

Nonisothermal Crystallization Behavior of Cu/LDPE Nanocomposites Prepared by Solution Blending Method

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ABSTRACT: The nonisothermal crystallization behavior of Copper/low-density polyethylene (LDPE) nanocomposites was investigated by differential scanning calorimetry (DSC). The nanocomposites were prepared by solution blending method, and the traditional extrusion melt method was also employed for comparison. The DSC results show that under identical copper content condition, the crystallization of the LDPE is facilitated owing to the higher degree of molecular regularity and the lesser chain entanglement for the nanocomposites prepared by the solution blending method in comparison with the traditional extrusion melt method. The differences of nonisothermal crystallization behavior diminish with the increase of copper content between the nanocomposites prepared

by the two methods. SEM/EDX was applied to study the dispersion of copper nanoparticles in the nanocomposites, and the results illustrate that the dispersion condition can be better when the solution blending method was employed. The investigation of the effective activation energy on the relative extent of crystallization implies that the agglomeration of copper nanoparticles can facilitate the crystallization of the LDPE, while the well-dispersed copper nanoparticles act as obstacles since the motion of the LDPE molecular chains is limited. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 3348–3356, 2012

Key words: nanocomposites; crystallization; thermal properties; solution blending method; extrusion melt method

INTRODUCTION

In recent decades, polymer and polymer-matrix composites have been widely applied in the industrial production. Meanwhile, polymer and nanoscale particles hybrid, called nanocomposites, have been receiving special attention owing to its various advantages in comparison with the traditional polymer composites. The addition of metal nanoparticles makes the nanocomposites display an unusual combination of physical, optical, electrical, and magnetical properties.^{1–4} Compared with the isothermal crystallization, the industrial processes proceed

generally under nonisothermal conditions. Therefore, the study of nonisothermal crystallization behavior is of practical significance and has gained much attention.

Over the past few years, a large number of studies on polymer/clay,⁵ polymer/carbon black,⁶ polymer/carbon nanotube,⁷ nanocomposites etc. were reported because of their promising industrial value. However, the investigation of the nonisothermal crystallization behavior of polymer/metal composites is rarely reported.

Low-density polyethylene (LDPE) is one of the most widely used polyolefin polymers since it possesses toughness, near-zero moisture absorption, excellent chemical inertness, low coefficient of friction, ease of processing, and unusual electrical properties.⁸ Huang et al.,⁹ have investigated the nonisothermal crystallization behavior of LDPE/Al nano- and microcomposites prepared by the melt blending and reported that the size of Al fillers can significantly affect the crystallization of LDPE. Since LDPE, as implantable material, is excellently biocompatible with human body, Cu/LDPE nanocomposites have been developed as novel kind of intrauterine contraception devices (IUDs) in our research. The structure of the LDPE has significant influence on the

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corrosion rate of the copper nanoparticles and the release rate of the copper ion. During the immersion process of IUDs in uterine fluid, copper nanoparticles are corroded constantly and Cu^{2+} is released into uterine fluid from LDPE matrix, thereby enhancing contraception effect.^{10–12} In the previous work, Xia has investigated the nonisothermal crystallization behavior of Cu/LDPE nanocomposites prepared by the extrusion melt method with single-screw extruder.¹³ It indicates that the addition of copper nanoparticles significantly influences the melting and crystallization behavior of the LDPE matrix. The presence of copper nanoparticles may act as a heterogeneous nucleation and hinder the transport of the molecule chains at the same time. However, there are still some questions puzzling us, like how LDPE matrix works to control copper ion release during the use of the IUDs and why the crystallization of LDPE matrix is facilitated or hindered by copper nanoparticles.

In this work, the copper/LDPE nanocomposites were prepared by the solution blending method, and the traditional extrusion melt method was also employed for comparison. SEM was applied to investigate the distribution of copper nanoparticles in the composites. DSC was used to study the differences of the nonisothermal crystallization behavior between the nanocomposites which were prepared by the two methods. Meanwhile, we made use of the combined Avrami-Ozawa theory to simulate and analyze the crystallization kinetics of the nanocomposites. Through the changing of blending method for the preparation of nanocomposites, the investigation results of the nonisothermal crystallization can guide us to realize the control mechanism of LDPE in IUDs use.

EXPERIMENTAL

Materials

The LDPE was purchased as pellets with an average particle size of 1000 μm from Qilu Petrochemical of China, and then was grinded into micro-sized powder with an average particle size of 250 μm . The nano-sized copper particles were prepared via our own patented techniques, i.e., hybrid induction and laser heating (HILH) evaporation condensation method.¹⁴ The cyclohexane (AR) was purchased from Guoyao Chemical reagent of Shanghai.

Preparation of Cu/LDPE nanocomposites

In this work, two groups of samples were studied. The first group of samples were obtained by a single-screw extruder and more details can be seen in the Ref.¹⁵ suggested. The nanocomposites with 0, 6.25, 12.5, and 18.75 wt % copper nanoparticles were obtained by this method.

The second group of samples were prepared by compounding the polymer with 0, 6.25, 12.5, and 18.75 wt % copper nanoparticles by means of the solution blending method. First, the LDPE and copper nanoparticles were dissolved in cyclohexane, respectively. It should be noted that the addition of the suitable dispersant Span-80 is necessary for the more effective dispersion of the copper nanoparticles into cyclohexane. Second, the two kinds of solution mentioned above were mixed for about 1 h under stirring and heating conditions to make LDPE mixed sufficiently with the copper nanoparticles. Thirdly, the mixture obtained from the second step was put into the vacuum drying oven (DZF-6020, made in Shanghai, China) until the cyclohexane was completely volatilized. Finally, the copper/LDPE nanocomposites were obtained.

Scanning electron microscopy

A SEM model Sirion 200 (manufactured by FEI of Holland) equipped with an EDX elemental composition analyzer was used to analyze the two groups of samples with the copper nanoparticles content of 18.75 wt %, which were prepared by the two methods mentioned above, respectively. The total scanning time during the elemental map generation was 4 min. The images show the distribution of copper element in the nanocomposites.

Differential scanning calorimetry

The nonisothermal crystallization behavior of the samples was analyzed using a PerkinElmer Diamond DSC differential scanning calorimeter. All samples were accurately weighted (≈ 5.0 mg) using analytical balance, and then placed in the DSC cell.

In the analysis process, the samples were divided into two groups. The first group contains the samples with the copper nanoparticles content of 0, 6.25, 12.5, and 18.75 wt %, which were equally obtained by the solution blending method and the extrusion melt method. Each sample was analyzed by the same process, i.e., being heated from 40 to 150°C at a rate of 10°C/min, kept for 2 min at 150°C to eliminate the heat history and then cooled to 40°C at a rate of 10°C/min. This process was carried out for evaluating the difference of the nonisothermal crystallization behavior of the nanocomposites prepared by different methods with increasing of copper nanoparticles content. The samples with an identical copper nanoparticles content of 12.5 wt %, prepared by the solution blending method and the extrusion melt method, were included in the second group. Each testing process for the samples was consistent: being heated from 40 to 150°C at a heating rate of 10°C/min, kept at 150°C for 2 min to eliminate the

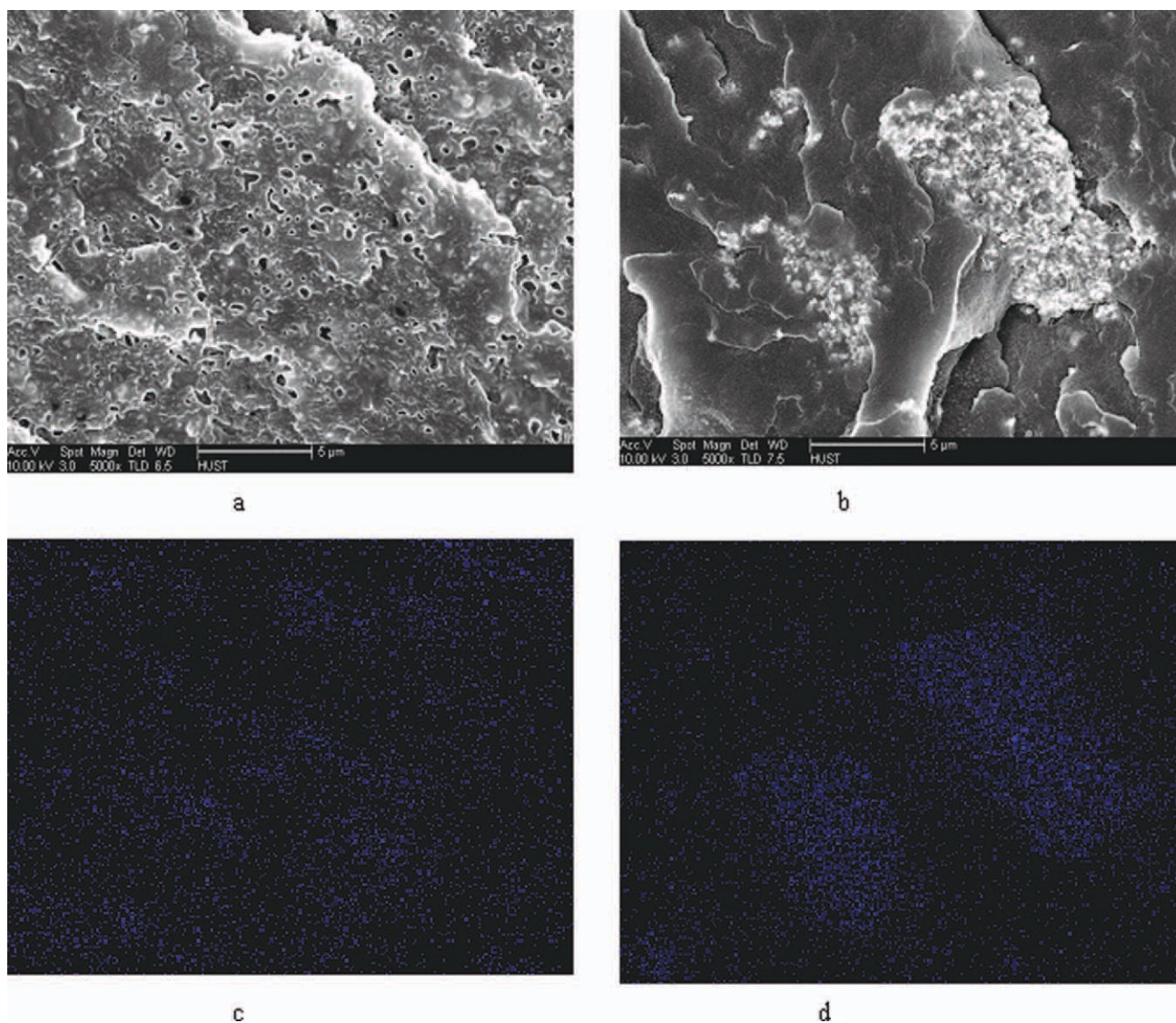


Figure 1 SEM-EDX mapping of the vertical section of the composites with a copper nanoparticles content of 18.75 wt % (a) SEM image for the *S*-nanocomposite, (b) SEM image for the *E*-nanocomposite, (c) the corresponding EDX mapping of copper for *S*-nanocomposite, (d) the corresponding EDX mapping of copper for *E*-nanocomposite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

heat history and then cooled to 40°C at a rate of 5, 10, 15, and 20°C/min, respectively. The purpose of this measurement was to study the variation and differences of nonisothermal crystallization kinetics at different cooling rates for the nanocomposites prepared by using the above two methods. During all the testing process, N_2 atmosphere was available for protection. And both the exothermic and endothermic curves were recorded as a function of temperature.

RESULTS AND DISCUSSION

SEM/EDX results

As shown in Figure 1, the distribution of copper nanoparticles is much more uniform in the *S*-nano-

composites with 18.75 wt % copper nanoparticles, compared with the *E*-nanocomposites. (*S*-nanocomposites and *E*-nanocomposites stand for the nanocomposites prepared by the solution blending method and the extrusion melt method, respectively) Apparent agglomeration of copper nanoparticles can be observed in the *E*-nanocomposites. Same but more obvious results could be obtained from the EDX maps in Figure 1(c,d). The reason for the results is that when the solution blending method was employed, the suspension liquid of copper nanoparticles and cyclohexane was obtained since the copper nanoparticles were dispersed evenly in the cyclohexane under the effect of Span-80. Then the suspension liquid can be mixed sufficiently with LDPE solution under stirring condition. However, it

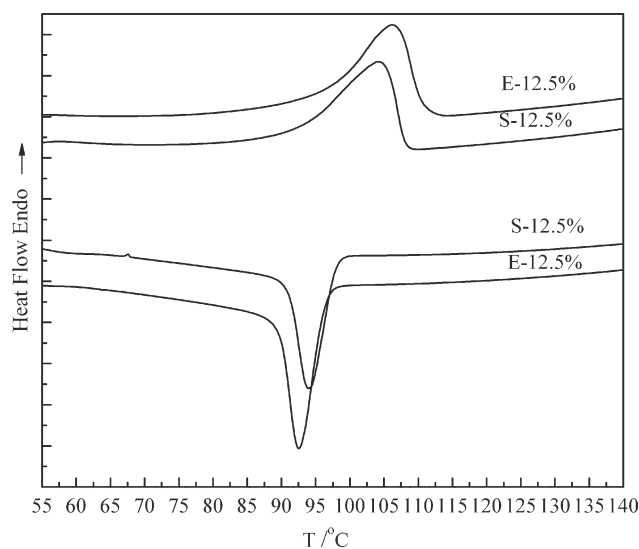


Figure 2 Heating and cooling scans of the composites with the copper nanoparticles content of 12.5 wt %.

could not be so effective with the traditional extrusion melt method. The distribution of copper nanoparticles has significant influence on the corrosion of copper and the release of copper ion in the using process of the IUDs, and the release of the copper ion would be erratical and the usability of IUDs may be instable if the copper nanoparticles agglomerate seriously in the nanocomposites. Therefore the properties of the IUDs could be improved remarkably by using the solution blending method.

General crystallization behavior

The melting and crystallization curves of the composites with the copper nanoparticles content of 12.5 wt % are shown in Figure 2. Similar results have been observed for the copper nanoparticles content of 0, 6.25, and 18.75 wt%, but not shown here. The temperature parameters of all specimens are collected in Table I, where T_{mp} , T_{cp} , ΔT_p , ΔH_f , and X_c denote the peak melting temperature, the peak crystallization temperature, the supercooling degree, the heat of fusion and the crystallinity, respectively. And $\Delta T_p = T_{mp} - T_{cp}$, $X_c = \frac{\Delta H_f / (1 - W_t\%)}{\Delta H_f^0}$, $\Delta H_f^0 = 289.9$ J/g.

As is shown in Figure 2 and listed in Table I, compared with the *E*-nanocomposites, the melting temperature and the degree of supercooling ΔT_p are lower, while the crystallization temperature and crystallinity are higher for the *S*-nanocomposites under the condition of identical copper content. The results illustrate that the crystallization of the LDPE matrix is facilitated when the solution blending method was employed, and the nanocomposites

prepared by the extrusion melt method require a greater degree of supercooling for crystallization.

On the basis of the molecular motion theory, the crystallization of polymer is affected by the quantity and density of the entanglements. Xie et al.,¹⁶ has approved that the molecular motion is lesser or no longer hindered by the molecular around and the crystallization ability is enhanced when the molecular chains are in disentanglement state. In this research, when the solution blending method is adopted, the LDPE chains unfold to fully extended conformation in the dilute solution. And the probability of folding and entanglement is very small for the molecular chains since the LDPE coils separate far away from each other. The disentanglement state would preserve when the LDPE extract from cyclohexane, and the chain segments show ordered arrangement to a certain extent. As for the *E*-nanocomposites, however, numerous entanglements hinder chain unfolding in the melt and the crystallization rate is decreased.

As is collected in Table I, although the regularity of the values of T_{mp} and T_{cp} with respect to the copper content is not clear for either *S*-nanocomposites or *E*-nanocomposites, the difference of every parameter between *S*-nanocomposites and *E*-nanocomposites ranges regularly in regard to the variation of the copper content. For example, the difference of peak crystallization temperature T_{cp} between *S*-nanocomposites and *E*-nanocomposites decreases from 2.1 to 1°C, and the difference of the degree of supercooling ΔT_p decreases from 4.4 to 3.4°C gradually with the addition of copper nanoparticles. Meanwhile, the difference of ΔH_f ranges from 28.2 to 7.4 J/g. This result illustrates that the increase of copper content can diminish the difference of crystallization behavior caused by different preparation methods. With increasing of the copper nanoparticles, the agglomeration becomes more obvious for the *E*-nanocomposites, while the phenomenon does not turn up for the *S*-nanocomposites. The well-dispersed copper nanoparticles may hinder the motion of the molecular chains. While the agglomerated copper nanoparticles act as heterogeneous

TABLE I
Melting and Cooling Parameters for the *S*-nanocomposites and *E*-nanocomposites

Samples (%)	T_{mp} (°C)	T_{cp} (°C)	ΔT_p	ΔH_f (J/g)	X_c (%)
S-0	104.5	94.6	9.9	103.3	35.6
E-0	108.2	92.5	14.3	75.1	25.9
S-6.25	104.0	93.9	10.1	86.1	31.7
E-6.25	106.3	92.5	13.8	61.9	22.8
S-12.5	104.4	93.2	10.6	71.1	28.0
E-12.5	106.1	92.0	14.1	52.0	20.5
S-18.75	104.4	93.7	10.7	61.4	26.1
E-18.75	106.8	92.7	14.1	54.0	22.9

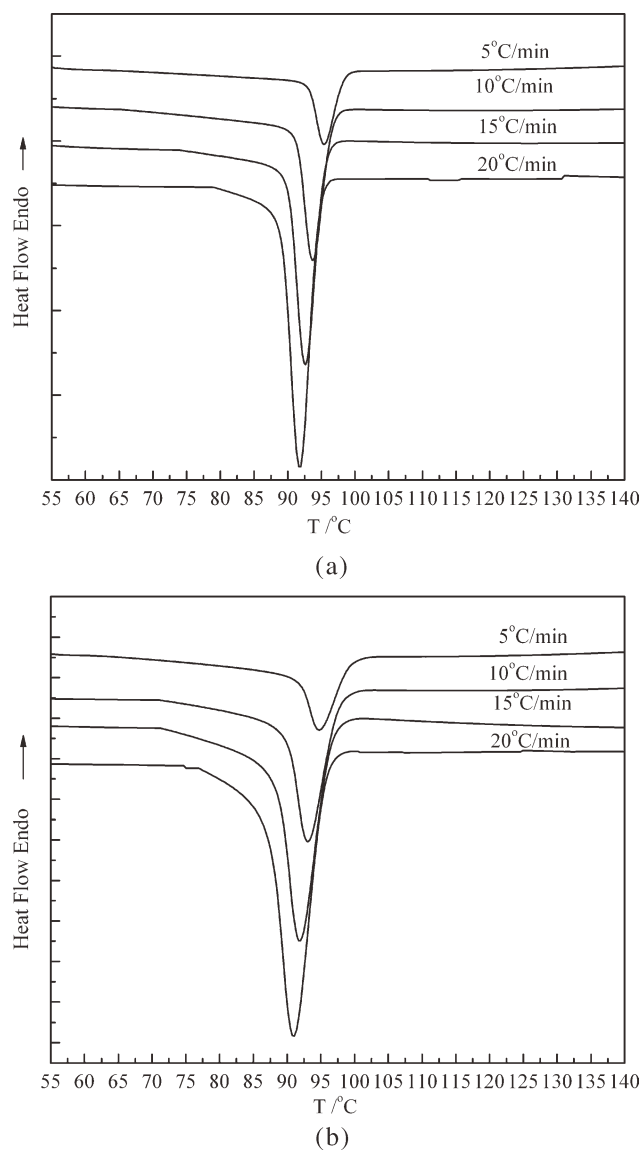


Figure 3 DSC thermograms of the nonisothermal crystallization for the the S-nanocomposite (a) and the E-nanocomposite (b) with the copper nanoparticles content of 12.5 wt % at various cooling rates.

nucleations for the crystallization of LDPE, and the agglomeration of copper nanoparticles can facilitate the crystallization of LDPE relatively. And it is similar to the effect of clay in PP/clay nanocomposites.¹⁷ Furthermore, as the copper content arise, the crystallinity for the S-nanocomposites and E-nanocomposites varies from 35.6 to 26.1% and 25.9 to 22.9%, respectively. It indicates that besides the nucleating agent role for the copper nanoparticles, the presence of the copper nanoparticles may hinder the arrangement of the molecular chains to the crystal region and result in the decrease of the crystallinity.

Figure 3 presents the T_{ci} , T_{cp} , and T_{cf} of the composites with a copper nanoparticles content of 12.5 wt % all shift to lower temperature with

increasing of cooling rate. The reason is that the entrance rate into crystalline regions of LDPE molecular chains is lesser than the cooling rate with increasing of cooling rate, and the crystallization process is restrained. To achieve the given crystallinity greater cooling rate is required. Meanwhile the increase of cooling rate makes the crystal structure imperfect and irregular.

Figure 4 clearly reflects the difference and relation of the crystallization temperature of the nanocomposites prepared by the two different methods at various cooling rates. At the identical cooling rate, the T_{ci} of the nanocomposites prepared by the solution blending method is higher than that of the nanocomposites prepared by the extrusion melt method, while T_{cp} and T_{cf} are lower relatively. The results also illustrate that the time for complete crystallization of the nanocomposites prepared by solution blending method is much shorter.

Nonisothermal crystallization kinetics

In nonisothermal crystallization kinetics, the functional relation of relative crystallinity $X(T)$ and the temperature T is given by:

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

where T_0 , T_c , and T_∞ denote the initial crystallization temperature, the crystallization temperature at time t and ultimate crystallization temperature, respectively. The dH_c is the enthalpy of crystallization released during an infinitesimal temperature range dT . Figure 5 shows the plots of the relative

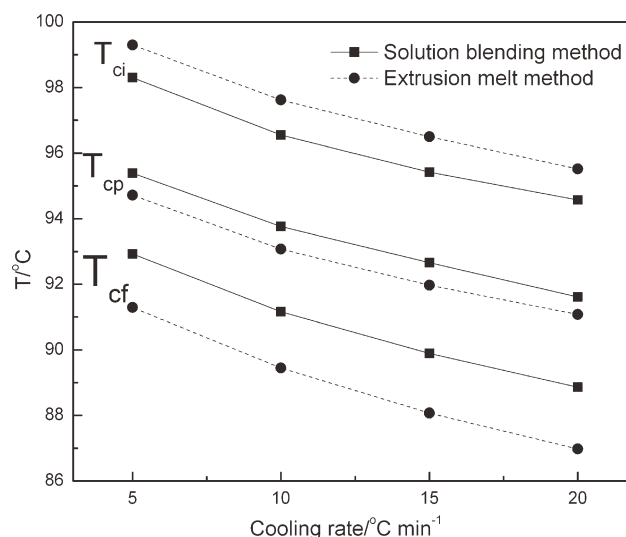
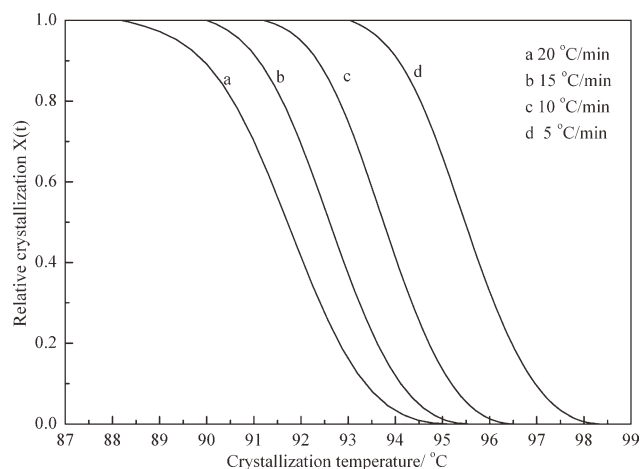
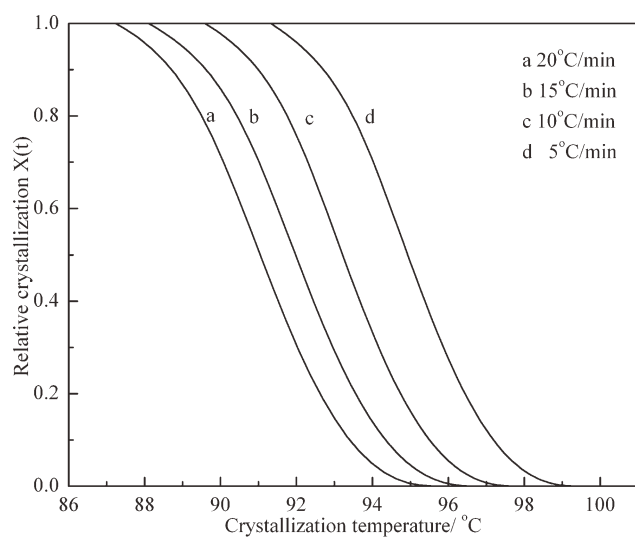


Figure 4 Plots of the influence of various cooling rates on crystallization temperature for the composites with the copper nanoparticles content of 12.5 wt %.



(a)



(b)

Figure 5 Plots of crystallization fraction as a function of temperature for the *S*-nanocomposite. (a) and the *E*-nanocomposite (b) with the copper nanoparticles content of 12.5 wt %.

degree of crystallinity (X_T) as a function of temperature T for the composites with a copper nanoparticles content of 12.5 wt %. All plots of the two kinds of nanocomposites appear the reversed “*S*” similarly. These curves would imply that only the lag effects of cooling rate on crystallization were observed.¹⁸

During the crystallization process, the time t has the following relation with the temperature T :

$$t = \frac{T_0 - T_c}{R} \quad (2)$$

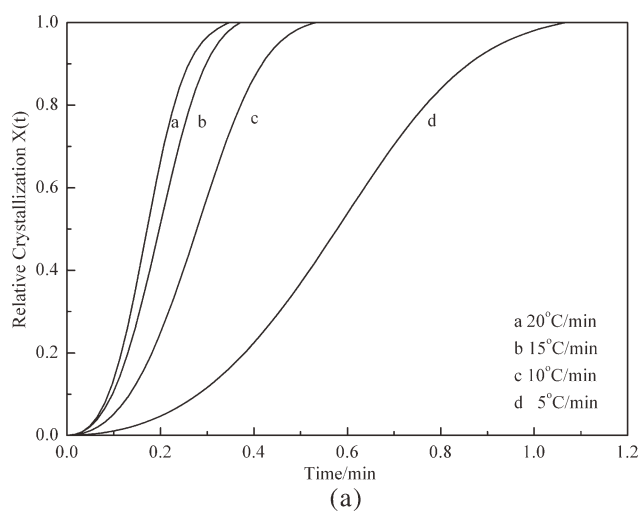
where R is the cooling rate. According to eq. (2), the plots of the relative degree of crystallinity (X_T) versus the temperature T in Figure 5 can be transformed to the plots of the relative degree of crystallinity (X_T) as a function of time t in Figure 6. Figure 6 clearly

shows that the greater the cooling rate is, the shorter the time is required to crystallize completely. Compared (1) with (2) in Figure 6, the crystallization time for the *S*-nanocomposites is shorter than that of the *E*-nanocomposites at a chosen cooling rate.

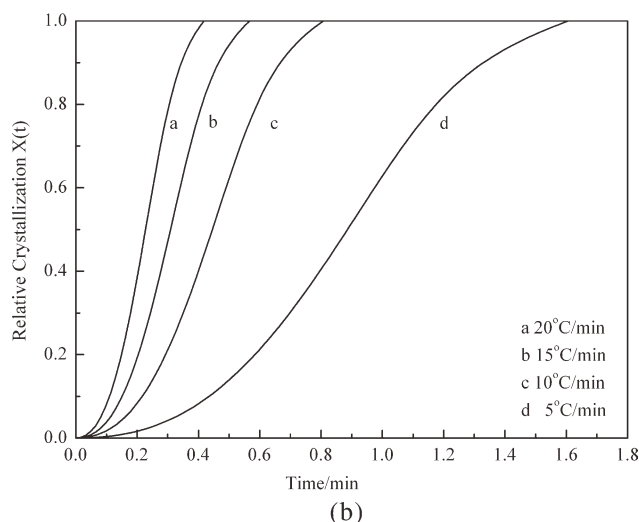
Many methods have been suggested to study the nonisothermal crystallization of polymer.^{19–28} However, no one method is universal. A novel kinetic equation proposed by Mo et al. to combine the Avrami with Ozawa equation is suitable to study the nonisothermal crystallization of many kinds of polymer.¹⁸ Therefore, the combined Avrami and Ozawa equation–Mo’s method is used in this article.

In the prior years, Avrami equation,^{29–31} was used to study the crystallization kinetics, the specific form is given by:

$$1 - X(t) = \exp(-Zt^n) \quad (3)$$



(a)



(b)

Figure 6 Plots of crystallization fraction as a function of time for the *S*-nanocomposite (a) and the *E*-nanocomposite (b) with the copper nanoparticles content of 12.5 wt %.

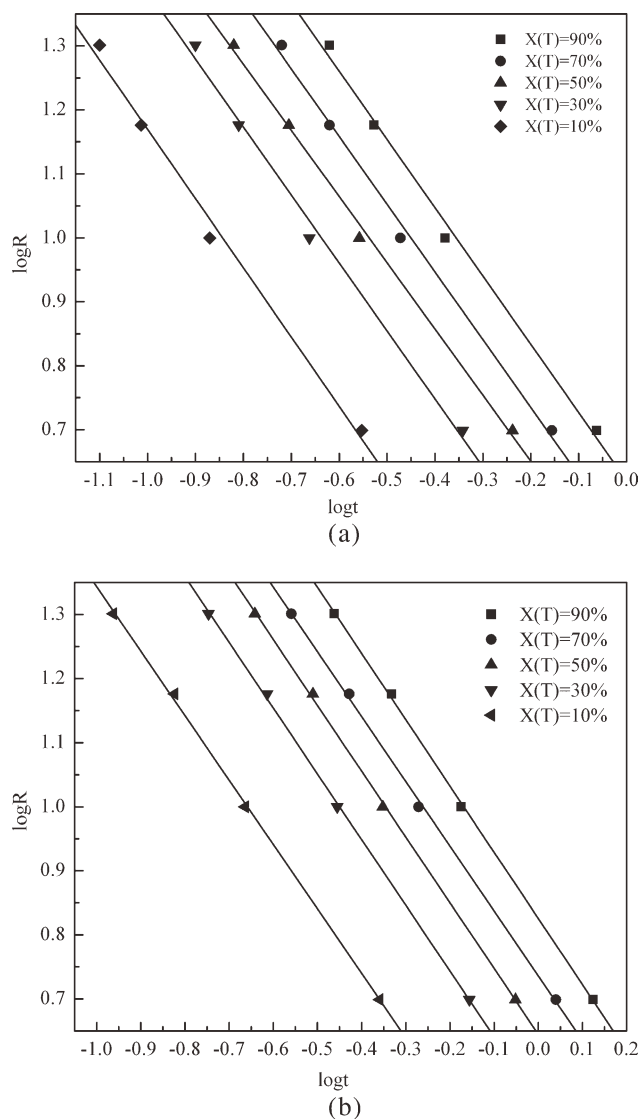


Figure 7 Plots of $\log R$ as a function of $\log t$ for the S-nanocomposite (a) and E-nanocomposite (b) with the copper nanoparticles content of 12.5 wt %.

The double logarithmic form of eq. (3) is:

$$\lg[-\ln(1 - X(t))] = \lg Z + n \lg t \quad (4)$$

where the parameter t denotes time, $X(t)$ refers to the relative degree of crystallinity at time t , Z is a composite rate constant involving both nucleation and growth rate parameters, n is a mechanism constant, the value of which depends on the type of nucleation and growth-process parameters.

The specific form of Ozawa Equation³² is given by:

$$1 - X(T) = \exp[-P(T)/R^m] \quad (5)$$

Similarly, the double logarithmic form of eq. (5) is:

$$\lg\{-\ln[1 - X(T)]\} = \lg P(T) - m \lg R \quad (6)$$

where $X(T)$ is the relative degree of crystallinity at temperature T , m is the Ozawa parameter, R denotes the cooling rate, $P(T)$ denotes the kinetic parameter at temperature T , which depends on the type of nucleation, nucleation rate and the growth rate of crystal. According to eq. (2), we know that the relative degree of crystallinity is available at the temperature T that corresponding to the time t . Therefore, the relation by combining eq. (4) with eq. (6) is derived as follows:

$$\lg[-\ln(1 - X(t))] = \lg\{-\ln[1 - X(T)]\} \quad (7)$$

Then combining eqs. (4), (6), (7), and (8) is obtained:

$$\lg Z + n \lg t = \log P(T) - m \log R \quad (8)$$

and is further written as:

$$\lg R = \lg \left[\frac{P(T)}{Z} \right]^{1/m} - \frac{n}{m} \lg t \quad (9a)$$

$$\lg R = \lg F(T) - a \lg t \quad (9b)$$

where the parameter $F(T) = \left[\frac{P(T)}{Z} \right]^{1/m}$ refers to the value of cooling rate, which has to be chosen at a unit crystallization time when the measured system amounts to a certain degree of crystallinity, a is the ratio of the Avrami exponent n to the Ozawa exponent m ($a = n/m$). According to eq. (9b), at a given degree of crystallinity, the plot of $\log R$ versus $\log t$ will give a straight line with the intercept of $\log F(T)$ and the slope of $-a$. Figure 7 shows the plots of $\log R$ versus $\log t$, t of the nanocomposites with the copper nanoparticles content of 12.5 wt % which were prepared by solution blending method and extrusion melt method. 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 collected in Table II, it can be seen that the values of $F(T)$ systematically increase with increasing of the relative crystallinity

TABLE II
Nonisothermal Crystallization Kinetics Parameters Obtained from the Combined Avrami-Ozawa Equations for the S-nanocomposite and E-nanocomposite with the Copper Nanoparticles Content of 12.5 wt %

X(T) (%)	S-12.5%		E-12.5%	
	F(T)	a	F(T)	a
10	1.22	1.08	2.17	1.01
30	2.01	1.06	3.44	1.03
50	2.78	1.03	4.41	1.03
70	3.33	1.06	5.46	1.01
90	4.16	1.07	6.67	1.03

for S-12.5% and E-12.5% nanocomposites. And at the given degree of crystallinity, the values of $F(T)$ of the S-nanocomposites are generally higher than that of the E-nanocomposites. This result indicates that the crystallization process of LDPE is slower when the extrusion melt method is adopted, and higher cooling rate is required to achieve the given crystallinity in unit time. And it is consistent with the results previously described. However, with the same addition of copper nanoparticles the values of a are relatively greater for the S-nanocomposites. It illustrates that the effect of the copper nanoparticles on the Avrami exponent and Ozawa exponent is different for S-nanocomposites and E-nanocomposites.

Crystallization activation energy

The crystallization activation energy E_a is often applied to study the crystallization ability of polymer in the nonisothermal crystallization kinetics. The smaller the value of E_a is, the greater the crystallization ability is.

Kissinger equation³³ is often used to calculate the whole crystallization activation energy in various temperature rate. Friedman model as well as Flynn and Wall model are the frequently-used isoconversional methods. Nevertheless, Vyazovkin,³⁴ commented that the Flynn method was not appropriate for melt crystallization, since this method requires the calculation of the logarithm of the heating rate, which is negative for cooling processes, while the Friedman method is most appropriate to evaluate the crystallization activation energy. Therefore, in this article, the Friedman method is used to evaluate the crystallization activation energy of the composites with the copper nanoparticles content of 12.5 wt %. The specific form of Friedman method is given by:

$$\ln\left(\frac{dX_t}{dt}\right)_{X_t} = A - \frac{E_a}{RT} \quad (10)$$

where dX_t/dt is the instantaneous crystallization rate at the given conversion X_t , A denotes the pre-exponential factor, R denotes the gas constant ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T and E_a stand for the temperature and activation energy of the given extent conversion, respectively. At a given degree of crystallinity, the plot of $\ln(dX_t/dt)$ versus $1/T$ is obtained, and the activation energy E_a can be evaluated according to the slope of the plot. Figure 8 presents the plots of E_a as a function of X_t for the composites with the copper nanoparticles content of 12.5 wt % prepared by the two methods.

From Figure 8 it can be seen that the values of E_a of the two groups of composites increase with

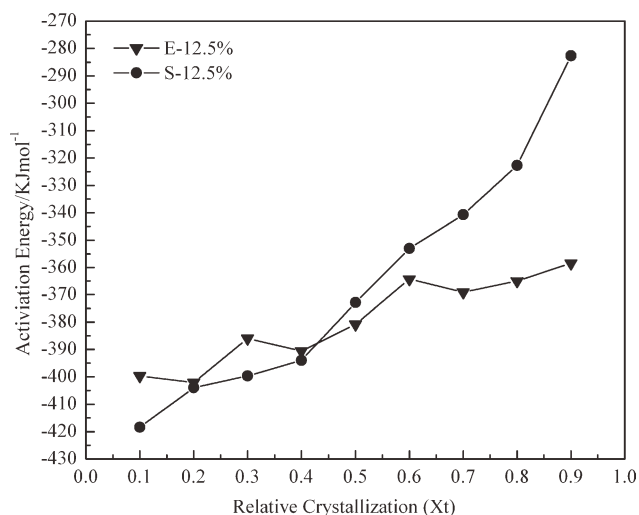


Figure 8 Dependence of the effective activation energy on the relative extent of crystallization for the composites with the copper nanoparticles content of 12.5 wt %.

increasing of the degree of crystallinity. In the range of $X_t = 10\text{--}90\%$, the values of E_a of the S-nanocomposite increase from -403.99 to $-282.67 \text{ KJ mol}^{-1}$ gradually, and the values rise from -399.66 to $-368.43 \text{ KJ mol}^{-1}$ gradually for the E-nanocomposites. However, at the points of $X_t = 20\%$, 40% , 70% the values of E_a of the E-nanocomposites display diminishing trend appreciably. May be it is owing to the uneven distribution of the copper nanoparticles, which results in the instability of the LDPE crystallization. It also can be seen that when $X_t < 50\%$, the values of E_a of the S-nanocomposites is lesser than that of the E-nanocomposites, while this result is opposite when $X_t \geq 50\%$. The probable reason is that when the solution blending method is adopted, the LDPE retains a high degree of molecular regularity, which results in the stronger crystallization ability in the initial phase. But along with the crystallizing processes, the agglomeration of copper nanoparticles facilitates the crystallization of the LDPE for the nanocomposites prepared by the extrusion melt method. And copper nanoparticles have nucleating effect during the crystallization procedure of the LDPE matrix. As for the nanocomposites prepared by the solution blending method, the movement of the LDPE molecular chains is hindered and the crystallization ability is weakened owing to the even distribution of copper nanoparticles. Therefore, the well-dispersed copper nanoparticles act as obstacles in the crystallization of the LDPE.

CONCLUSIONS

Solution blending method was employed to obtain the Cu/LDPE nanocomposites, also the extrusion melt method was used for comparison. The SEM/

EDX results reveal that the copper nanoparticles can be well-dispersed in the *S*-nanocomposites, while obvious agglomeration is observed for the *E*-nanocomposites.

DSC has been used to investigate the differences of melting and crystallization behavior of the LDPE for *S*-nanocomposites and *E*-nanocomposites. The LDPE crystallization is facilitated for the *S*-nanocomposites in comparison to the *E*-nanocomposites when the copper content is constant. The crystallization differences between *S*-nanocomposites and *E*-nanocomposites are diminished with increasing of copper content, which shows that the well-dispersed copper nanocomposites may hinder, while the agglomerated copper nanoparticles facilitate the crystallization ability of the LDPE. From the Mo method, we have found the values of $F(T)$ for *E*-nanocomposites are greater than that of the *S*-nanocomposites, which implies that greater cooling rate is required for the *E*-nanocomposites than that of the *S*-nanocomposites when they arrives at the same crystallinity degree at the unit crystallization time.

Friedman model was applied to investigate the activation energy E_a of the composites with the copper nanoparticle content of 12.5 wt %, and it shows that the values of E_a are lower and the crystallization ability of the LDPE is stronger when the extent of conversion is lower than 0.5 for the *S*-nanocomposites. While when the extent conversion is higher than 0.5, agglomeration of the copper nanoparticles facilitates the crystallization of the LDPE for the *E*-nanocomposites.

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