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Non-isothermal crystallization behavior of low-density polyethylene/copper nanocomposites

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Abstract

The influences of copper nanoparticles content and cooling rate on non-isothermal crystallization behavior of low-density polyethylene/copper (LDPE/Cu) nanocomposites were investigated. Nanocomposites were prepared by extruding mixtures of pure LDPE and copper nanoparticles using melt-blending method in a single-screw extruder. Differential scanning calorimetry (DSC) was used to analyze their non-isothermal crystallization behavior. The results indicate that both the incorporation of copper nanoparticles and cooling rates influence the crystallization behaviors of the LDPE matrix significantly. Especially, the dependence of the effective activation energy on the relative extent of crystallization implies that the copper nanoparticles dispersed in the nanocomposites may act as a heterogeneous nucleation for the crystallization of the LDPE matrix, and that the presence of the copper nanoparticles may hinder the transport of the molecule chains at the same time, resulting in a decrease of the crystallization growth rate of the LDPE matrix.

Keywords: Polyethylene; Copper nanoparticles; Nanocomposites

1. Introduction

Polymer-based metal nanocomposites are a very important branch of nanocomposites based on polymer matrix. They have combined the advantages of the matrix polymer with the unique characteristics of metal nanoparticles organically. The incorporation of metal nanoparticles makes the nanocomposites gain a series of unique properties, such as optical properties [1–3], electronic properties [4–6], magnetic properties [7], catalytic properties [8], sensitive properties [9], wear properties [10] and so on. Polymer-based metal nanocomposites have become a novel kind of functional materials that has great potential application in many fields.

The polyethylene (PE) is one of the most widely used thermoplastics resins. Considering the fact that the LDPE possesses excellent biocompatibility with human body and usually used as implantable material, LDPE/Cu nanocomposites have been developed as a new kind of intrauterine contraceptive devices (IUDs) materials by using their properties of controlled release in our research. As we know, the cupric ions released from copper-containing IUDs in uterine fluid can enhance their contraceptive effect [11–13], and the larger the release rate of cupric ions, the better the contraceptive effect is. But the release rate of cupric ions in uterine fluid is affected by the structure, i.e. the crystallinity degree, of this new IUDs material. Therefore, it is necessary to study the crystallization behavior of this new IUDs material.

In addition, compared with the investigation of the crystallization behavior of polymer-based non-metal nanocomposites, such as the PTT/clay nanocomposites [14], the PA/clay nanocomposites [15], the PP/P-g-MAH/Org-MMT nanocomposites [16], and so on, the investigation of the crystallization behavior of polymer-based metal nanocomposites is lagged behind relatively. Whether both of them have the similar crystallization behavior or not is not clear, this is an-

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other reason why it is necessary to study the crystallization behavior of LDPE/Cu nanocomposites.

Compared with the isothermal crystallization conditions, the non-isothermal crystallization conditions are much more closer to the real industrial processing conditions, and the results of investigation on non-isothermal crystallization can guide us to control the structure of this new IUDs material. Consequently, the non-isothermal crystallization behavior of LDPE/Cu nanocomposites was investigated in this paper.

The LDPE/Cu nanocomposites were analyzed using differential scanning calorimeter (DSC) to examine the influences of copper nanoparticles content and cooling rate on their non-isothermal crystallization behavior. Simultaneously, pure LDPE was analyzed in the same process for comparison.

2. Experimental

2.1. Materials

The LDPE (melt index at 463 K/2.16 kg is 1.8–3.2 g/10 min) was bought as pellets from Qilu Petrochemical Corporation of China. The copper nanoparticles were prepared via our own patent techniques, i.e. hybrid induction and laser heating (HILH) evaporation condensation method [17]. Their mean diameter is about 50 nm, and purity is over 99.9%.

2.2. Preparation of nanocomposites

The LDPE/Cu nanocomposites were formed by compounding the polymer with 2.0, 6.0, 7.5, and 11.0 wt.% of copper nanoparticles by using melt-blending process in a single-screw extruder (SJ20, made in Jiangshu, China) at a screw speed about 15–20 rpm, respectively. The temperature of the extruder was maintained at 145, 160, and 180 °C from hopper to die, respectively. The composites are referred to here as LC-2.0, LC-6.0, LC-7.5, and LC-11.0, respectively. For comparison, samples of pure polymer were processed in the same way. Table 1 shows the amount of copper nanoparticles in LDPE/Cu nanocomposites.

Table 1
Amount of copper nanoparticles in LDPE/Cu nanocomposites

Samples	LC-2.0	LC-6.0	LC-7.5	LC-11.0
Copper nanoparticles (wt.%)	2.0	6.0	7.5	11.0

2.3. Differential scanning calorimetry (DSC) procedures

The non-isothermal crystallization behavior of the pure LDPE and its nanocomposites was analyzed using a Perkin-Elmer DSC 7 differential scanning calorimeter. The temperature scale of the DSC was calibrated from the melting point (156.60 °C) of high purity (99.999%) indium metal. The power response of the calorimeter was calibrated from the enthalpy of fusion of indium, taken to be 28.45 J/g. The specimens were excised from extruded strands. Each sample is less than 5 mg and was accurately weighed using analytical balance, and then placed in the DSC cell. All DSC analyses were performed under argon atmosphere.

The samples were composed of two groups. The first group was used for evaluating the influence of copper nanoparticles content on the non-isothermal crystallization behavior of the nanocomposites. It contains five samples, of which copper nanoparticles content were 0, 2.0, 6.0, 7.5, and 11.0 wt.%, respectively. Each sample was analyzed using the same process, i.e. heated from 30 to 160 °C at a rate of 10 °C/min, held for 2 min at 160 °C to ensure melting, and then cooled to 30 °C at 10 °C/min. Both the exothermic and endothermic curves were recorded. The second group was used for evaluating the influence of cooling rate on the non-isothermal crystallization behavior of the pure LDPE and its nanocomposites. It includes two samples. One is pure LDPE and the other is its nanocomposites with 7.5 wt.% copper nanoparticles. Both of them were performed as follows: heated from 30 to 160 °C at a rate of 10 °C/min, kept for 2 min at 160 °C to eliminate the heat history before cooled at a specified cooling rate, then cooled to 30 °C at constant cooling rate of 5, 10, 15 and 20 °C/min, respectively. After kept at 30 °C for 2 min, samples were heated to 160 °C at a rate of 10 °C/min, then followed by the next cooling cycle. Both the exothermic and endothermic curves were recorded too.

Heating scans were analyzed for the initial melting temperature T_{fi}, the peak melting temperature T_{fp}, the final melting temperature T_{ff}, and the heat of fusion ΔH_{f}; while cooling scans were used to obtain the initial crystallization temperature T_{ci}, the peak crystallization temperature T_{cp}, the final crystallization temperature T_{cf}, and the heat of crystallization ΔH_{c}. The heat of fusion ΔH_{f}, which was determined by integrating the heat flow from 60 to 115 °C, was used to calculate the crystallinity degree of the pure LDPE and the matrix of the LDPE/Cu nanocomposites, X_{c}, defined by the ratio of $\Delta H_{\mathrm{f}}/(1-x)$ (where x is the content of copper nanoparticles) to the heat of fusion of the purely crystalline form of PE, $\Delta H_{\mathrm{f}}^{\circ}$, i.e. 289.9 J/g [18], as indicated in Table 2. The heats of crystallization ΔH_{c}, were determined by integrating cooling scans from 60 to 105 °C. Fig. 1 shows a representative example of a full heating and cooling cycle and the analytical technique used to calculate ΔH_{f}, ΔH_{c}, T_{fi}, T_{fp}, T_{ff}, T_{ci}, T_{cp} and T_{cf}.

3. Results and discussion

3.1. Influence of copper nanoparticles content on non-isothermal crystallization behavior

The non-isothermal crystallization exothermic and endothermic curves of the neat LDPE and its nanocomposites with various copper nanoparticles contents are illustrated in Figs. 2 and 3, respectively, and the values of ΔH_{f}, ΔH_{c}, T_{fi},

Table 2
Values of ΔH_f, ΔH_c, T_{fi}, T_{fp}, T_{ff}, T_{ci}, T_{cp}, T_{cf} and X_c for LDPE and its nanocomposites

Samples	Heating				Cooling				X_c (%)
	ΔH_f (J/g)	T_{fi} (°C)	T_{fp} (°C)	T_{ff} (°C)	ΔH_c (J/g)	T_{ci} (°C)	T_{cp} (°C)	T_{cf} (°C)	
LDPE	87.84	99.8	108.0	111.0	−72.24	94.1	90.1	85.3	30.30
LC-2.0	85.43	99.6	107.5	110.6	−69.20	94.3	90.2	85.9	30.07
LC-6.0	79.72	99.2	107.1	110.1	−63.60	94.6	90.5	86.4	29.25
LC-7.5	76.92	99.0	107.0	109.7	−61.41	94.7	90.7	86.8	28.68
LC-11.0	73.46	98.7	106.4	108.6	−60.29	95.2	91.1	87.4	28.47

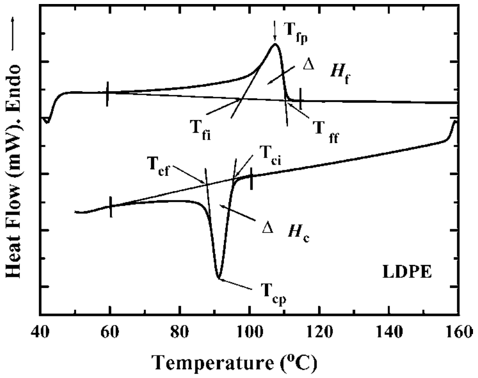

Fig. 1. Representative example of a complete DSC heating and cooling scan and the analytical technique used to determine ΔH_f, ΔH_c, T_{fi}, T_{fp}, T_{ff}, T_{ci}, T_{cp} and T_{cf}.

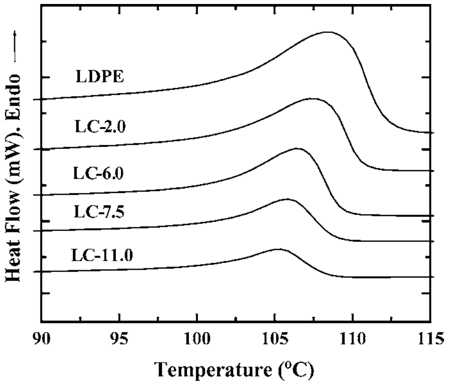

Fig. 2. Heating scans of samples taken from the extruded pure LDPE and its nanocomposites with various content of copper nanoparticles.

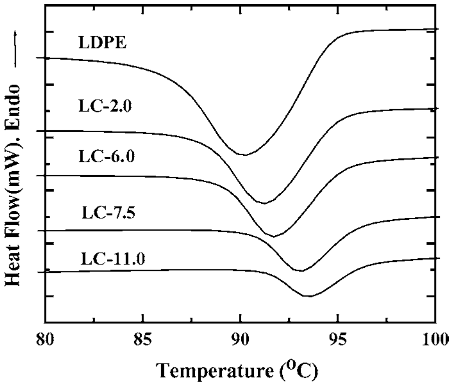

Fig. 3. Cooling scans of samples taken from the extruded pure LDPE and its nanocomposites with various content of copper nanoparticles.

T_{fp}, T_{ff}, T_{ci}, T_{cp}, T_{cf} and X_c at a cooling rate of 10 °C/min for the pure LDPE and its nanocomposites are listed in Table 2.

Figs. 2 and 3 show that both the melting temperatures range and the crystallization temperatures range decrease with increasing of copper nanoparticles content. Data in Table 2 indicate that the melting temperatures decrease but the crystallization temperatures increase with increasing of copper nanoparticles content, and that the higher the content of copper nanoparticles, the lower the crystallinity degree is. Especially, the value of T_{ci} of the LDPE/Cu nanocomposites increase with increasing of copper nanoparticles content can indicate that the copper nanoparticles dispersed in the nanocomposites may act as nucleation agents. Compared with the literature [19], the influence of copper nanoparticles content on the crystallinity degree of the matrix of the LDPE/Cu nanocomposites is similar to the influence of clay content on the crystallinity degree of the s-PS/clay nanocomposites. In addition, the absolute value of ΔH_c is smaller than ΔH_f for the same sample, as shown in Table 2, is because that ΔH_c was determined by integrating cooling scans from 60 to 105 °C and ΔH_f was determined by integrating the heat flow from 60 to 115 °C.

3.2. Influence of cooling rate on non-isothermal crystallization behavior

The non-isothermal crystallization exothermic curves of the neat LDPE and the LDPE/Cu nanocomposite with a copper nanoparticles content of 7.50 wt.% are illustrated in Fig. 4. The influence of various cooling rates on crystallization temperatures (i.e. T_{ci}, T_{cp}, and T_{cf}) of the pure LDPE and the LDPE/Cu nanocomposite with a copper nanoparticles content of 7.50 wt.% is shown in Fig. 5. From Figs. 4 and 5, the following trends can been seen: (a) the crystallization temperatures shift to lower temperature with increasing cooling rate; (b) the values of crystallization temperatures of the LDPE/Cu nanocomposites are larger than those of the neat LDPE; and (c) the bigger the cooling rate, the more obvious the trend of (b) is.

All these results show that the influence of cooling rate on non-isothermal crystallization behavior of the LDPE/Cu nanocomposite is similar to that of the polymer/non-metal nanocomposites, such as the PTT/clay nanocomposites [14], the PA/clay nanocomposites [15], the PP/P-g-MAH/Org-MMT nanocomposites [16], and so on.

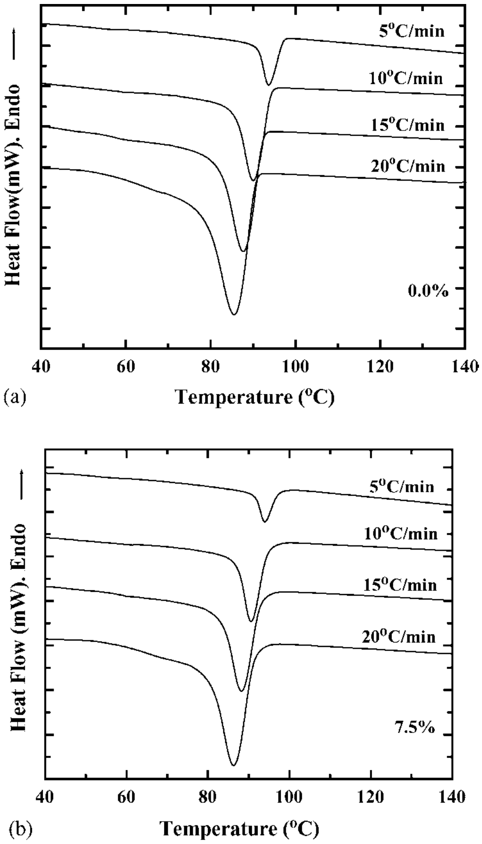

Fig. 4. Heat flow as a function of temperature during non-isothermal crystallization at different cooling rates by DSC for (a) neat LDPE and (b) LDPE/Cu nanocomposite with a copper nanoparticles content of 7.5 wt.%.

3.3. Non-isothermal crystallization analysis

Many methods have been suggested to study the non-isothermal crystallization of polymer. Weng et al. [20], Liu et al. [14,15] have verified that the novel kinetics equation by combining Avrami and Ozawa equation proposed by Mo et al. is suitable to study the non-isothermal crystallization of polymer. Therefore, the combined Avrami and Ozawa equation was used in this paper.

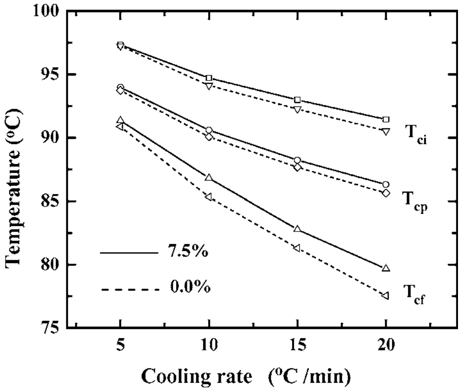

Fig. 5. Plots of the influence of various cooling rates on crystallization temperatures for pure LDPE and its nanocomposites with a copper nanoparticles content of 7.5 wt.%.

As mentioned above, in the non-isothermal crystallization, the time t has the following relation with the temperature T:

$$t = \frac{|T_0 - T|}{\phi} \tag{1}$$

where T is the temperature at time t, T_0 the temperature at the beginning of crystallization ($t = 0$), ϕ the cooling rate.

The Avrami equation is described as follows:

$$1 - X(t) = \exp(-Z_t t^n) \tag{2}$$

where $X(t)$ is the relative crystallinity degree, n the Avrami exponent, t the time and Z_t the growth rate constant. Here, n represents the nucleation mechanism and growth dimension.

And the Ozawa equation is given by

$$1 - C(T) = \exp\left[-\frac{K(T)}{\phi^m}\right] \tag{3}$$

where $C(T)$ is the relative crystallinity degree, m the Ozawa exponent, ϕ the cooling rate and $K(T)$ the kinetic parameter at temperature T. Here, the Ozawa exponent is similar to the Avrami exponent, which depends on the type of nucleation and growth mechanism.

Using Eq. (1) and combining Eqs. (2) and (3), the following equation can be obtained under a certain crystallinity degree:

$$\log Z_t + n \log t = \log K(T) - m \log \phi \tag{4a}$$

$$\log \phi = \frac{1}{m} \log \left[\frac{K(T)}{Z_t}\right] - \frac{n}{m} \log t \tag{4b}$$

$$\log \phi = \log F(T) - a \log t \tag{4c}$$

where $F(T) = [K(T)/Z_t]^{1/m}$, $a = n/m$. The physical meaning of $F(T)$ is the necessary cooling rate when the measured system arrives at a certain crystallinity degree at unit crystallization time.

According to Eq. (4c), at a given degree of crystallinity, the plot of $\log \phi$ as a function of $\log t$ gives a straight line with $\log F(T)$ as the intercept and $-a$ as the slope.

Plots of $\log \phi$ versus $\log t$ at various degree of crystallinity for the pure LDPE and the LDPE/Cu nanocomposite with a copper nanoparticles content of 7.50 wt.% during non-isothermal crystallization are presented in Fig. 6. From Fig. 6, it can be seen that the plots show a good linearity, which verifies the advantage of the combined approach applied in this case.

The values of $F(T)$ and a are listed in Table 3, from which it can be seen that the values of $F(T)$ increase systematically with increasing of relative crystallinity degree, indicating that at unit crystallization time, a higher cooling rate should be required in order to obtain a higher crystallinity degree. The values of $F(T)$ for neat LDPE is larger than that for LDPE/Cu nanocomposites, implying that the necessary cooling rate for neat LDPE is larger than that for LDPE/Cu nanoparticles

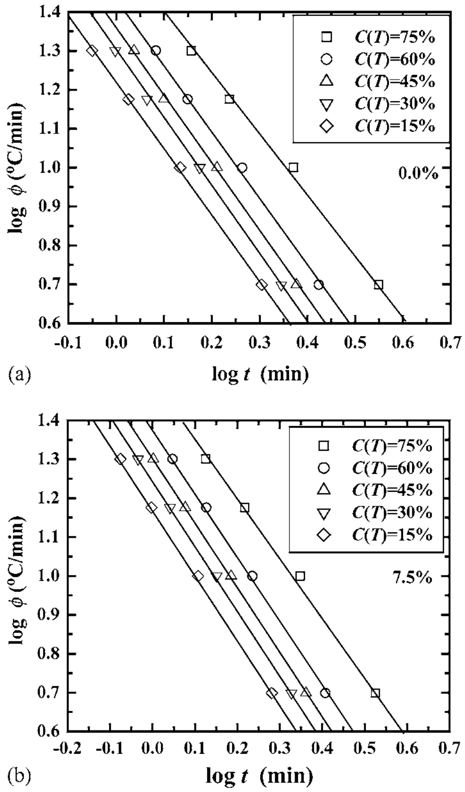

Fig. 6. Plots of $\log\phi$ vs. $\log t$ for (a) neat LDPE and (b) LDPE/Cu nanocomposite with a copper nanoparticles content of 7.50 wt.% during non-isothermal crystallization.

when they arrives at the same crystallinity degree at unit crystallization time. Nevertheless, the values of the parameter a are almost constant.

3.4. Crystallization activation energy

Frequently, the activation energy, E, of non-isothermal crystallization of polymer melts has been evaluated by the Kissinger equation with positive rates of temperature variation β. Vyazovkin [21,22] has demonstrated that dropping the negative sign for β in order to make the Kissinger equation applicable to cooling processes is an invalid procedure. Reversing the sign for β, is a mathematically invalid procedure that generally invalidates the Kissinger method. In addition, the use of the Kissinger method with positive values of the cooling rate may result in erroneous values of the activation energy. That is to say, the Kissinger equation is generally inapplicable for evaluating the activation energy of the processes that occur on cooling. As an alternative, the isoconversional methods that developed by Friedman and by Vyazovkin [21,22] can be used for evaluating the effective activation energy, E_α, of non-isothermal crystallization of the polymer melts, this method can be used for heating as well as for cooling. Therefore, the advanced isoconversional method that has been developed by Vyazovkin [21,22] was used to evaluate the effective activation energy in this paper.

Table 3
Non-isothermal crystallization kinetics parameters obtained from combination of Avrami–Ozawa equation

$C(T)$ (%)	0.0 wt.%		7.5 wt.%	
	$F(T)$	a	$F(T)$	a
15	3.39	1.71	3.25	1.60
30	3.68	1.75	3.49	1.61
45	3.90	1.74	3.69	1.61
60	4.19	1.70	3.96	1.59
75	4.76	1.60	4.53	1.55

The advanced isoconversional method is described as follows:

$$\Phi(E_\alpha)=\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{J[E_\alpha, T_i(t_\alpha)]}{J[E_\alpha, T_j(t_\alpha)]} \tag{5}$$

where

$$J[E_\alpha, T_i(t_\alpha)]=\int_{t_{\alpha-\Delta\alpha}}^{t_\alpha}\exp\left[\frac{-E_\alpha}{RT_i(t_\alpha)}\right]\mathrm{d}t \tag{6}$$

In Eqs. (5) and (6), t is the time, α the extent of conversion, it varies from $\Delta\alpha$ to $1-\Delta\alpha$ with a step $\Delta\alpha=m^{-1}$, where m is the number of the equidistant values of α chosen for the analysis. We usually set $m=50$ that gives $\Delta\alpha=0.02$; n is the number of a series of experiments carried out under different temperature programs; the subscripts i and j represent ordinal numbers of two experiments performed under different heating or cooling programs; $T_i(t_\alpha)$ is the temperature of the given extent of conversion; R is the gas constant.

The activation energy is determined at any particular value of α by finding E_α, which minimizes the function $\Phi(E_\alpha)$. The minimization procedure is repeated for each value of α to find the dependence of the activation energy on the extent of conversion.

As one know, these mathematics equations were given in higher mathematics as follows:

$$\int_a^b c\,\mathrm{d}x=c(b-a) \tag{7}$$

$$\frac{\mathrm{e}^a}{\mathrm{e}^b}=\mathrm{e}^{(a-b)} \tag{8}$$

$$\mathrm{e}^x=\sum_{n=0}^{\infty}\frac{x^n}{n!}\quad(-\infty<x<+\infty) \tag{9}$$

Using mathematical equations (7)–(9), Eqs. (5) and (6) can be changed into the following type:

$$\Phi(E_\alpha)=AE_\alpha^2+BE_\alpha+C \tag{10}$$

Minimizing the function $\Phi(E_\alpha)$ that shows in Eq. (10), the value of activation energy, E_α, at any particular value of α can be got:

$$E_\alpha=-\frac{B}{2A} \tag{11}$$

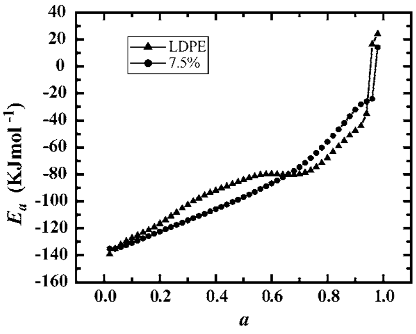

Fig. 7. Dependence of the effective activation energy on the relative extent of crystallization.

The use of this advanced isoconversional method developed by Vyazovkin yields a set of E_α shown in Fig. 7.

From Fig. 7, it can be seen that the experimental activation energy increases with the extent of the melt conversion α from around −140 to +20 kJ mol^{-1}. And the experimental activation energy of the LDPE/Cu nanocomposite with a copper nanoparticles content of 7.50 wt.% is smaller than that of the neat LDPE when the extents of conversion is lower than 0.65, when the extents of conversion is higher than 0.65, the experimental activation energy of the LDPE/Cu nanocomposite with a copper nanoparticles content of 7.50 wt.% is bigger than that of the neat LDPE. This trend suggesting that the copper nanoparticles dispersed in the LDPE/Cu nanocomposites may act as a heterogeneous nucleation for the crystallization of LDPE and accelerate the crystallization process, at the same time the presence of copper nanoparticles hinders the transport of the molecule chains, resulting in a decrease of the crystallization growth rate.

4. Conclusions

DSC has been used to investigate the influence of various copper nanoparticles contents and various cooling rates on the non-isothermal crystallization behavior of LDPE/Cu nanocomposites. When heating rate and cooling rate are constant, the DSC results show that the melting temperatures decrease but the crystallization temperatures increase with increasing copper nanoparticles content, and that the higher the content of copper nanoparticles, the lower the crystallinity degree is. When the copper nanoparticles loading of the nanocomposites is constant, the following results can be seen: (a) the crystallization temperatures shift to lower temperature with increasing cooling rate; (b) the values of crystallization temperatures of the LDPE/Cu nanocomposites are larger than those of the neat LDPE, the bigger the cooling rate, the more obvious the trend is; and (c) the value of T_{ci} of the LDPE/Cu nanocomposites is larger than that of the neat LDPE, indicating that the copper nanoparticles dispersed in the nanocomposites may act as nucleation agents.

The values of $F(T)$ for neat LDPE is larger than that for LDPE/Cu nanocomposites, implying that the necessary cooling rate for neat LDPE is larger than that for LDPE/Cu nanoparticles when they arrives at the same crystallinity degree at unit crystallization time.

The experimental activation energy of the LDPE/Cu nanocomposite with a copper nanoparticles content of 7.50 wt.% is smaller than that of the neat LDPE when the extents of conversion is lower than 0.65, when the extents of conversion is higher than 0.65, the experimental activation energy of the LDPE/Cu nanocomposite with a copper nanoparticles content of 7.50 wt.% is bigger than that of the neat LDPE.

All these results indicate that the incorporation of copper nanoparticles significantly influences the melting and crystallization behaviors of the LDPE matrix of the nanocomposites. Especially, the dependence of the effective activation energy on the relative extent of crystallization implies that the copper nanoparticles dispersed in the nanocomposites may act as a heterogeneous nucleation for the crystallization of the LDPE matrix, and that the presence of the copper nanoparticles may hinder the transport of the molecule chains at the same time, resulting in a decrease of the crystallization growth rate of the LDPE matrix.

Acknowledgements

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