

NON-ISOTHERMAL CRYSTALLIZATION KINETICS OF KEVLAR FIBER-REINFORCED WOOD FLOUR/HDPE COMPOSITES

Rongxian Ou, Chuigen Guo, Yanjun Xie, and Qingwen Wang*

Non-isothermal crystallization of neat high density polyethylene (HDPE), wood flour (WF)/HDPE composite (WPC), virgin Kevlar fiber (KF) reinforced WPC (KFWPC), and grafted Kevlar fiber (GKF) reinforced WPC (GKFWPC) was investigated by means of differential scanning calorimetry (DSC) and wide angle X-ray diffraction (WAXD). Several theoretical models were applied to describe the process of non-isothermal crystallization. The results showed that the Avrami analysis modified by Jeziorny and a method developed by Mo and coworkers successfully described the non-isothermal crystallization behavior of HDPE and composites. The Ozawa analysis, however, failed to provide an adequate description of non-isothermal crystallization. The values of crystallization peak temperature (T_p), half-time of crystallization ($t_{1/2}$), and kinetic parameters K_j and $F(T)$ showed that the crystallizability followed the order: FKFWPC > GKFWPC > HDPE > WPC. The effective activation energy for non-isothermal crystallization of HDPE and composites based on both Kissinger and Friedman methods was evaluated. WAXD indicated that the crystalline thickness perpendicular to the reflection plane (L_{hkl}) increased with the addition of KF. The results demonstrated that KF and GKF can act as nucleating agents and increase the crystallization rate of HDPE. Compared with GKF, KF is a more effective nucleating agent for HDPE, and wood flour cannot act as a nucleating agent for HDPE.

Keywords: High density polyethylene; Kevlar fiber; Non-isothermal crystallization; Wood plastic composites

Contact information: Key Laboratory of Bio-Based Material Science and Technology (Ministry of Education), Northeast Forestry University, Harbin 150040, China; *Corresponding author: qwwang@nefu.edu.cn

INTRODUCTION

High density polyethylene (HDPE) is an important polymer with high-tonnage production due to its superior mechanical and physical properties. However, its brittleness and inadequate stiffness restrict the versatility of its applications to some extent. Reinforcing HDPE with filler is an efficient measure to improve its tensile and flexural properties (Xiong et al. 2009), creep resistance (Xu et al. 2001), and impact strength (Liu et al. 2002).

During the past decade, wood plastic composites (WPCs) have received extensive attention from both academia and industry (Liu et al. 2008). WPCs are considered to be a new way to efficiently utilize natural lignocellulosic materials and reduce environmental

problems arising from wastes of lignocellulosic materials and plastic products. WPCs are mainly used as exterior nonstructural or semistructural building materials, automobile components, and transportation materials (Liu et al. 2008).

In spite of the advantages mentioned above, WPC's application in many fields (structural and engineering construction) is still restricted because of poor interfacial bonding between hydrophilic wood and hydrophobic plastic matrices. The resulting composites therefore exhibit poor mechanical properties (Lai et al. 2003; Park and Balatinecz 1996), especially lower impact toughness (Matuana et al. 1998).

Our recent work has indicated that the addition of a small amount (2 to 3%) of Kevlar fiber could significantly improve the tensile, flexural, and impact properties of wood flour/HDPE composite. Both reinforcing and toughening effects were realized (Ou et al. 2010).

For composites based on semicrystalline polymers, morphological features such as degree of crystallinity, spherulite size, lamella thickness, crystallite orientation, and the formation of transcrystalline layer influence the ultimate properties of the polymer matrix and the resulting reinforced composite (Choudhury 2008). Both morphology and crystallinity of the thermoplastic polymer matrix are substantially affected by the reinforcement used (Arroyo et al. 2000; Piorkowska 2001; Quan et al. 2005). The transcrystalline layer formation has been found to improve the interfacial strength and mechanical properties of WPC (Zafeiropoulos et al. 2001; Zhang et al. 1996). However, no effect or even a negative effect on interfacial and mechanical properties has been reported (Wang and Hwang 1996).

Since the crystalline structure of the polymer matrix can influence the physical and mechanical properties of the reinforced polymer composites, it is of great importance to investigate the crystallization behavior of polymer composites (Yuan et al. 2006). Generally, non-isothermal kinetics analysis is used to study crystallization behavior of crystalline polymers.

The study of the non-isothermal crystallization of polymer composites has a practical meaning because the processes of composites are commonly run under non-isothermal conditions (Yuan et al. 2006). The crystallization kinetics of polyethylenes and polyethylene composites (Huang et al. 2008; Kundu et al. 2003; Li et al. 2006; Qian and He 2003; Xu et al. 2005; Zou et al. 2009) have been extensively reported previously, but few studies have focused on the crystallization kinetics of WPCs (Zou et al. 2009), especially Kevlar fiber (KF) reinforced wood flour/HDPE composites.

The objective of the present work is to compare the non-isothermal crystallization kinetics between the neat HDPE and its composites (with wood flour (WF), WF and KF, WF and grafted Kevlar fiber (GKF)) using differential scanning calorimeter (DSC) and wide-angle X-ray diffraction (WAXD). The kinetics are further analyzed using the theoretical approaches of Avrami, Ozawa, and Mo and coworkers (Avrami 1940; Liu et al. 1997; Ozawa 1971) for non-isothermal crystallization. The activation energy is calculated based on the Kissinger method (Kissinger 1956), and the differential iso-conversional method of Friedman (1964).

EXPERIMENTAL

Materials

HDPE (5000S resin, density 0.954 g cm^{-3} , melt flow index 0.7 g/10 min) from Daqing Petrochemical Co., China, was used in the study as the matrix. Kevlar-29 fibers (6 mm in length, diameter $12 \mu\text{m}$) were purchased from Du Pont, USA. Poplar wood flour that passed through a sieve of 40-mesh size ($425 \mu\text{m}$) and had been retained on a 70-mesh ($212 \mu\text{m}$) sieve was supplied by Harbin Yongxu, China. Kevlar fiber co-grafted with the mixture of γ -chloropropyltrimethoxysilane and allyl chloride was prepared according to our previous study (Ou et al. 2010).

Preparation of HDPE and the Composite Samples

To avoid the influence of heating history in processing of the polymer crystallization, all the samples, including neat HDPE, wood flour/HDPE composite (WPC), KF reinforced WPC (KFWPC), and GKF reinforced WPC (GKFWPC) were prepared under the same conditions.

Wood flour (WF) was dried at $105 \text{ }^\circ\text{C}$ for 24 h to remove moisture. HDPE was mixed with WF, KF, or GKF in a high-speed mixer for 8 min, subsequently melted, and extruded by a twin-screw/single-screw extruder system to form HDPE and its composite sheets.

The processing temperatures for extrusion were set at $150 \text{ }^\circ\text{C}$ in the melting zone, $155\text{--}175 \text{ }^\circ\text{C}$ in the pumping zone, and $170 \text{ }^\circ\text{C}$ in the die zone, respectively. The rotation speeds of the twin-screw and single-screw were 40 rpm and 20 rpm respectively. The weight ratios of HDPE/WF/KF/GKF were 40/0/0/0 for HDPE, 40/60/0/0 for WPC, 40/57/3/0 for KFWPC, and 40/57/0/3 for GKFWPC, respectively.

DSC Analysis

The non-isothermal crystallization kinetics were investigated using a Pyris Diamond differential scanning calorimeter from Perkin-Elmer instruments, Shelton, Connecticut.

The instrument's operating temperature was calibrated with indium. Samples of about 5 mg were used and were initially heated to 443 K at a rate of 20 K min^{-1} , melted for 5 min to erase the thermal history, and then cooled down to 298 K at four different cooling rates: 2.5, 5, 10, and 15 K min^{-1} , respectively.

The crystallized samples were re-heated at a rate of 10 K min^{-1} to investigate the melting behavior of HDPE. All the measurements were carried out in a nitrogen atmosphere at a flow rate of 20 ml min^{-1} .

WAXD Analysis

The WAXS experiment was carried out on a Rigaku D/max-2200 (Rigaku Corporation, Tokyo, Japan) with CuK_α radiation ($\lambda = 1.5406 \text{ \AA}$) operated at 40 kV and 30 mA. The 2θ range was from 5° to 40° with a scanning speed of 4 deg min^{-1} .

RESULTS AND DISCUSSION

Non-isothermal Crystallization Behavior

The effects of wood flour and Kevlar fiber on the crystallization behavior of HDPE were quantitatively analyzed through non-isothermal DSC experiments (Fig. 1). The onset temperature (T_c), which is the temperature at the crossing point of the tangents of the baseline and the high temperature side of the exotherm, and the crystallization peak temperature (T_p) of HDPE or its composites were determined from the plots (Table 1).

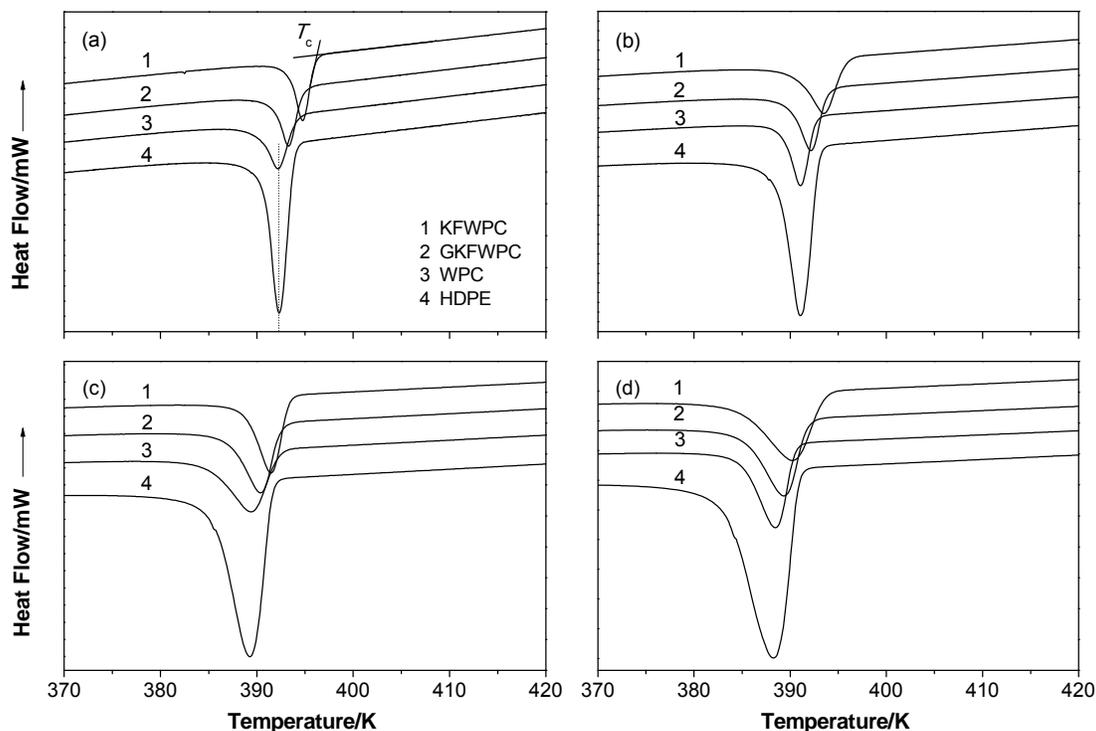


Fig. 1. DSC thermograms for non-isothermal crystallization of HDPE and its composites at cooling rates of (a) 2.5, (b) 5, (c) 10, and (d) 15 K min⁻¹

Both T_c and T_p decreased with increasing the cooling rate. T_p of neat HDPE decreased approximately 4 K as the cooling rate increased from 2.5 to 15 K min⁻¹. A similar behavior was observed for the composites. A slower cooling rate provides better fluidity and diffusivity for molecules due to low viscosity and allows much more time to activate nuclei at a higher temperature. On the contrary, at faster cooling rates, the activation of the nuclei occurs at a lower temperature (DiLorenzo and Silvestre 1999; Qian and He 2003). The addition of wood flour to neat HDPE did not change the T_p . This implies that the wood flour does not act as a nucleating agent for the HDPE matrix. Similar results were obtained in previous studies (Mucha and Królikowski 2003; Zou et al. 2009). However, some studies also showed that wood particles act as effective nucleating agents (Borysiak and Doczekalska 2006; Bouafif et al. 2009; Garbarczyk and Borysiak 2004; Garbarczyk et al. 2002; Mathew et al. 2006). Consequently, further

investigations are needed to clarify the effect of the size, chemical composition, surface polarity, and surface topography of wood particles in the nucleation activity and crystallization kinetics of polymers. The presence of Kevlar fiber in HDPE caused an obvious increase in T_p (Fig. 1). This implies that Kevlar fiber is an effective nucleating agent to increase the rate of crystallization of HDPE. When the Kevlar fiber surface was co-grafted with the mixture of γ -chloropropyltrimethoxysilane and allyl chloride, grafted KF still can function as a heterogeneous nucleating agent in the composite, but exhibited less effect than the virgin KF. This may be ascribed to the weakened nucleating ability of GKF and the improved interfacial adhesion between HDPE and GKF in the composites, where the movement of HDPE segments is inhibited, thus reducing the crystallization rate of HDPE in the composites.

Table 1. Non-isothermal Parameters for HDPE and its Composites at Various Cooling Rates Determined from DSC Exotherms

Sample	Cooling rate (K min ⁻¹)	T_c (K)	T_p (K)	$t_{1/2}$ (s)
HDPE	2.5	393.9	392.4	39.0
	5	392.9	390.9	23.3
	10	391.6	389.3	15.6
	15	390.7	388.1	12.4
WPC	2.5	393.4	392.2	44.2
	5	392.5	390.9	28.4
	10	391.2	389.4	18.5
	15	390.3	388.3	15.0
KFWPC	2.5	396.5	394.7	30.2
	5	395.6	393.4	19.2
	10	394.3	391.6	11.9
	15	393.4	390.1	9.4
GKFWPC	2.5	394.7	393.3	33.8
	5	393.7	392.0	21.3
	10	392.4	390.4	13.7
	15	391.6	389.2	11.1

In the non-isothermal crystallization process, the relative crystallinity X_t , a function of crystallization temperature T , can be formulated as (Herrero et al. 1994),

$$X_t = \int_{T_0}^T \left(\frac{dH_c}{dH} \right) dT \bigg/ \int_{T_0}^{T_\infty} \left(\frac{dH_c}{dH} \right) dT \quad (1)$$

where T_0 is the initial crystallization temperature, T and T_∞ represent the crystallization temperature at time t and the ultimate crystallization temperature, respectively. The term ΔH_c is the enthalpy of crystallization released during an infinitesimal temperature range dT (Cebe and Hong, 1986). The crystallization time (t) can be calculated by,

$$t = (T_0 - T)/\Phi \quad (2)$$

where T_0 is the temperature at the beginning of crystallization ($t = 0$), T is the temperature at a crystallization time t , and Φ is the cooling rate. Figure 2 shows the relationship between the relative degree of crystallinity as a function of temperature for HDPE and KFWPC at various cooling rates (the plots of WPC and GKFPC are omitted). At higher the cooling rate, HDPE started to crystallize at lower temperature range. This is attributed to the dependence of nucleation and crystal growth on the degree of supercooling.

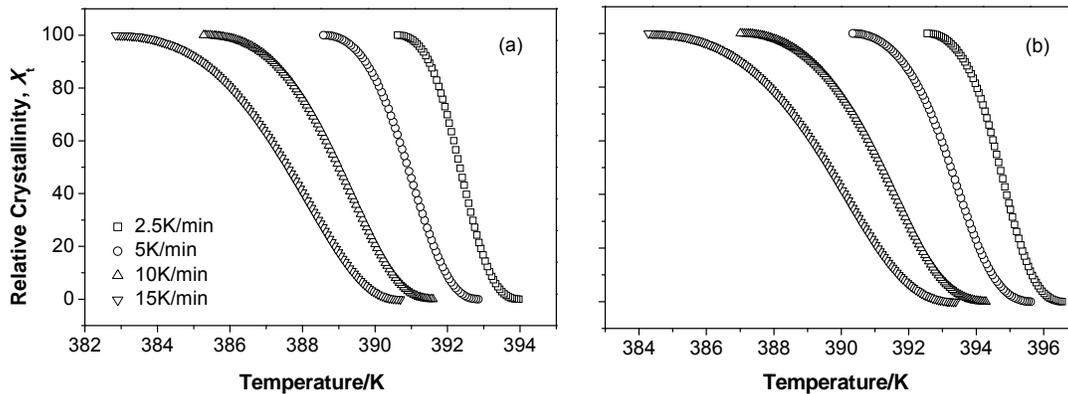


Fig. 2. Relative crystallinity as a function of temperature for non-isothermal crystallization of (a) neat HDPE and (b) KFWPC at various cooling rates

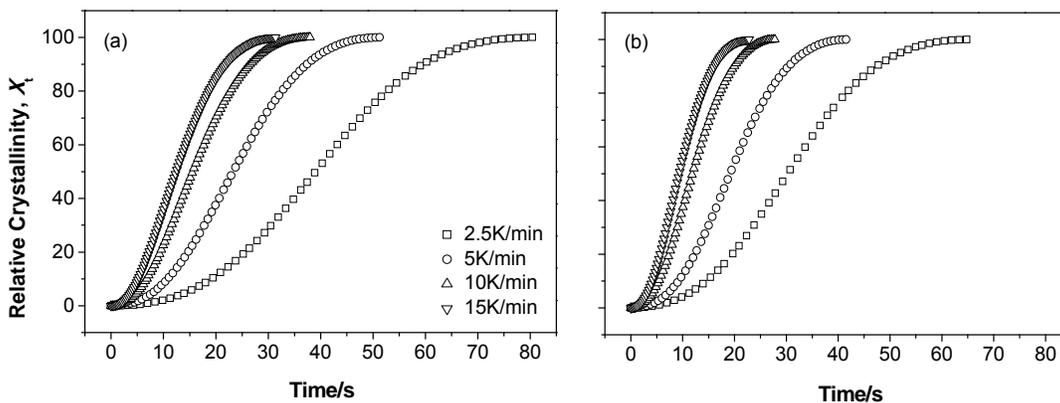


Fig. 3. Relative crystallinity as a function of time for non-isothermal crystallization of (a) neat HDPE and (b) KFWPC at various cooling rates

According to Eq. 2, the X-axis in Fig. 2 can be changed into a time axis, as shown in Fig. 3. It can be clearly seen that increasing the cooling rate reduced the time for

completion of crystallization. From these curves, an important parameter that can be derived is the half-time of crystallization ($t_{1/2}$), which is the value of the time from the onset of crystallization to the time at which X_t is 50%; these values are listed in Table 1. As expected, with increasing cooling rate, the crystallization half time decreased. This indicates that the crystallization of the HDPE can be conducted faster at a higher cooling rate. At the same cooling rate, $t_{1/2}$ for the four samples follows the order: $t_{1/2}$ (KFWPC) < $t_{1/2}$ (GKFWPC) < $t_{1/2}$ (neat HDPE) < $t_{1/2}$ (WPC). Clearly, the crystallization rate of HDPE has been accelerated after addition of virgin and grafted Kevlar fibers, but wood flour retarded the crystallization of HDPE. This indicates that wood flour cannot act as a nucleating agent for the HDPE matrix, because larger size of wood flour may limit the flow of polymer, and restrict its rearrangement due to steric hindrance. After addition of virgin Kevlar fiber, the values of $t_{1/2}$ for KFWPC decreased significantly compared to that of WPC, and was even lower than that of neat HDPE. This means that virgin Kevlar fiber has a remarkable heterogeneous nucleation effect on the HDPE matrix.

Avrami Method

Isothermal crystallization kinetics of polymers is commonly studied by the Avrami method (Avrami 1939, 1940, 1941). Based on the assumption that the crystallization temperature is constant, Mandelkern (1980) considered that the primary stage of non-isothermal crystallization could also be described by the Avrami equation, just like isothermal analysis,

$$1-X_t = \exp(-K t^n) \quad (3)$$

where X_t is the relative crystallinity, t is the time, K is the kinetic rate constant involving nucleation and growth parameters, and n is the Avrami exponent, which is a parameter depending on the geometry of the growing crystals and the nucleation process.

The above equation can be rearranged as follows by taking its double logarithm:

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

Plotting $\ln[-\ln(1-X_t)]$ against $\ln t$ for each cooling rate, a straight line was obtained with the data at a lower degree of crystallinity in the linear regression (Fig. 4). The slope of the line is n and the intercept with the ordinate yields $\ln K$. It should be taken into account that in non-isothermal crystallization, the values of the n and K do not have the same physical significance as in isothermal crystallization, due to the fact that the temperature changes constantly under non-isothermal conditions. It affects the rates of both nuclei formation and spherulite growth, since they are temperature dependent. In this case, n and K might be only considered as two adjustable parameters to fit the data. Although the physical meaning of n and K cannot be related to the isothermal case in a simple way, Eq. 3 provides further insight into the kinetics of non-isothermal crystallization.

Considering the non-isothermal character of the process investigated, the rate parameter K should be corrected for the influence of cooling rate Φ of the polymer, as is suggested for poly(ethylene terephthalate) (Jeziorny 1978). Assuming Φ to be constant or approximately constant, the final form of the parameter characterizing the kinetics of non-isothermal crystallization was given as follows,

$$\ln K_J = \ln K/\Phi \quad (5)$$

where K_J is the corrected kinetic rate constant and Φ is the cooling rate. The results obtained from the Avrami plots and Jeziorny method are summarized in Table 2. The Avrami exponents, n , were non-integer and ranged from 2.27 to 2.46 for the neat HDPE, which is consistent with the results of Zou's for rape straw flour/HDPE composite (Zou et al. 2009), from 2.21 to 2.26 for WPC, 2.22 to 2.40 for KFWPC, and 2.26 to 2.36 for GKFwPC, respectively. The fact that the range of the n value was 2 to 3 suggests that the non-isothermal crystallization of the neat HDPE and HDPE matrix in the composites corresponds to a tridimensional growth with heterogeneous nucleation (Zou et al. 2009). K and K_J for KFWPC and GKFwPC are higher than that of neat HDPE at the same cooling rate, suggesting a higher crystallization rate for HDPE in the Kevlar fiber reinforced composites. K and K_J for KFWPC are larger than that for GKFwPC, i.e. the crystallization rate of KFWPC is faster than that of GKFwPC, which is in agreement with the results of $t_{1/2}$. K and K_J for WPC are lower than that of neat HDPE at the same cooling rate, indicating that wood flour cannot act as a nucleating agent for the HDPE matrix.

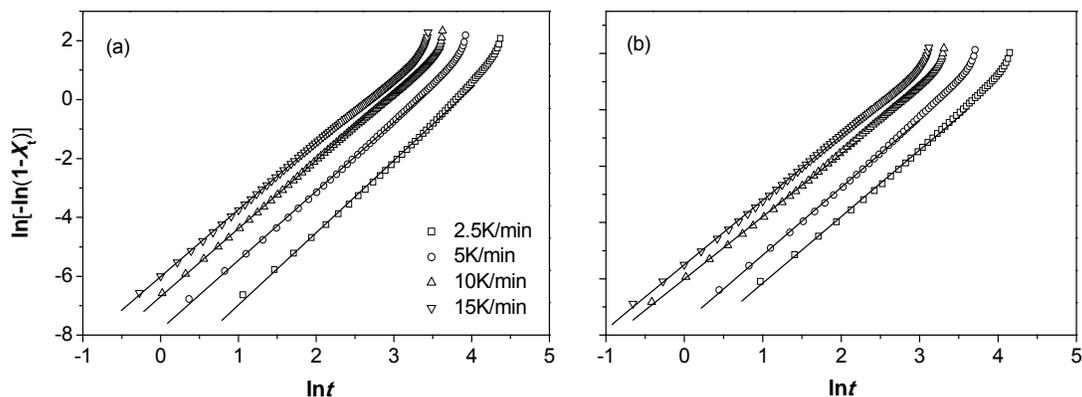


Fig. 4. Pots of $\ln[-\ln(1-X_t)]$ versus $\ln t$ for the non-isothermal crystallization of (a) neat HDPE and (b) KFWPC at various cooling rates

The Ozawa Method

Considering the non-isothermal character of the process, cooling rate (Φ) is the factor that needs to be considered. Based on the mathematical derivation of Evans, Ozawa modified the Avrami equation by incorporating the cooling rate (Φ) factor and is given by (Ozawa 1971),

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

where $K(T)$ and m are the Ozawa crystallization rate constant and exponent, respectively. Eq. 6 in the logarithmic form can be written as:

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

Table 2. Avrami Kinetics Parameters

Sample	Cooling rate (K min ⁻¹)	n	$K(\text{min}^{-1})$	K_J	R^2
HDPE	2.5	2.46	0.00008	0.0229	0.998
	5	2.34	0.00041	0.2101	0.999
	10	2.31	0.00124	0.5120	0.999
	15	2.27	0.00245	0.6697	0.999
WPC	2.5	2.21	0.00012	0.0270	0.997
	5	2.26	0.00028	0.1947	0.999
	10	2.23	0.00085	0.4931	0.999
	15	2.20	0.00153	0.6491	0.999
KFWPC	2.5	2.36	0.00017	0.0310	0.998
	5	2.40	0.00053	0.2212	0.999
	10	2.22	0.00246	0.5483	0.999
	15	2.29	0.00407	0.6928	0.999
GKFWPC	2.5	2.32	0.00012	0.0270	0.998
	5	2.36	0.00045	0.2141	0.999
	10	2.29	0.00162	0.5259	0.998
	15	2.26	0.00291	0.6775	0.998

Plots based on Eq. 7 for the non-isothermal crystallization data of neat HDPE and KFWPC for a series of temperatures are presented in Fig. 5. In our study, the Ozawa plots of neat HDPE and KFWPC show deviation from linearity when cooling rate varies from 2.5 to 15 K min⁻¹, suggesting that the Ozawa equation is not appropriate to describe the non-isothermal crystallization of neat HDPE and its composites because it does not consider the issue of secondary crystallization.

The Mo Method

In order to find a method that exactly describes the non-isothermal crystallization process, Mo and Liu (Liu and Mo 1991; Liu et al. 1997) suggested a novel kinetic approach by combining the Avrami equation (Eq. 3) with the Ozawa equation (Eq. 6),

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

where $F(T) = [K(T)/K]^{1/m}$ refers to the value of the cooling rate chosen at a unit crystallization time, when the system has a certain degree of crystallinity. The smaller the value of $F(T)$, the higher the crystallization rate. Therefore, $F(T)$ has a definite physical and practical meaning. Meanwhile, α refers to the ratio of the Avrami exponent n to the Ozawa exponent m (i.e. $\alpha = n/m$). At a given degree of crystallinity, plotting $\ln \Phi$ versus $\ln t$ (a typical plot is shown in Fig. 6) yields a good linear relationship between $\ln \Phi$ and $\ln t$. The data of kinetic parameter, $F(T)$ and α , can be estimated from the intercept and slope.

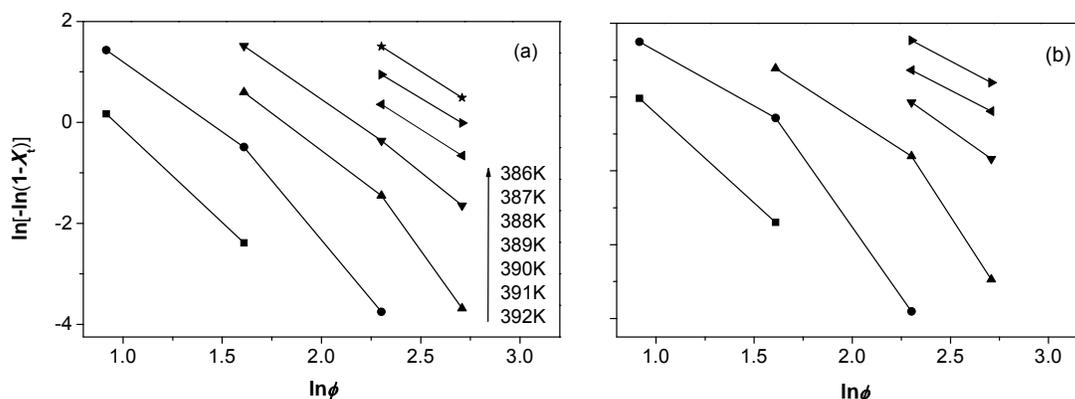


Fig. 5. Ozawa plots of $\ln[-\ln(1-X_t)]$ versus $\ln \Phi$ for non-isothermal crystallization of a neat HDPE and b KFWPC

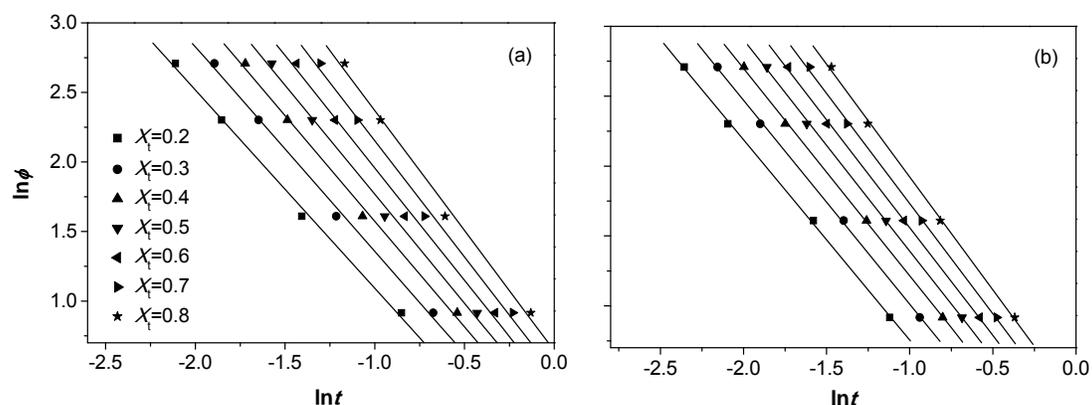


Fig. 6. Plots of the $\ln \Phi$ versus $\ln t$ for non-isothermal crystallization of a neat HDPE and b KFWPC

The value of α ranged from 1.42 to 1.73 for neat HDPE, 1.56 to 1.76 for WPC, 1.43 to 1.61 for KFWPC, and 1.50 to 1.69 for GKFwPC, respectively (Table 3). The variation in the values of α for all the neat HDPE and its composites was small, indicating that the method of Mo and coworkers (Eq. 8) was successful in describing the non-isothermal process of neat HDPE and its composites in a manner similar to rape straw flour/HDPE composites (Zou et al. 2009), PP-clay nanocomposites (Yuan et al. 2006), and PP-surface-treated SiO_2 nanocomposites (Papageorgiou et al. 2005). It can be seen from Table 3 that the values of $F(T)$ increased systematically with increasing relative

degree of crystallinity. At a given degree of crystallinity, the higher the $F(T)$ value, the higher the cooling rate needed within unit crystallization time, indicating the difficulty of polymer crystallization. For the same relative crystallinity, the $F(T)$ for the four samples follows the order: KFWPC < GKFwPC < neat HDPE < WPC. This suggests that the crystallization rate follows the order: KFWPC > GKFwPC > neat HDPE > WPC. The trend is in good agreement with the statement made from the Avrami equation and $t_{1/2}$.

Table 3. Value of $F(T)$ and a for HDPE and Blends

Sample	X_t	$F(T)$	α	R^2	Activation energy ΔE (kJ mol ⁻¹)
HDPE	0.2	0.72	1.42	0.9967	538.0
	0.3	0.89	1.47	0.9963	
	0.4	1.06	1.52	0.9959	
	0.5	1.22	1.57	0.9953	
	0.6	1.40	1.62	0.9946	
	0.7	1.62	1.67	0.9938	
	0.8	1.90	1.73	0.9934	
WPC	0.2	0.79	1.56	0.9991	590.0
	0.3	1.03	1.58	0.9990	
	0.4	1.25	1.61	0.9988	
	0.5	1.49	1.65	0.9986	
	0.6	1.75	1.68	0.9985	
	0.7	2.07	1.72	0.9984	
	0.8	2.51	1.76	0.9984	
KFWPC	0.2	0.51	1.43	0.9994	502.3
	0.3	0.64	1.46	0.9995	
	0.4	0.76	1.48	0.9995	
	0.5	0.89	1.51	0.9995	
	0.6	1.02	1.54	0.9994	
	0.7	1.17	1.58	0.9992	
	0.8	1.36	1.61	0.9990	
GKFwPC	0.2	0.55	1.50	0.9992	562.7
	0.3	0.70	1.53	0.9990	
	0.4	0.84	1.56	0.9987	
	0.5	0.99	1.59	0.9984	
	0.6	1.15	1.62	0.9982	
	0.7	1.35	1.65	0.9980	
	0.8	1.61	1.69	0.9978	

Effective Activation Energy

It is known that the crystallization of polymers is controlled by two factors: one is the dynamic factor, which is related to the activation energy ΔE for the transport of crystalline units across the phase, and the other is the static factor that is related to the free energy barrier for nucleation (Yuan et al. 2006). Considering the variation of T_p with the cooling rate (Φ), the ΔE of non-isothermal crystallization can be evaluated from the Kissinger method (Kissinger 1956),

$$\frac{d[\ln(\phi/T_p^2)]}{d[1/T_p]} = -\frac{\Delta E}{R} \quad (9)$$

where T_p , R , and Φ are the peak temperature, the universal gas constant, and the cooling rate, respectively. Figure 7 shows the plots based on the Kissinger method and the slopes of the least-square lines drawn through these plots ($\Delta E/R$), enabling determination of the activation energy, ΔE . The results of ΔE are listed in Table 3. The activation energies of non-isothermal melt crystallization of neat HDPE, WPC, KFWPC, and GKFPC are 538.0, 590.0, 502.3, and 562.7 kJ mol⁻¹, respectively. The addition of virgin KF caused a decrease in ΔE , which made the molecular chains of HDPE easier to crystallize, and increased the crystallization rates due to the nucleation activity of KF. The value of ΔE for WPC is higher than that of neat HDPE, suggesting that wood flour cannot act as an effective nucleating agent and decelerate the crystallization of HDPE in the composites. These results are in agreement with the experimental results observed above.

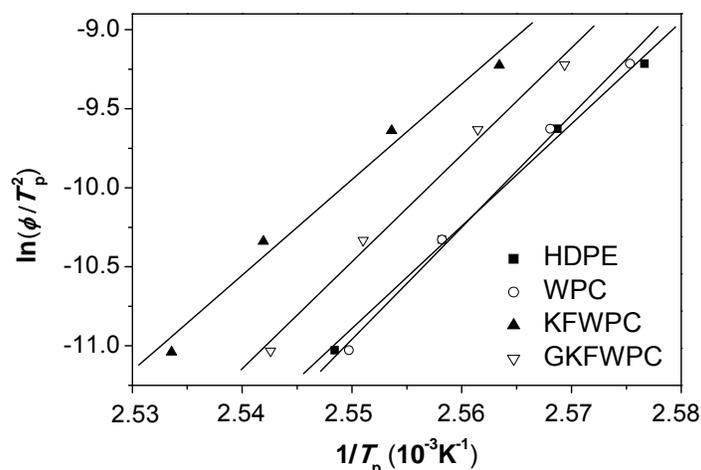


Fig. 7. Determination of the activation energy (ΔE) describing the non-isothermal crystallization process of the HDPE and its composites based on Kissinger method

Recently, Vyazovkin (2002) has demonstrated that dropping the negative sign for Φ is a mathematically invalid procedure that generally makes the Kissinger equation inapplicable to the processes that occur on cooling. The use of this invalid procedure may result in erroneous values of the effective energy barrier, ΔE . Therefore, the differential iso-conversional method of Friedman (1964) and the integral iso-conversional method of

Vyazovkin (2001) are appropriate for melt crystallization. In this work, the Friedman method will be used, mainly due to the reliability and simplicity of the method (Vyazovkin 2001). The Friedman equation is expressed as follows,

$$\ln\left(\frac{dX_t}{dt}\right)_{X_t} = \text{constant} - \frac{\Delta E_{X_t}}{RT_{X_t}} \quad (10)$$

where dX_t/dt is the instantaneous crystallization rate as a function of time for a given value of the relative crystallinity (X_t), R is the universal gas constant, and ΔE_{X_t} is the effective energy barrier of the process for a given value of X_t . At various cooling rates, the values of dX_t/dt at a specific X_t are correlated to the corresponding crystallization temperature at this X_t , that is, T_{X_t} , a straight line can be obtained by plotting $\ln(dX_t/dt)$ versus $1/T_{X_t}$, and the slope is $-\Delta E_{X_t}/R$.

Figure 8 illustrates a typical plot of $\ln(dX_t/dt)$ as a function of $1/T_{X_t}$ for neat HDPE at different relative crystallinities. As can be seen, there was a good linear relation between $\ln(dX_t/dt)$ and $1/T_{X_t}$ at each relative crystallinity, and all the values of the regression coefficient (R^2) were larger than 0.98, indicating the Friedman equation was successful in calculating the effective activation energy barrier at different crystallinities.

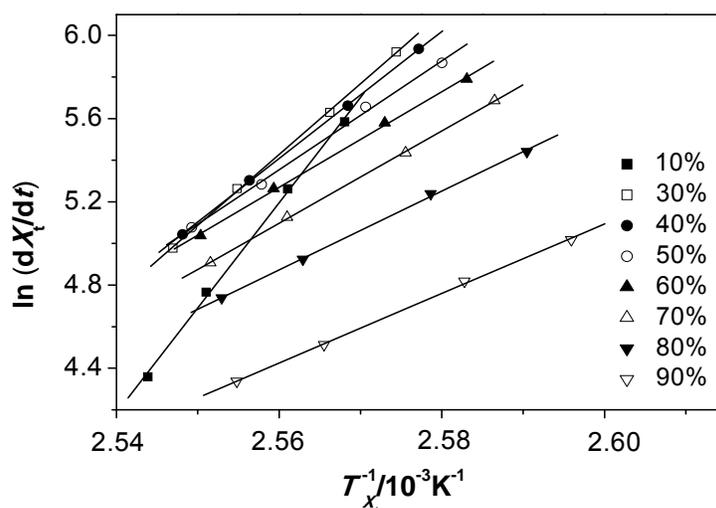


Fig. 8. Plots of $\ln(dX_t/dt)$ versus $1/T_{X_t}$ of neat HDPE at different relative crystallinities

The dependence of the effective activation energy on conversion based on the Friedman equation is shown in Fig. 9. The activation energy is negative, which indicates that the crystallization increases as the temperature decreases. For all of the samples studied, the experimental activation energy generally increased with increasing relative crystallinity, suggesting that as the crystallization proceeded it was more difficult for each polymer system to crystallize.

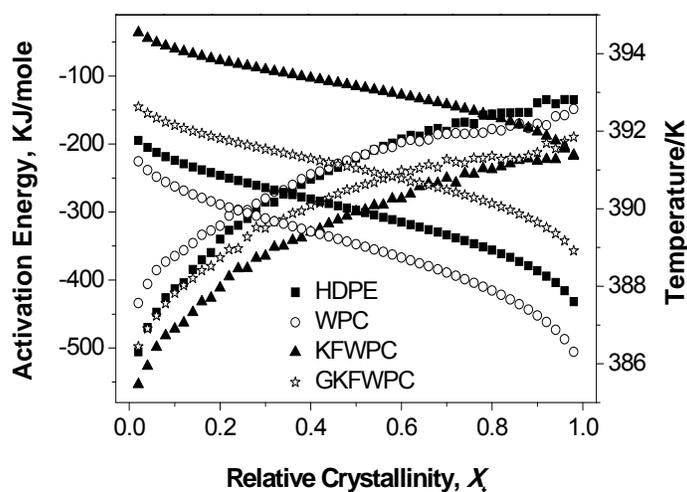


Fig. 9. Dependence of the effective activation energy and temperature on the relative crystallinity for HDPE and its composites

The activation energy of KFWPC and GKFwPC were lower than that of neat HDPE at all relative crystallinities. Also, the activation energy of KFWPC was lower than that of GKFwPC. It should be noted that the lower the activation energy, the higher the crystallization ability of the polymer system (Supaphol et al. 2004). Therefore, this trend shows that virgin and grafted KF dispersed in the composites act as a heterogeneous nucleation for the crystallization of HDPE and accelerate the crystallization process. The effect of virgin KF is stronger than that of modified KF. The activation energy of WPC is higher than neat HDPE when relative crystallinity is lower than 0.5, and is equivalent to that of neat HDPE at higher relative crystallinities, suggesting that wood flour cannot act as a nucleating agent.

Wide Angle X-ray Diffraction

Figure 10 shows the X-ray diffraction patterns of HDPE and composites that were cooled down to room temperature at a rate of 10 K min^{-1} . As listed in Table 4, the characteristic X-ray peaks for neat HDPE were observed at the scattering angles of 21.6, 24.1, 30.2, and 36.4, which correspond to the reflections from the (110), (200), (210), and (020) planes, respectively (Rizzo et al. 2001). In addition to the sharp diffraction peaks, the shoulder on Fig. 10 is the characteristic diffraction band of the amorphous regions. The characteristic peaks of WPC, KFWPC, and GKFwPC are similar to those of neat HDPE, as shown in Fig. 10 and Table 4. There are no new characteristic peaks or significant differences appearing in the X-ray patterns of the composites, indicating that the crystalline structure of HDPE remains unchanged upon blending with WF or KF. As can be seen in Fig. 10, however, the intensity of the crystalline peaks of HDPE decreases as WF and KF were added. This decrease in the peak intensity could be due to the decrease in crystallinity (Karger-Kocsis et al. 1979; Moly et al. 2005). As mentioned in Table 4, when grafted KF is added to WPC composites, all the crystalline thicknesses perpendicular to the reflection plane (L_{hkl}) are increased. The increased values may result from the nucleating ability of KF (Arroyo et al. 2000) and crystal perfection.

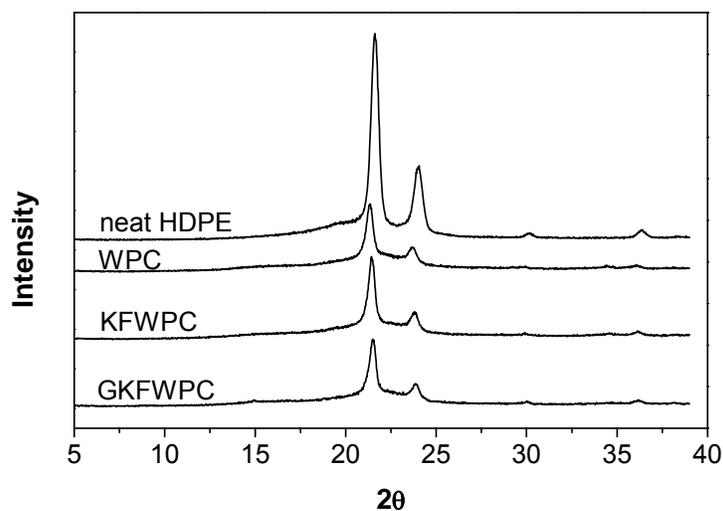


Fig. 10. WAXM patterns of neat HDPE and its composites

Table 4. Crystalline Peaks and Thickness of HDPE and its Composites by XRD

Sample	hkl	Angle (°)	FWHM (°)	L_{hkl} (nm)
HDPE	(110)	21.6	0.468	17.09
	(200)	24.1	0.523	15.36
	(210)	30.1	0.482	16.88
	(020)	36.4	0.497	16.64
WPC	(110)	21.3	0.452	17.68
	(200)	23.7	0.493	16.28
	(210)	29.9	0.577	14.09
	(020)	36.1	0.593	13.93
KFWPC	(110)	21.4	0.434	18.42
	(200)	23.8	0.437	18.37
	(210)	29.9	0.481	16.90
	(020)	36.2	0.445	18.57
GKFWPC	(110)	21.5	0.446	17.93
	(200)	23.9	0.577	13.92
	(210)	30.0	0.520	15.64
	(020)	36.2	0.489	16.90

CONCLUSIONS

1. The results demonstrate that Kevlar fiber (KF) and grafted Kevlar fiber (GKF) can act as nucleating agents to promote the crystallization rate of high density polyethylene (HDPE). Compared with GKF, KF was a more effective nucleator for HDPE; however, wood flour cannot act as a nucleating agent for HDPE.
2. The Avrami equation modified by Jeziorny's method and the Mo method are fit to describe the non-isothermal crystallization behavior of HDPE and its composites; however, the Ozawa equation is inapplicable. The crystallization ability of all samples followed the order: FKWPC > GKFWPC > HDPE > WPC.
3. The effective activation energy for non-isothermal crystallization of all samples based on Friedman equation was ranked: FKWPC < GKFWPC < HDPE \approx WPC.
4. Incorporation of KF in the composite system can increase the crystalline thicknesses perpendicular to the reflection plane (L_{hkl}) as evidenced by WAXD.

ACKNOWLEDGMENTS

We thank the financial supports from National Natural Science Foundation of China (31010103905 and 31070507). In addition, the Fundamental Research Funds for the Central Universities (DL09EB02-1) and the Breeding Plan of Excellent Doctoral Dissertation of Northeast Forestry University (OPTP10-NEFU) are also appreciated.

REFERENCED CITED

- Arroyo, M., Zitzumbob, R., and Avalosc, F. (2000). "Composites based on PP/EPDM blends and aramid short fibres. Morphology/behaviour relationship," *Polymer* 41, 6351-6359.
- Avrami, M. (1939). "Kinetics of phase change. I. General theory," *J. Chem. Phys.* 7, 1103-1112.
- Avrami, M. (1940). "Kinetics of phase change. II. Transformation-time relations for random distribution of nuclei," *J. Chem. Phys.* 8, 212-224.
- Avrami, M. (1941). "Granulation, phase change and microstructure. Kinetics of phase change, 111," *J. Chem. Phys.* 9, 177-184.
- Borysiak, S., and Doczekalska, B. (2006). "Influence of chemical modification of wood on the crystallisation of polypropylene," *Holz. Roh. Werkst.* 64, 451-454.
- Bouafif, H., Koubaa, A., Perré, P., Cloutier, A., and Riedl, B. (2009). "Wood particle/high-density polyethylene composites: Thermal sensitivity and nucleating ability of wood particles," *J. Appl. Polym. Sci.* 113, 593-600.
- Cebe, P., and Hong, S. (1986). "Crystallization behaviour of polyetheretherketone," *Polymer* 27, 1183-1192.
- Choudhury, A. (2008). "Isothermal crystallization and mechanical behavior of ionomer treated sisal/HDPE composites," *Mat. Sci. Eng. A-Struct.* 491, 492-500.

- DiLorenzo, M., and Silvestre, C. (1999). "Non-isothermal crystallization of polymers," *Prog. Polym. Sci.* 24, 917-950.
- Friedman, H. L. (1964). "Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic," *J. Polym. Sci. C.* 6, 183-195.
- Garbarczyk, J., and Borysiak, S. (2004). "Influence of the pulling of embedded natural fibers on the crystal structure of polypropylene matrix," *Int. J. Polym. Mater.* 53, 725-733.
- Garbarczyk, J., Paukszta, D., and Borysiak, S. (2002). "Polymorphism of isotactic polypropylene in presence of additives, in blends and in composites," *J. Macromol. Sci. Phys.* 41, 1267-1278
- Herrero, C. R., and Acosta, J. L. (1994). "Effect of poly(epichlorhydrin) on the crystallization and compatibility behavior of poly(ethylene oxide)/polyphosphazene blends," *Polym. J.* 26, 786-796.
- Huang, J. W., Wen, Y. L., Kang, C. C., Tseng, W. J., and Yeh, M. Y. (2008). "Nonisothermal crystallization of high density polyethylene and nanoscale calcium carbonate composites," *Polym. Eng. Sci.* 48, 1268-1278.
- Jeziorny, A. (1978). "Parameters characterizing the kinetics of the non-isothermal crystallization of poly(ethylene terephthalate) determined by D.S.C.," *Polymer* 19, 1142-1144
- Karger-Kocsis, J., Kallo, A., Szafner, A., and Bodor, G. (1979). "Morphological study on the effect of elastomeric impact modifiers in polypropylene system," *Polymer* 20, 37-43.
- Kissinger, H. E. (1956). "The crystallization kinetics with heating rate in differential thermal analysis," *J. Res. Natl. Bur. Stand. (U.S.)* 57, 217-221.
- Kundu, P. P., Biswas, J., Kim, H., and Choe, S. (2003). "Influence of film preparation procedures on the crystallinity, morphology and mechanical properties of LLDPE films," *Eur. Polym. J.* 39, 1585-1593.
- Lai, S. M., Yeh, F. C., Wang, Y., Chan, H. C., and Shen, H. F. (2003). "Comparative study of maleated polyolefins as compatibilizers for polyethylene/wood flour composites," *J. Appl. Polym. Sci.* 87, 487-496.
- Li, M., He, X. F., Liu, J. J., Zhang, X. Q., Sun, G., Cai, H. G., and Zhang, C. Y. (2006). "Crystallization behavior of polyethylene/montmorillonite (MMT) nanocomposites by in situ polymerization," *Chem. J. Chinese. U.* 27, 779-783.
- Liu, H., Wu, Q., Han, G., Yao, F., Kojima, Y., and Suzuki, S. (2008). "Compatibilizing and toughening bamboo flour-filled HDPE composites: Mechanical properties and morphologies," *Compos. Part A-Appl. S.* 39, 1891-1900.
- Liu, J., and Mo, Z. (1991). "Crystallization kinetics of polymers," *Chinese. Polym. Bull.* 4, 199-207.
- Liu, T., Mo, Z., Wang, S., and Zhang, H. (1997). "Nonisothermal melt and cold crystallization kinetics of poly(aryl ether ether ketone ketone)," *Polym. Eng. Sci.* 37, 568-575.
- Liu, Z. H., Kwok, K. W., Li, R. K. Y., and Choy, C. L. (2002). "Effects of coupling agent and morphology on the impact strength of high density polyethylene/CaCO₃ composites," *Polymer* 43, 2501-2506.

- Mandelkern, L. (1980). *Mandelkern Methods of Experimental Physics*, Academic Press, New York.
- Mathew, A. P., Oksman, K., and Sain, M. (2006). "The effect of morphology and chemical characteristics of cellulose reinforcements on the crystallinity of polylactic acid," *J. Appl. Polym. Sci.* 101, 300-310.
- Matuana, L. M., Park, C. B., and Balatinecz, J. J. (1998). "Cell morphology and property relationships of microcellular foamed pvc/wood-fiber composites," *Polym. Eng. Sci.* 38, 1862-1872.
- Moly, K. A., Radusch, H. J., Androsh, R., Bhagawan, S. S., and Thomas, S. (2005). "Nonisothermal crystallisation, melting behavior and wide angle X-ray scattering investigations on linear low density polyethylene (LLDPE)/ethylene vinyl acetate (EVA) blends: Effects of compatibilisation and dynamic crosslinking," *Eur. Polym. J.* 41, 1410-1419.
- Mucha, M., and Królikowski, Z. (2003). "Application of dsc to study crystallization kinetics of polypropylene containing fillers," *J. Therm. Anal. Calorim.* 74, 549-557.
- Ou, R., Zhao, H., Sui, S., Song, Y., and Wang, Q. (2010). "Reinforcing effects of Kevlar fiber on the mechanical properties of wood-flour/high-density-polyethylene composites," *Compos. Part A-Appl. S.* 41, 1272-1278.
- Ozawa, T. (1971). "Kinetics of non-isothermal crystallization," *Polymer* 12, 150-158.
- Papageorgiou, G., Achilias, D., and Bikiaris, D. (2005). "Crystallization kinetics and nucleation activity of filler in polypropylene/surface-treated SiO₂ nanocomposites," *Thermochim. Acta.* 427, 117-128.
- Park, B. D., and Balatinecz, J. J. (1996). "Effects of impact modification on the mechanical properties of wood-fiber thermoplastic composites with high impact polypropylene (HIPP)," *J. Thermoplast. Compos.* 9, 342-364.
- Piorkowska, E. (2001). "Modeling of crystallization kinetics in fiber reinforced composites," *Macromol. Symp.* 169, 143-148.
- Qian, J., and He, P. (2003). "Non-isothermal crystallization of HDPE/nano-SiO₂ composite," *J. Mater. Sci.* 38, 2299-2304.
- Quan, H., Li, Z. M., Yang, M. B., and Huang, R. (2005). "On transcrystallinity in semi-crystalline polymer composites," *Compos. Sci. Technol.* 65, 999-1021.
- Rizzo, P., Baione, F., Guerra, G., Martinotto, L., and Albizzati, E. (2001). "Polyethylene unit cell and crystallinity variations as a consequence of different cross-linking processes," *Macromolecules* 34, 5175-5197.
- Supaphol, P., Dangseeyun, N., and Srimoan, P. (2004). "Non-isothermal melt crystallization kinetics for poly(trimethylene terephthalate)/poly(butylene terephthalate) blends," *Polym. Test.* 23, 175-185.
- Vyazovkin, S. (2001). "Modification of the integral isoconversional method to account for variation in the activation energy," *J. Comput. Chem.* 22, 178-83.
- Vyazovkin, S. (2002). "Is the Kissinger equation applicable to the processes that occur on cooling?" *Macromol. Rapid. Comm.* 23, 771-775.
- Wang, C., and Hwang, L. M. (1996). "Transcrystallization of PTFE fiber/PP composites. II. Effect of transcrystallinity on the interfacial strength," *J. Polym. Sci. B-Polym. Phys.* 34, 1435-1442.

- Xiong, C., Qi, R. R., Wang, Y. L. (2009). "Wood-thermoplastic composites from wood flour and high-density polyethylene," *J. Appl. Polym. Sci.* 114, 1160-1168.
- Xu, B., and Simonsen, J. (2001). "Creep resistance of wood-filled polystyrene/high-density polyethylene blends," *J. Appl. Polym. Sci.* 79, 418-425.
- Xu, J. T., Zhao, Y. Q., Wang, Q., and Fan, Z. Q. (2005). "Observation of regime III Crystallization in polyethylene/montmorillonite nanocomposites," *Macromol. Rapid. Comm.* 26, 620-625.
- Yuan, Q., Awate, S., and Misra, R. D. K. (2006). "Nonisothermal crystallization behavior of polypropylene-clay nanocomposites," *Eur. Polym. J.* 42, 1994-2003.
- Zafeiropoulos, N. E., Baillie, C. A., and Matthews, F. L. (2001). "A study of transcrystallinity and its effect on the interface in flax fibre reinforced composite materials," *Compos. Part A-Appl. S.* 32, 525-43.
- Zhang, M., Xu, J., Zhang, Z., Zeng, H., and Xiong, X. (1996). "Effect of transcrystallinity on tensile behaviour of discontinuous carbon fibre reinforced semicrystalline thermoplastic composites," *Polymer* 37, 5151-5158.
- Zou, P., Tang, S., Fu, Z., and Xiong, H. (2009). "Isothermal and non-isothermal crystallization kinetics of modified rape straw flour/high-density polyethylene composites," *Int. J. Therm. Sci.* 48, 837-846.

Article submitted: May 12, 2011; Peer review completed: July 4, 2011; Revised version received: September 13, 2011; Accepted: September 16, 2011; Published: September 21, 2011.