nanocomposite

Nonisothermal Crystallization Behavior

The study of nonisothermal crystallization behavior is important because most of the current processing techniques of polymeric materials follow the nonisothermal crystallization process. Figure 2 shows typical DSC

curves of heat flow as a function of temperature at different cooling rates for PBS and PBS/LDH1 nanocomposite. From DSC thermograms (Figs. 2(A and B) and Table 1) at various cooling rates, it is clear that the crystallization peak temperature for nanocomposites is higher than those of pure PBS and decreases with increasing cooling rates.

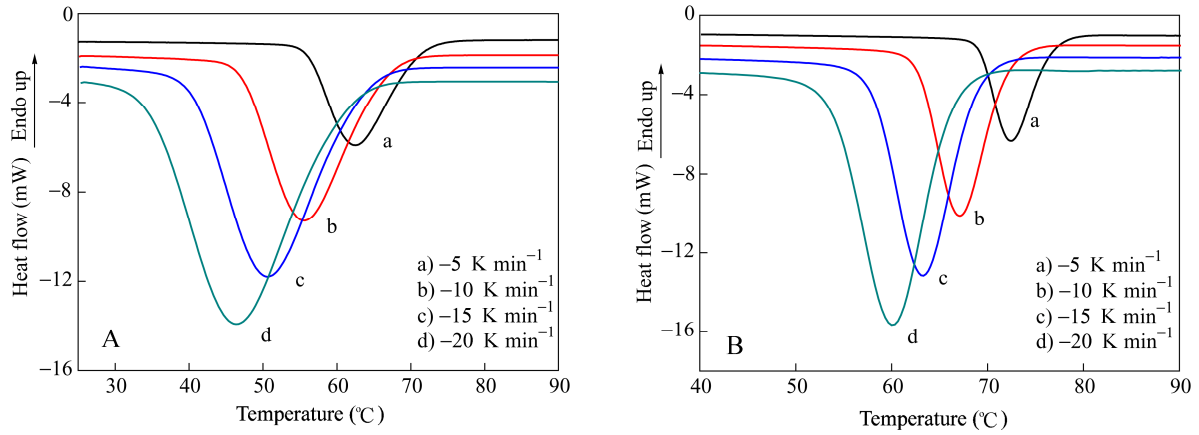


Fig. 2 DSC thermograms of nonisothermal crystallization at different cooling rates: (A) PBS and (B) PBS/LDH1 nanocomposite

From the data for the crystallization exotherms as a function of temperature dH_c/dT , the relative crystallinity as a function of temperature $X(T)$ can be calculated as follows^[30]:

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

where T_0 and T_∞ represent the temperatures at the initial and end of crystallization process, respectively.

The development of relative degree of crystallinity $X(T)$ as a function of temperature, T , for PBS/LDH1 nanocomposites at various cooling rates is shown in Fig. 3(A). The plots of $X(T)$ versus T for PBS and PBS/LDH nanocomposites are similar and all these curves have the same sigmoidal shape, implying that only a lag effect of cooling rate on crystallization is observed.

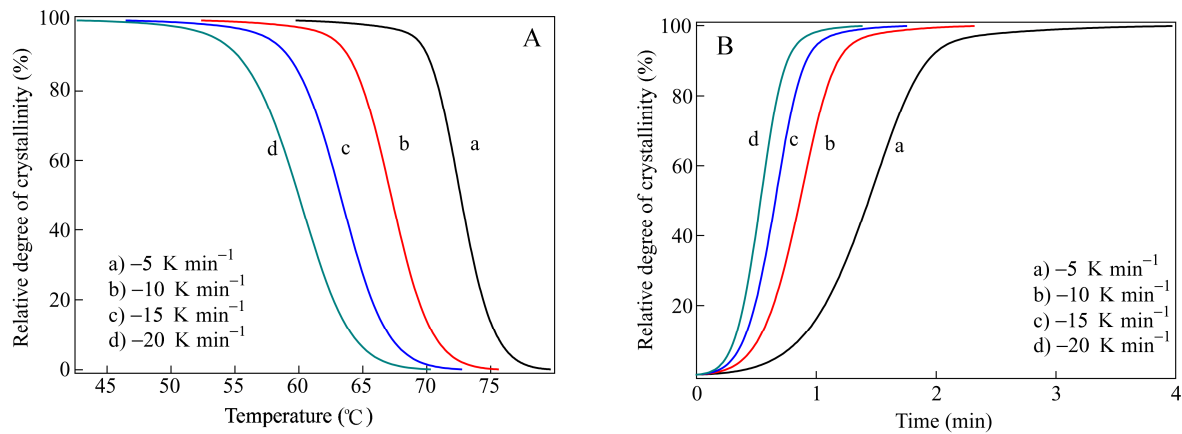


Fig. 3 Relative degree of crystallinity versus temperature (A) and time (B) for nonisothermal crystallization of PBS/LDH1 nanocomposites at different cooling rates

During the melt nonisothermal crystallization process, the relation between crystallization time t and corresponding temperature T is given by

$$t = \frac{T_0 - T}{\Phi} \quad (2)$$

where Φ is cooling rate. According to Eq. (2), the temperature-dependent relative crystallinity $X(T)$ can be transformed into the time-dependent relative crystallinity $X(t)$. The results show that the higher the cooling rate, the shorter the time for completing crystallization. According to Eq. (2) the value of T on the X -axis can be transposed into the crystallization time (t) as shown in Fig. 3(B). All data give S-type curves, and it shows a slow process during the later crystallization stage.

On the basis of these curves, some useful parameters for the nonisothermal crystallization analysis, such as the onset temperature of crystallization (T_{onset}), the crystallization peak temperature (T_{peak}) and the end temperature of crystallization (T_{end}) can be obtained and summarized in Table 1. The results indicate that the crystallization of PBS was promoted and occurred at a relatively low crystallization temperature, and a distinct increase of about 10 K in the crystallization temperature of PBS was achieved in the presence of LDH nanoparticles. It can be explained by the heterogeneous nucleation effect of LDH nanoparticles on the PBS chain segments, which could be easily attached to the surface of the LDH nanoparticles^[18]. However, the crystallization peak temperature (T_{peak}) of PBS nanocomposites does not increase with the LDH content monotonically. The values of T_{peak} increment reached a maximum at 1 wt% LDH, and then decreased with the more addition of LDH. It should be attributed to the reduction of the transportability of polymer chains caused by the addition of LDH. Although the addition of LDH would cause a heterogeneous nucleation effect, the hindrance effect of LDH seemed to be unnegligible at higher LDH loadings.

Table 1. Kinetics parameters of nonisothermal crystallization of PBS and PBS/LDH nanocomposites

Sample	Φ (K/min)	T_{onset} (°C)	T_{peak} (°C)	T_{end} (°C)	$t_{1/2}$ (min)
PBS	5	76.43	62.60	38.8	2.66
	10	72.25	55.63	34.76	1.59
	15	69.59	50.64	31.02	1.21
	20	67.13	46.47	28.77	0.99
PBS/LDH0.2	5	79.92	71.92	55.63	1.52
	10	75.99	66.45	49.38	0.92
	15	73.14	62.61	45.38	0.69
	20	70.86	59.42	42.62	0.56
PBS/LDH0.5	5	79.57	72.09	59.82	1.48
	10	75.50	66.61	53.58	0.87
	15	72.92	62.63	48.34	0.66
	20	70.66	59.79	43.93	0.54
PBS/LDH1	5	79.65	72.37	59.85	1.40
	10	75.59	67.00	52.47	0.83
	15	72.77	63.17	46.61	0.63
	20	70.29	59.83	42.97	0.52
PBS/LDH3	5	79.23	70.68	56.7	1.64
	10	74.65	64.79	48.16	0.97
	15	71.46	60.37	44.54	0.72
	20	68.79	57.11	42.52	0.58
PBS/LDH5	5	79.12	70.50	55.42	1.67
	10	74.45	64.28	49.50	0.99
	15	71.11	59.86	45.23	0.74
	20	68.50	56.44	42.17	0.60

The half crystallization time ($t_{1/2}$) is defined as the half period (*i.e.* 50% relative crystallinity), from the onset of crystallization and the end of crystallization. The $t_{1/2}$ values for PBS and its nanocomposites can be obtained from Fig. 3(b), and the results are listed in Table 1. It is apparent that the value of $t_{1/2}$ decreases with increasing cooling rate. Moreover, at a given cooling rate, the $t_{1/2}$ values for PBS/LDH nanocomposites are lower than those for PBS, and they decrease first and then increase with increasing of LDH content. Incorporation of clay into a polymer matrix either increases or decreases the crystallization rate of the polymer matrix, which is dependent of the competition between the nucleation action and the restricting effect of the clay. When the nucleation is the rate determining step for the crystallization, then addition of clay should raise the overall crystallization rate. However, with increase in the clay content, the nucleating action of clay does not have a significant influence on the nucleation rate, in contrast, the overall crystallization rate decreases because of restriction of the motion of the polymer molecules by the clay layers. Such a similar trend was observed in the case of PHB/LDH nanocomposites^[22].

Nonisothermal Crystallization Kinetics Analysis

In order to quantitatively describe the evolution of crystallinity during nonisothermal crystallization, the Ozawa, the Avrami and the Mo models (modified Avrami-Ozawa method) were employed to analyze the nonisothermal crystallization kinetics of PBS and its nanocomposites.

Nonisothermal crystallization kinetics by Ozawa model

Ozawa^[31] extended the use of the Avrami macrokinetic model to describe the kinetics of nonisothermal crystallization. In this approach, the nonisothermal crystallization process is the result of an infinite number of small isothermal crystallization steps, and the degree of conversion at temperature T , $X(T)$, can be calculated as:

$$1 - X(T) = \exp \frac{-K(T)}{\Phi^m} \quad (3)$$

where Φ is cooling rate, m is the Ozawa exponent that depends on the crystal growth and nucleation mechanism, and $K(T)$ is the function of cooling crystallization. $K(T)$ is related to the overall crystallization rate and indicates how fast crystallization occurs. Taking the double-logarithmic form of Eq. (3), it follows:

$$\ln [-\ln (1 - X(T))] = \ln K(T) - m \ln \Phi \quad (4)$$

According to the Ozawa analysis, if the relative crystallinities at different cooling rates at a given temperature are chosen, the plots of $\ln [-\ln (1 - X(T))]$ versus $\ln \Phi$ should give a series of parallel lines. Indicative Ozawa plots for crystallization of PBS/LDH1 nanocomposite are shown in Fig. 4(a). The linearity in the plots is not satisfactory in the range from 62°C to 70°C. The changing of slopes indicates that the Ozawa exponent m is not constant with temperature during the primary crystallization process. The general curvature seen in Fig. 4(a) makes it impossible to determine the cooling function by the Ozawa's method.

The reason why the nonisothermal crystallization of PBS/LDH nanocomposites does not follow the Ozawa equation is probably that the crystallization processes with different cooling rates are at different stages at a given temperature. In other words, the low cooling rate process takes place toward the end of the crystallization process, whereas at the high cooling rate, the crystallization process is at an earlier stage. In addition, the secondary crystallization of later stage could not be neglected. Thus, the Ozawa method was found to be inapplicable for the nonisothermal kinetic model of PBS/LDH nanocomposites, similar with PP/LDH nanocomposites^[18].

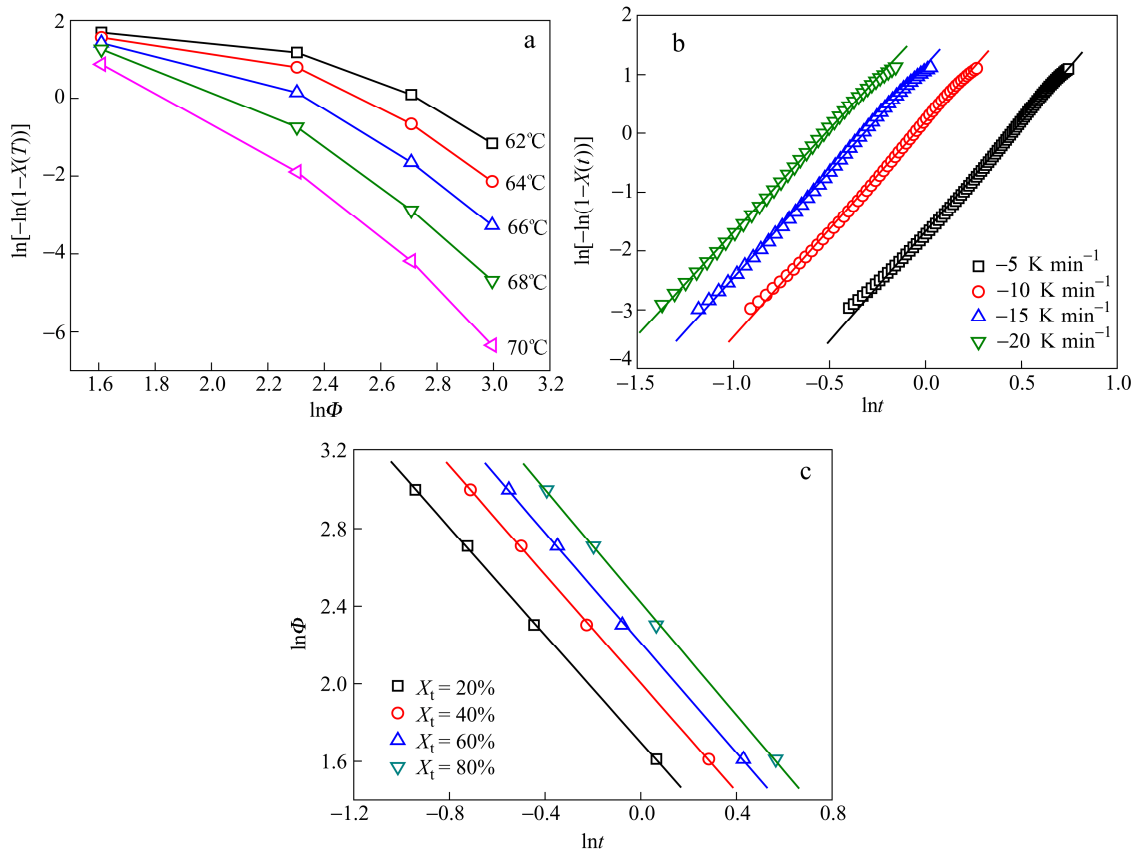


Fig. 4 (a) Ozawa plots of $\ln[-\ln(1-X(T))]$ versus $\ln\Phi$, (b) Avrami plots of $\ln[-\ln(1-X(t))]$ versus $\ln t$ and (c) Mo plots of $\ln\Phi$ versus $\ln t$ during nonisothermal crystallization process of PBS/LDH1 nanocomposite

Nonisothermal crystallization kinetics by modified Avrami model

According to the modified Avrami method^[32], the relative degree of crystallinity, $X(t)$, can be calculated from:

$$1 - X(t) = \exp(-Z_t t^n) \quad (5)$$

where Z_t and n denote the growth rate constant and the Avrami exponent, respectively.

By fitting the experimental data ($5\% \leq X(t) \leq 95\%$) to Eq. (5), the values of n and Z_t can be obtained from the slope and intercept of the plots of $\ln[-\ln(1-X(t))]$ against $\ln t$ for each cooling rate as shown in Fig. 4(b). From the figure, it can be seen that straight lines are obtained in each cooling rate. It should be taken into account that in nonisothermal crystallization, Z_t and n do not have the same physical significance as in isothermal crystallization because under nonisothermal crystallization, the temperature changes constantly. Since the rate of nonisothermal crystallization depends on the cooling rate, Jeziorny^[32] suggested that the rate parameter Z_t should be corrected for the influence of cooling rate Φ of the polymer. The parameters Z_c characterizing the kinetics of nonisothermal crystallization were given as follows:

$$\ln Z_c = \frac{\ln Z_t}{\Phi} \quad (6)$$

where Z_t is the crystallization rate parameter and Z_c is the modified crystallization rate parameter with respect to cooling rate, Φ .

Table 2 summarizes the values of $\ln Z_t$, Z_c , and n calculated using Equation (6) for PBS/LDH nanocomposites at each cooling rate. The crystallization constant Z_c increases, while the exponent n decreases as the cooling rate increases, or in other words as the supercooling increases. The Z_c values of the PBS/LDH

nanocomposites are, as expected, higher than those of the pure PBS at the same cooling rate, showing that incorporation of LDH could crystallize PBS at a quicker rate. All the values of n obtained for PBS and PBS/LDH nanocomposites were near 4, and they should possibly be related with a three-dimensional crystallization growth by homogeneous nucleation mechanism. Avrami parameters n and Z_c for PBS were found to be similar values reported by Yoon^[9]. The results indicated that the addition of LDH has not greatly altered the dimension of PBS crystalline growth.

Table 2. Nonisothermal crystallization kinetic parameters obtained by Avrami and Jeziorny methods

Sample	Φ (K/min)	$\ln Z_t$	Z_c	n
PBS	5	-3.970	0.452	3.66
	10	-1.990	0.820	3.49
	15	-1.025	0.934	3.40
	20	-0.337	0.983	3.27
PBS/LDH0.2	5	-1.922	0.681	3.75
	10	-0.071	0.993	3.79
	15	1.002	1.069	3.72
	20	1.700	1.089	3.67
PBS/LDH0.5	5	-1.828	0.694	3.66
	10	0.077	1.008	3.69
	15	1.080	1.075	3.76
	20	1.799	1.094	3.71
PBS/LDH1	5	-1.676	0.715	3.73
	10	0.193	1.019	3.66
	15	1.151	1.080	3.61
	20	1.815	1.095	3.50
PBS/LDH3	5	-2.392	0.620	3.98
	10	-0.310	0.969	3.86
	15	0.787	1.054	3.73
	20	1.534	1.080	3.64
PBS/LDH5	5	-2.384	0.621	3.88
	10	-0.400	0.961	3.85
	15	0.704	1.048	3.78
	20	1.435	1.074	3.74

Nonisothermal crystallization Kinetics by Mo model (modified Avrami-Ozawa models)

Nonisothermal crystallization is difficult to describe with a single equation since there are a lot of parameters that have to be taken into account simultaneously. Liu and Mo^[33] proposed a different kinetic model by combining the Ozawa and Avrami equations. The importance of this method is that it correlates the cooling rate to temperature, time, and morphology. As the degree of crystallinity was related to the cooling rate (Φ) and the crystallization time (t) or temperature (T), the relation between Φ and t could be defined for a given degree of crystallinity. Consequently, combining Eqs. (3) and (5) derived a new kinetic model for nonisothermal crystallization:

$$\ln Z_t + n \ln t = \ln K(T) - m \ln \Phi \quad (7)$$

By rearrangement at a given crystallinity and solving for the cooling rate, Eq. (7) becomes:

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

where $F(T) = [K(T)/Z_t]^{1/m}$ refers to the value of cooling rate that must be selected within a unit of crystallization time when the measured systems reach a certain degree of crystallinity; and α is the ratio of Avrami exponent (n) to Ozawa exponent (m) that is n/m . It can be seen that $F(T)$ has a definite physical and practical meaning.

According to Eq. (8) at a given degree of crystallinity the plot of $\ln \Phi$ against $\ln t$ will give a straight line with an intercept of $\ln F(T)$ and a slope of $-\alpha$. As it is shown in Fig. 4(c), plotting $\ln \Phi$ versus $\ln t$, at a given

degree of crystallinity, a series of good straight lines is observed. The values of $F(T)$ and the slope α are listed in Table 3. The α values keep constant, while the values of $F(T)$ systematically increase with increasing relative degree of crystallinity and are lower in the presence of LDH nanoparticles, which indicates that PBS/LDH nanocomposites crystallize at a faster rate than PBS.

Table 3. Kinetic parameters obtained by Mo method at different relative degrees of crystallinity

Sample	X_t (%)	α	$F(T)$
PBS	20	1.36	12.58
	40	1.39	17.62
	60	1.42	22.31
	80	1.43	27.74
PBS/LDH0.2	20	1.41	5.94
	40	1.38	8.00
	60	1.40	9.82
	80	1.43	12.22
PBS/LDH0.5	20	1.41	5.75
	40	1.39	7.85
	60	1.40	9.64
	80	1.41	11.78
PBS/LDH1	20	1.38	5.46
	40	1.40	7.40
	60	1.41	9.12
	80	1.45	11.22
PBS/LDH3	20	1.31	6.81
	40	1.33	8.97
	60	1.35	10.86
	80	1.38	13.20
PBS/LDH5	20	1.36	6.93
	40	1.36	9.24
	60	1.38	11.26
	80	1.40	13.71

Effective Activation Energy Barrier

As demonstrated by Vyazovkin^[34], the above Kissinger method usually provides unacceptable values of activation energy (ΔE_a) because the dependence of temperature on the overall rate cannot be described by a single Arrhenius equation over a wide temperature range. However, evaluation of the effective activation energy as a function of the relative crystallinity has an additional benefit of detecting changes in the process mechanism that are likely to occur in such complex processes as polymer crystallization. Such dependence has been quite helpful in detecting and elucidating complex kinetics in polymeric systems. In this study, the differential isoconversional method of Friedman^[35] was used to calculate the effective energy barrier (ΔE_X), and the equation is expressed as:

$$\ln\left(\frac{dX}{dt}\right)_{X,t} = \text{Constant} - \frac{\Delta E_X}{RT_{X,i}} \quad (9)$$

where dX/dt is the instantaneous crystallization rate as a function of time at a given conversion X . ΔE_X is the effective energy barrier at a given conversion X , $T_{X,i}$ is the set of temperatures related to a given conversion X at different cooling rates, Φ and the subscript i refers to every individual cooling rate used.

According to this method, the $X(t)$ function obtained from the integration of the experimentally measured crystallization rates is initially differentiated with respect to time to obtain the instantaneous crystallization rate, dX/dt . Furthermore, by selecting appropriate degrees of crystallinity (*i.e.* from 10% to 90%) the values of dX/dt at a specific X are correlated to the corresponding crystallization temperature at this X , *i.e.* T_X . Then by plotting the left hand side of Eq. (9) with respect to $1/T_X$ a straight line must be obtained with a slope equal to $-\Delta E_X/R$.

The dependence of the effective activation energy on the context of relative crystallization of the PBS and PBS/LDH nanocomposites is presented in Fig. 5(a). As it can be seen, ΔE_X is strongly dependent on the LDH content and increases with the increase in relative degree of crystallinity for PBS and its nanocomposites. In all the cases, ΔE_X takes great negative values at lower extent of conversion that corresponds to temperatures closer to the melting point. The value of ΔE_X increases as the extent of conversion rises and the temperature decreases. This suggests that, as the crystallization progresses, it is more difficult for the polymer to crystallize. As crystallization proceeds, diffusion of the crystallizing molecular segments from the melt to the growth front will be deterred by the rejected molecular segments. The shape of the curve obtained is similar to that observed for PP/SiO₂ nanocomposites^[36].

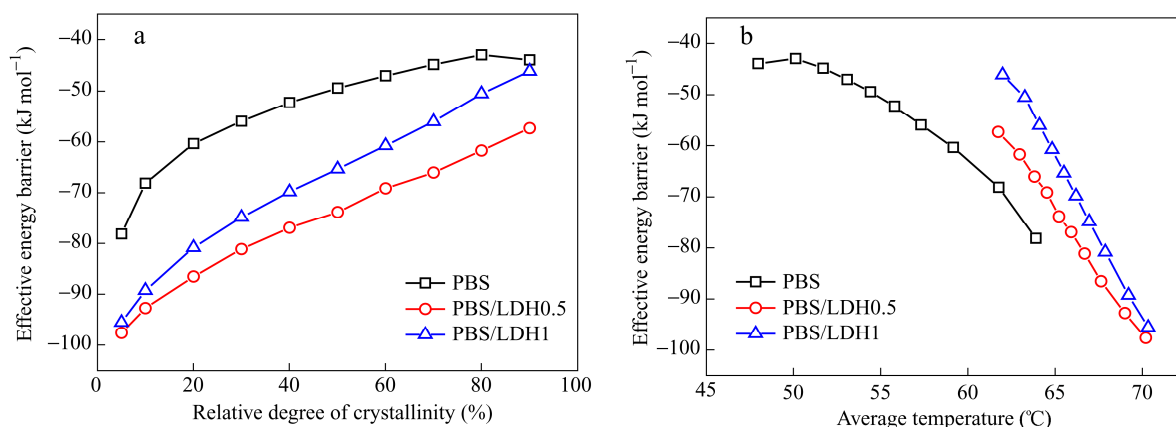


Fig. 5 Dependence of effective activation energy barrier on relative degree of crystallinity (a) and average temperature (b) for PBS and PBS/LDH nanocomposites

For PBS/LDH nanocomposites, it is observed that samples with 0.5 wt% LDH show rather low values of ΔE_X , and the ΔE_X values increase with increasing LDH content. These results indicate that the addition of 0.5 wt% LDH into PBS causes heterogeneous nucleation (low ΔE_X). The addition of more LDH is expected to cause more heterogeneous nucleation, but increasing the content of LDH also reduces the transportation ability of polymer chains and prevents the PBS macromolecule segments from rearranging, and as a result, increases the ΔE_X during crystallization process. Accordingly, the addition of LDH may accelerate the overall nonisothermal crystallization process of PBS.

Furthermore, according to recent reports, the effective activation energy barrier can be plotted as a function of temperature by taking an average temperature associated with a certain value shown in Fig. 5(b). It can be seen, again at a given crystallization temperature, the 0.5 wt% LDH nanocomposite exhibits lower value of the effective activation energy while the 1 wt% LDH one shows higher ΔE_X . The values of ΔE_X were negative, indicating that the rate of crystallization increased with decreasing temperatures. The absolute value of ΔE_X for LDH nanocomposites was higher than that of PBS, which revealed that PBS segments require more energy to rearrange in presence of LDH, since LDH nanolayers might hinder the mobility of chain segments. However, such trend is different from the earlier report for PP/SiO₂ nanocomposites, in which the effective energy barrier of the nanocomposites was higher than the pure PP^[36].

Melting Behavior after Nonisothermal Crystallization

In this work, a wide range of cooling rate was used for the evaluation of melting behavior of PBS/LDH nanocomposites after nonisothermal crystallization. The DSC heating thermograms of pure PBS and the PBS/LDH1 nanocomposite are presented in Figs. 6(a and b), respectively. It is observed that both PBS and PBS/LDH nanocomposites showed a multiple melting behavior. There are two endothermic peaks labeled as T_{m1} and T_{m2} from low to high temperatures and one exothermic peak (T_{exo}), which is located between the two

melting peaks. However, some discrepancies still existed in the multiple thermograms of PBS and PBS/LDH1 nanocomposites at the same cooling rate. The low melting peak T_{m1} of pure PBS and PBS/LDH1 nanocomposite appears when the cooling rate is lower than 1 and 10 K/min, respectively. In contrast, the crystallization exothermic T_{exo} of pure PBS and PBS/LDH1 nanocomposite starts to disappear at the corresponding cooling rate. However, the high melting endothermic T_{m2} seems unchanged with the cooling rate and locates at around 105°C. The magnitude of the area of T_{m1} increases and that of T_{m2} decreases by decreasing the cooling rate, especially for the PBS/LDH nanocomposite.

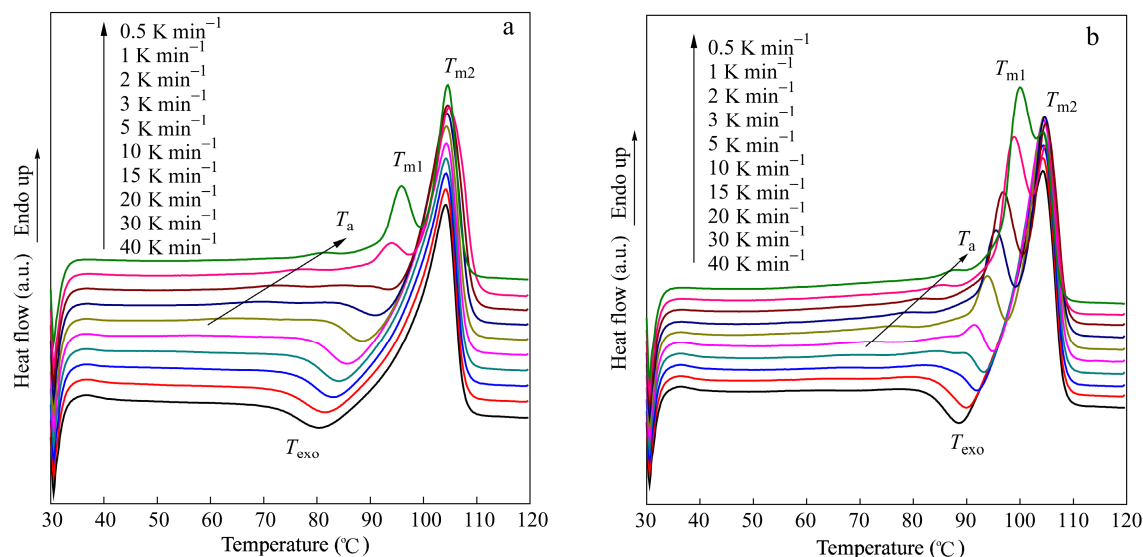


Fig. 6 DSC heating scans recorded at 10 K/min of (a) PBS and (b) PBS/LDH1 nanocomposite after nonisothermal crystallization at various cooling rates as indicated

Apparently, the melting behavior of PBS and PBS/LDH nanocomposites is dependent on the cooling rate. Generally, the slower the cooling rate, the higher temperature region the crystallization starts, because there was sufficient time to overcome the nucleation barrier. Although the nonisothermal crystallization occurred over a range of temperatures, most of the crystallization in every case happened at about the peak temperature T_{peak} . Thus, it would be reasonable to suppose that the resulting morphology is similar to that generated during an isothermal crystallization at a T_c equal to the respective T_{peak} observed in the cooling process^[37]. For example, the peak temperature observed on cooling at 0.5 K/min was 77.9°C (not shown here). The subsequent heating showed the melting peak profile that was very similar to that of the isothermally crystallized PBS at 78°C, as reported in another article in this series. As discussed in nonisothermal crystallization kinetics, the crystallization of PBS was promoted and occurred at an elevated crystallization temperature by 10 K, due to the heterogeneous nucleation effect of LDH nanoparticles on the PBS chain segments. Therefore, the melting peak profile of PBS/LDH nanocomposites shifted to that of PBS isothermally crystallized at an elevated temperature. Accordingly, the cooling rate is the direct cause, and the temperature that the crystallization occurred is the underlying cause.

It is of interest to note that a small shoulder peak in the DSC curves newly appeared at the low melting peak T_{m1} . An arrow indicates the shoulder peak in DSC curves with cooling rate lower than 10 K/min in Fig. 6(a) and Fig. 6(b). Similar DSC curves of the melting peaks have not been reported for nonisothermally crystallized PBS^[38]. However, the shoulder peak is usually observed in the DSC melting curve of an isothermally crystallized PBS. As shown in Fig. (6), the magnitude and the peak temperature of the shoulder peak increases with decreasing cooling rate. This small transition is similar to the “annealing peak” characteristics of isothermally crystallized PBS^[39].

Crystal Structure and Spherulitic Morphology

Figure 7 illustrates the WAXD patterns of pure PBS and its nanocomposites with various loadings of LDH. A typical diffraction peak of LDH is at about 11.6° ^[28], which indicates that the sheet-sheet distance in the lamellar sample, perpendicular to the sheet plane (003), is 0.76 nm. The sharp Bragg peak in the composites existed at the same location indicates that the dispersed LDH still retains an ordered structure after melt extrusion. This indicates that the LDH microcrystals remain essentially integral within the polymeric matrix. From Fig. 7, both PBS and its nanocomposites exhibit nearly the same diffractions at the identical locations. The three main characteristic peaks located at around 19.5° , 21.9° and 22.6° , corresponding to the (020), (021) and (110) planes of PBS, respectively^[12]. Therefore, the incorporation of LDH does not affect the crystalline structure of PBS matrix.

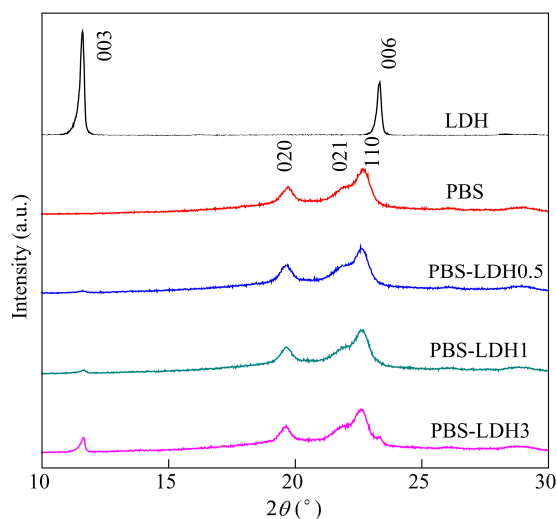


Fig. 7 X-ray diffraction patterns of LDH, PBS and PBS/LDH nanocomposites

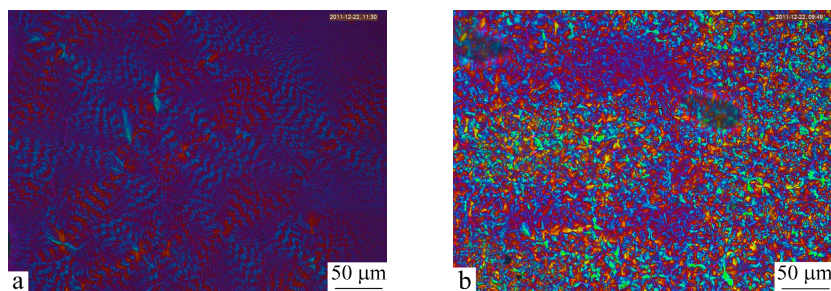


Fig. 8 Polarized optical micrographs of (a) PBS and (b) PBS/LDH5 nanocomposite after nonisothermal crystallization at a cooling rate of 10 K/min

In order to investigate the influence of LDH nanoparticles on the morphology development and size of spherulites of PBS, POM characterization was carried out. Figure 8 displays the spherulitic morphology of the pure PBS and its nanocomposite after crystallizing at the cooling rate of 10 K/min. As shown in Fig. 8(a), besides the typical spherulitic structure (*i.e.*, Maltese cross), the ring-banded extinction patterns with periodic distance along the radial direction are also observed in the spherulites of PBS. Although the morphology of PBS seems to be obscure, distinct boundaries can still be seen through the PBS matrix. Some smaller and imperfect spherulites are observed in the nanocomposite (Fig. 8b), which grow rapidly, impinge quickly with surrounding spherulites, and their further growth is restricted. This phenomenon is attributed to the nucleation effect of the LDH nanoparticles, which provide much more heterogeneous nuclei and reduce the size of the spherulites. Because of the impingement effect, it is hard to form perfect or well-developed spherulites in the presence of a

large number of heterogeneous nuclei (*i.e.*, LDH nanoparticles), and the growth of the PBS spherulites is restricted^[18]. In brief, the addition of LDH and its content in the PBS matrix are the main factors, which influence the spherulitic size and the overall crystallization process of PBS significantly.

CONCLUSIONS

Biodegradable poly(butylene succinate) (PBS) and layered double hydroxide (LDH) nanocomposites were successfully prepared *via* melt blending in a twin-screw extruder. The microstructure, nonisothermal crystallization and subsequent melting behavior, crystal structure and spherulitic morphology of PBS and its nanocomposites were studied by TEM, DSC, WAXD and POM in detail. The LDH nanoparticles were well dispersed in PBS matrix at the nanometer level. The addition of LDH is found to enhance the crystallization of PBS, due to the heterogeneous nucleation effect. In nonisothermal crystallization kinetics, it was found that the Ozawa model was rather inapplicable, probably due to the inaccurate assumption in the approach regarding secondary crystallization. In contrast, the Avrami analysis modified by Jeziorny as well as the Mo analysis successfully described the nonisothermal crystallization process of PBS/LDH nanocomposites. The cooling rate is the direct reason, but the temperature at which the crystallization occurs under cooling is the underlying one, which causes the discrepancy of melting behavior between pure PBS and PBS/LDH nanocomposites. The isoconversional analysis was successfully employed to determine the effective activation energy barrier for nonisothermal crystallization. It was found to vary with relative degree of crystallinity and strongly dependent on the LDH content. The addition of LDH and its content in the PBS matrix influence the spherulitic size and the overall crystallization process of PBS significantly, but it does not affect the crystallization mechanism and the crystalline structure of PBS matrix.

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