Studies on Nonisothermal Crystallization of Ultra–High Molecular Weight Polyethylene in Liquid Paraffin

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ABSTRACT: The nonisothermal crystallization kinetics for ultra–high molecular weight polyethylene (UHMWPE) in liquid paraffin (LP) systems was investigated through differential scanning calorimetry (DSC) measurement. The influence of UHMWPE concentration and cooling rate on crystallization mechanism and spherulitc structure as implied by the modified Avrami equation and Mo's analysis was determined, whereas the Ozawa's approach fails to describe the crystallization behaviors of these UHMWPE-diluent systems. As a result, in the modified Avrami analysis, it was found that the Avrami exponent is constant around five at various concentrations of UHMWPE and cooling rates. Further, the value of $F(T)$ in the Mo's approach increases with the increasing of relative crystallinity and UHMWPE content in the blends. The nonisothermal crystallization kinetics presented here are the first for UHMWPE-diluent systems. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 2782–2788, 2006

Key words: ultra–high molecular weight polyethylene; crystallization; kinetics; Avrami equation; differential scanning calorimetry

INTRODUCTION

The formation of microporous, semicrystalline membranes via thermally induced phase separation (TIPS) has been reported and commercialized.[1–3] TIPS can proceed via either solid–liquid phase separation or liquid–liquid phase separation. Solid–liquid phase separation usually results from the crystallization of the polymer from the homogeneous solution phase. The crystallization kinetics of the polymer plays important roles in determining the structure of the membrane from the solid–liquid phase separation. In most cases, the solid–liquid phase separation is induced using nonisothermal crystallization.[4] The objective of this study was to determine the effects of polymer concentration and cooling rate on the overall nonisothermal crystallization kinetics of ultra–high molecular weight polyethylene (UHMWPE) as it crystallizes in a melt-blend with liquid paraffin.

UHMWPE is a kind of polyethylene (PE) with the molecular weight in excess of 1×10^6. This kind of PE is superior to a similar PE with a lower molecular weight in the physical properties including nonadherent surface, low coefficient of friction, high abrasion resistance, impact resistance, and so on. Therefore, UHMWPE is the most advantageous as a material for the membrane. There have been previous studies on nonisothermal crystallization kinetics of pure PE and PE-thermoplastic blends.[5–11] But, most of such studies were concentrated on PE with general molecular weight, such as LDPE, HDPE, and so on. For UHMWPE, the nucleation type and growth process of crystallization are probably influenced by the high viscosity, which brought about by the ultra–high molecular weight. However, no such study has so far been carried out to analyze the nonisothermal crystallization behavior of neat UHMWPE or UHMWPE blends. The nonisothermal crystallization kinetics presented here are the first for UHMWPE/LP systems. The kinetic information gained from this study will be useful in determining the processing conditions (cooling rate and melt-blend composition) for nonisothermal TIPS membrane formation.

EXPERIMENTAL

Materials

All crystallization kinetic experiments were conducted with UHMWPE kindly supplied by Beijing No.2 Auxiliary Agent Factory. The viscosity average molecular weight was 1.5×10^6. Liquid paraffin, supplied by Hangzhou Chemical Reagent Co., was used as the diluent without further purification.

Preparation of UHMWPE/LP blends samples

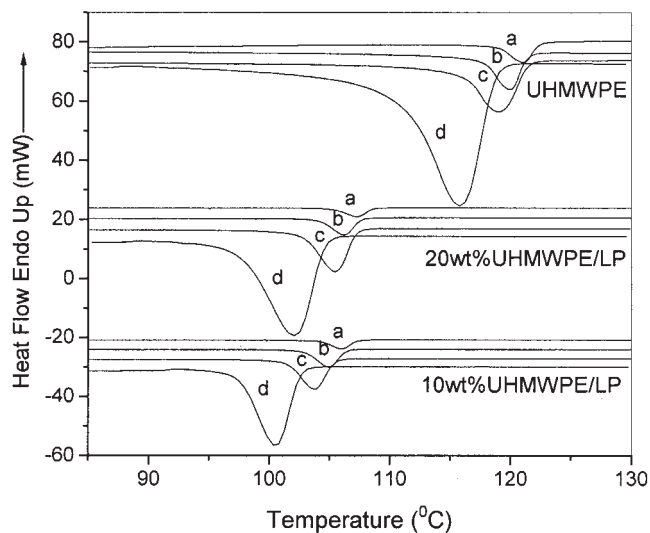UHMWPE/LP blends were prepared in the mixing chamber of the rheometer (HAAKE HBI System 90).

Figure 1 DSC curves of nonisothermal crystallization of UHMWPE and UHMWPE/LP composites at different cooling rate. (a) ~2, (b) ~4, (c) ~8, and (d) ~30°C/min.

The mixing condition: melting temperature is 170°C; roll speed is 64 rpm; and mixing time is 10 min. Then, the blends were cooled at room temperature for crystallization kinetic tests.

Nonisothermal crystallization process

Nonisothermal crystallization kinetics was studied using a Perkin–Elmer DSC-7 differential scanning calorimeter (Perkin–Elmer Cetus Instruments, Norwalk, CT). All DSC measurements were performed under the nitrogen atmosphere, and sample weights varied from 6 to 9 mg.

To reveal the nonisothermal crystallization kinetics, the sample was first heated to 200°C and maintained at this temperature for 5 min to erase thermal history, and then the sample was cooled at a rate of 2, 4, 8, 30°C/min to a final temperature of 30°C. The exothermic curves of heat flow with temperature decreasing at various rates were recorded and investigated.

RESULTS AND DISCUSSION

Nonisothermal crystallization analysis

Figure 1 shows typical DSC curves of UHMWPE and UHMWPE/LP blends recorded as the change of heat flow with the temperature decreasing at different cooling rates.

It is clear that the peak temperature, at which the crystallization rate is maximum, shifts to a lower temperature region with increasing cooling rates and decreasing concentration of UHMWPE. This observation is typical and common for most semicrystalline polymer while crystallizing nonisothermally. When the

polymer is undergoing crystallization at a lower cooling rate, it has a relatively long time remaining within the temperature range that promotes sufficient mobility of segments for the growth of crystallization. When cooled at a relatively rapid rate, however, segments are frozen before the formation of regular crystallite, thereby decreasing the crystallization temperature. Because the addition of diluent lowers the chemical potential of the blends and depresses the equilibrium melting point of the polymer,[12] the crystallization temperature decreases with increasing the concentration of LP.

Though the absolute crystallinity is a very important factor, the determination of the absolute crystallinity is not practically required for the analysis of crystallization kinetics. The relative degree of crystallinity $X(T)$ is considered and defined as

$$X(T) = -\frac{\int_{T_o}^{T}(dH_c/dT)dT}{\int_{T_o}^{T_e}(dH_c/dT)/dT} \quad (1)$$

where T_o and T_e are the onset and end crystallization temperatures respectively, and dH_c/dT is the heat flow rate.[13] In nonisothermal crystallization, the time t is related with the temperature T as follows

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

where T is the temperature at time t, and Φ is the cooling rate.

The developments of relative crystallinity with time for UHMWPE and UHMWPE/LP blends are shown in Figure 2. A series of S-shaped curves is obtained because of the spherulitic impingement in the later crystallization stage. The values of t (the proceeding time of crystallization) at the various cooling rates can be obtained at a random relative crystallinity (Fig. 2). The crystallization half-time $t_{1/2}$ is defined as the time at which the relative crystallization degree is completed 50%. Figure 3 shows $t_{1/2}$ in the crystallizing process at different cooling rates for UHMWPE and UHMWPE/LP blends. The half-time $t_{1/2}$ presents the overall crystallization rate. The shorter the half-time, the faster is the overall crystallization rate. It can be seen that with increase of the concentration of LP, the half-time of crystallization reduced. The overall crystallization rate is controlled by two factors, namely, nucleation and growth. The addition of LP to UHMWPE leads to lower nucleation density and higher growth rate of UHMWPE crystallization. Compara-
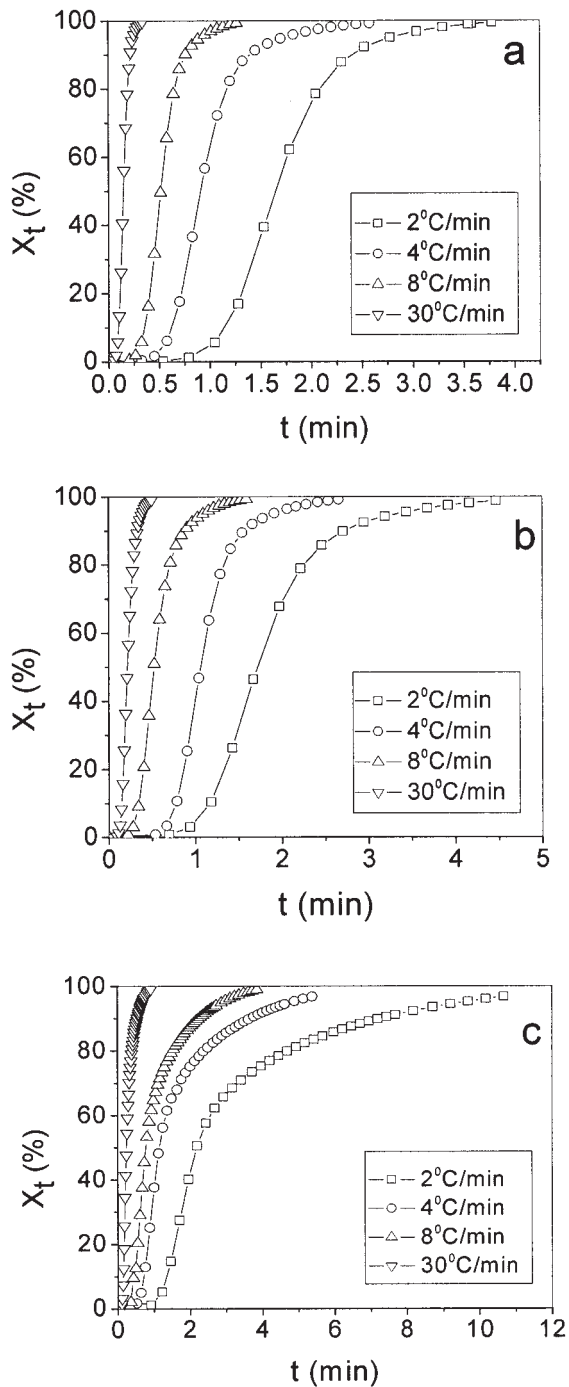
Figure 2 Development of relative crystallinity with crystallization time for (a) 10 wt % UHMWPE/LP, (b) 20 wt % UHMWPE/LP, and (c) UHMWPE.

tively, the effect of the latter is more important to speed the crystallization rate while increasing concentration of LP. On the contrary, increasing cooling rate can raise the nucleation density and reduce the growth rate of UHMWPE crystallization. In this case, the nucleation effect is dominant for crystallizing rate. So, the overall crystallization rate increases with increasing cooling rate.

Ozawa analysis of nonisothermal crystallization

Generally, the Ozawa theory has been successfully in describing the nonisothermal crystallization kinetics of polymers. Assuming that the polymer melt was cooled at a constant rate and the mathematical derivation of Evans[14] was valid, Ozawa[15] modified the Avrami equation to the nonisothermal situation. However, this theory does not take into account many factors. For example, secondary crystallization and dependence of fold length on temperature are ignored, and the exponent m is assumed to be constant independent of temperature.[8] According to Ozawa theory, the relative crystallinity $X(T)$ at a temperature T can be calculated as

$$1 - X(T) = \exp\left[-k(T)/\Phi^m\right] \tag{3}$$

where Φ is cooling rate, m is Ozawa exponent depending on the dimension of crystal growth, k is the cooling crystallization function related to the overall crystallizing rate. The above equation can also be written in another expression as

$$\log[-\ln(1 - X(T))] = \log k(T) - m \log \Phi \tag{4}$$

If this equation correctly describes the kinetics of nonisothermal crystallization, the plot of $\log[-\ln(1 - X(T))]$ against $\log \Phi$ should give a straight line. Kinetic parameter $k(T)$ and Ozawa exponent m should be obtained from the intercept and the slope of the line, respectively.

For UHMWPE and UHMWPE/LP blends, the Ozawa plots of $\log[-\ln(1 - X(T))]$ vs. $\log \Phi$ are shown in Figure 4. Obviously, the plots show as curvature rather than straight lines. The change in the slope
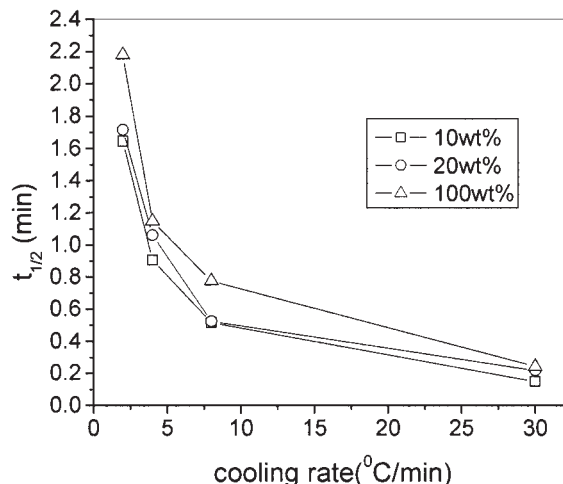

Figure 3 Half-time of crystallization, $t_{1/2}$, in the nonisothermal process at different cooling rates for UHMWPE and UHMWPE/LP blends.

secondary crystallization effect sometimes contributes >40% in the total crystallinity.[16] The failure of the Ozawa model to describe the nonisothermal behavior of the UHMWPE and UHMWPE/LP blends probably lies in ignoring secondary crystallization and dependence of lamellar thickness on crystallization temperature. In addition, it also can be seen from Figure 4
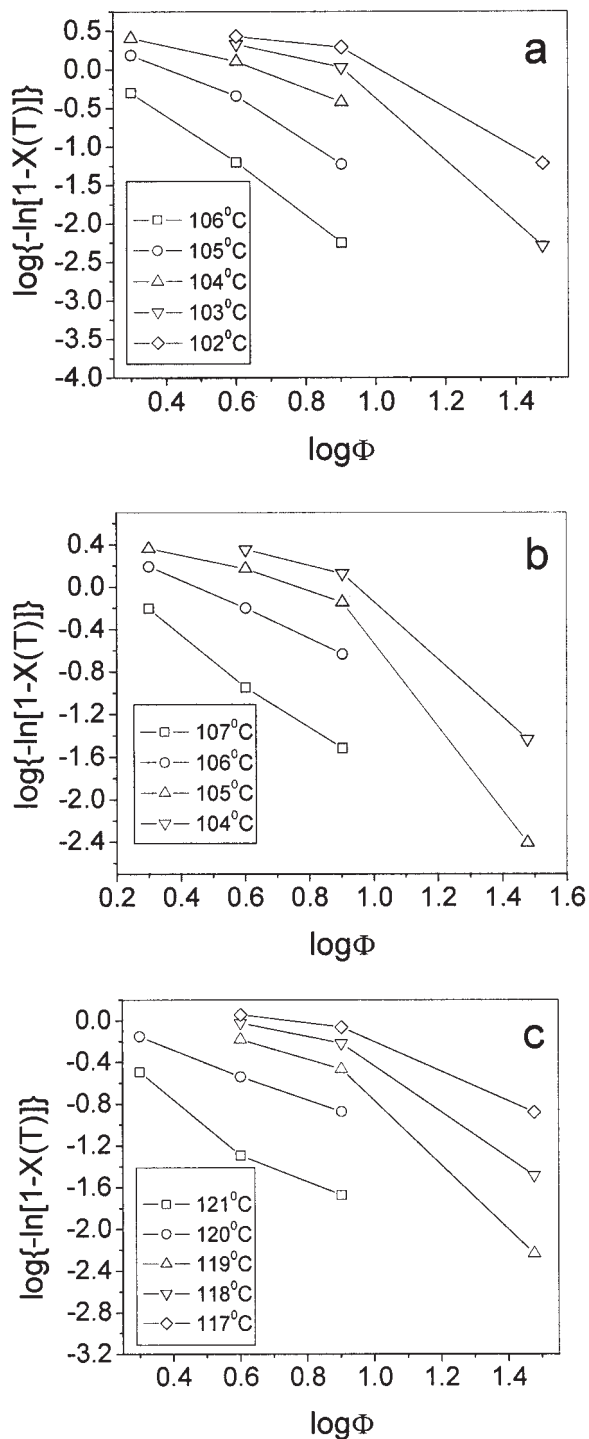

Figure 4 Ozawa plots for nonisothermal crystallization of (a) 10 wt % UHMWPE/LP, (b) 20 wt % UHMWPE/LP, and (c) UHMWPE.

indicates that m is not constant with temperature, and the cooling function $k(T)$ cannot be determined. The most probable reason for this may be the occurrence of secondary crystallization in cooling process. For PE, a large portion of the overall crystallization should be attributed to the secondary crystallization, and the
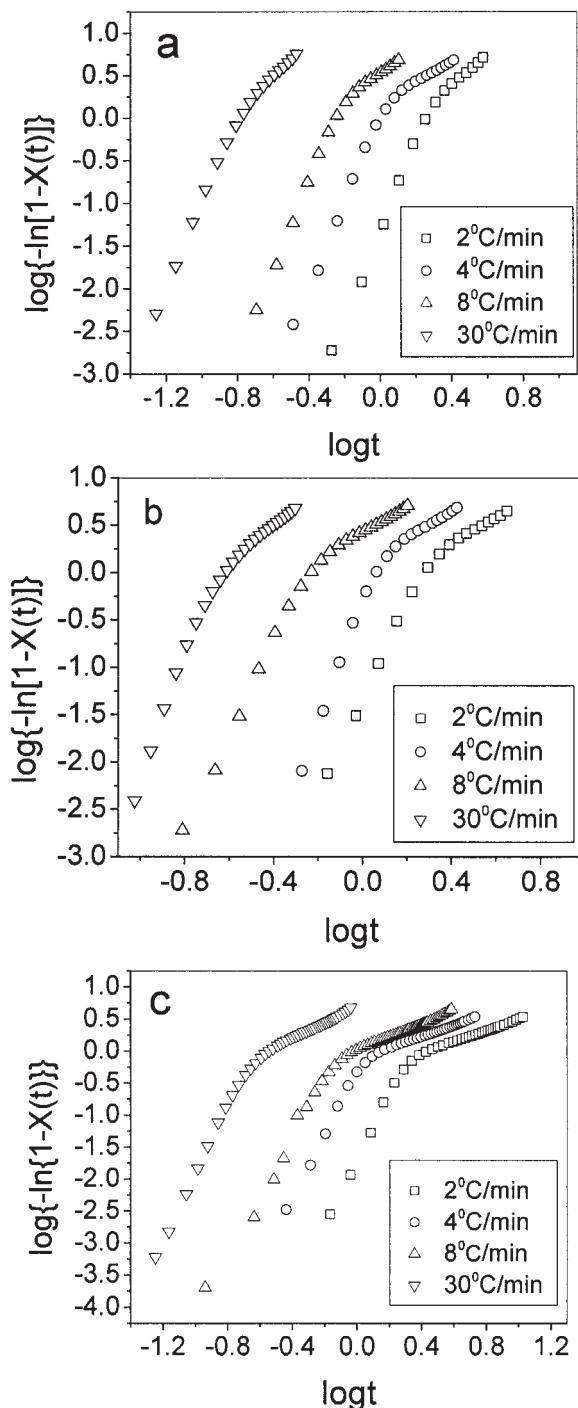

Figure 5 Avrami plots of $\log[-\ln(1 - X)]$ vs. $\log T$ for nonisothermal crystallization of (a) 10 wt % UHMWPE/LP, (b) 20 wt % UHMWPE/LP, and (c) UHMWPE.

TABLE I
Kinetic Parameters for UHMWPE and UHMWPE/LP Blends from Extended Avrami Analysis

Sample Φ(°C/min)	Primary crystallization stage			Secondary crystallization stage		
	n_1	Z_{t1}	Z_{c1}	n_2	Z_{t2}	Z_{c2}
10 wt %UHMWPE						
2	5.14	0.05	0.229	1.64	0.57	0.755
4	5.06	1.16	1.039	1.22	1.56	1.117
8	5.02	19.33	1.448	1.30	3.39	1.165
30	4.97	1.03×10^4	1.361	1.76	35.99	1.127
20 wt %UHMWPE						
2	5.18	0.04	0.218	1.29	0.671	0.819
4	5.78	0.48	0.834	1.39	0.807	0.948
8	5.16	22.51	1.476	1.28	2.70	1.132
30	5.40	3.08×10^6	1.645	1.96	19.72	1.104
UHMWPE						
2	5.08	0.02	0.142	0.80	0.49	0.400
4	5.07	1.86	1.167	0.89	0.75	0.931
8	4.94	4.46	1.205	1.04	1.00	1.000
30	5.09	1.63×10^3	1.280	1.27	5.13	1.056

that the deviation of the plots from Ozawa linearity increased with increasing cooling rates, which means that Ozawa exponent m increased for higher cooling rates. The probable reason is that the nucleation type and growth process of crystallization become more complicated at higher super cooling degree.

Avrami analysis modified by Jeziorny

The Avrami analysis modified by Jeziorny is an extended expression to analyze the nonisothermal crystallization process. In this case, the time-dependent relative crystallinity function $X(t)$ is shown as the following two forms

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

$$\log[-\ln(1 - X(t))] = n \log t + \log Z_t \quad (6)$$

where the Avrami exponent n is a mechanism constant depending on the nucleation type and growth process; Z_t is the Avrami rate constant involving nucleation and growth parameters; and t is the crystallization time. Since the process is nonisothermal, Jeziorny[11] suggested that the rate parameter Z_t should be corrected by the influence of cooling rate Φ of the polymer. The final form of the parameter characterizing the kinetics of nonisothermal crystallization Z_c was given as follows

$$\log Z_c = \frac{\log Z_t}{\Phi} \quad (7)$$

If eq. (6) adequately describes the nonisothermal crystallization behavior of a polymer, the straight-line relationship of $\log[-\ln(1 - X(t))]$ vs. $\log t$ would give

the values of n and Z_t or Z_c from the slopes and the intercepts, respectively. The Avrami plots of $\log[-\ln(1 - X(t))]$ vs. $\log t$ for UHMWPE and UHMWPE/LP blends are shown in Figure 5.

As can be seen, all plots consist of two sections corresponding to the primary crystallization stage and the secondary crystallization stage. The secondary crystallization takes place at 50–60% relative crystallinity of UHMWPE. These results clearly indicate the existence of secondary crystallization in the process of nonisothermal crystallization for UHMWPE.

The values of n, Z_t, and Z_c are shown in Table I. At the primary stage, the Avrami exponent n_1 is invariable and equal to five when the concentration of UHMWPE or the cooling rate is increased. Generally, the reported values of n for PE range from 2 to 4 (mostly for isothermal crystallization) and vary continuously with composition and cooling rate.[17–19] High and constant values of n_1 for UHMWPE and UHMWPE/LP blends may be caused by high viscosities, which would lead to a more complicated crystallization mechanism. Increasing the cooling rate can provide the system with more energy to improve the activity of chain segment, thus result in the increasing of crystallization rate parameter Z_{c1}. At the secondary stage, the Avrami exponent n_2 ranging from 1.96 to 0.80 indicates the spherulites' impingement and crowding. The form of spherulites' growth transforms into the mixture mode of one-dimensional and needle-like crystal growth, and the crystallization mode becomes simpler.

Mo's approach

By combining eqs. (4) and (6), Mo and coworkers derived another kinetic equation for nonisothermal

crystallization behavior to relate the crystallinity with the cooling rate Φ and the crystallization time t (or temperature T).[20] The relation between Φ and t was defined for a given degree of crystallinity. Thus

$$\log Z_t + n \log t = \log k(T) - m \log \Phi \quad (8)$$

$$\log \Phi = \log F(T) - b \log t \quad (9)$$

where the parameter $F(T) = [k(T)/Z_t]^{1/m}$ refers to the necessary value of cooling rate to reach a defined crystallinity within unit crystallization time, and b is the ratio between Avrami and Ozawa exponents, i.e., $b = n/m$. It is apparent that $F(T)$ has a definite physical and practical meaning. From eq. (9), it is followed that, at a given degree of crystallinity, the plot of log Φ vs. log t should be a straight line with an intercept of log $F(T)$ and a slope of b. From the obtained plots for UHMWPE and UHMWPE/LP blends presented in Figure 6, it is found that there is a linear relationship between log Φ and log t. The corresponding values of $F(T)$ and b are listed in Table II. $F(T)$ increases not only with the increasing of relative crystallinity for all samples, but also with the increasing of UHMWPE content in the blends at a given relative crystallinity value. In other words, increasing the concentration of UHMWPE can reduce the crystallizing rate. This result is consistent with the earlier analysis. The size of b ranges from 1.088 to 1.349. So, it can be clearly concluded that Mo's approach well describes the nonisothermal crystallization behavior of UHMWPE and UHMWPE/LP blends satisfactorily.

CONCLUSIONS

The nonisothermal crystallization kinetics of UHMWPE and UHMWPE/LP systems was studied by means of DSC technique. Compared with neat UHMWPE, the crystallization rate of UHMWPE in UHMWPE/LP blend systems is faster. The higher the concentration of LP in UHMWPE/LP blend systems, the faster the crystallization rate of UHMWPE. In the process of analyzing UHMWPE crystallization, the Ozawa model fails to adequately describe the crystallization behavior probably due to the inaccurate assumption in this approach about the secondary crystallization. The Avrami plots of UHMWPE and UHMWPE/LE blends show good linearity. At the primary stage, the Avrami exponent n_1 is constant and ~5 while increasing the concentration of UHMWPE or the cooling rate. High values of n_1 for UHMWPE and UHMWPE/LP blends may be generated from their high viscosities yielding a more complicated crystallization mechanism. The Avrami exponent n_2, ranging from 0.80 to 1.96, indicate the more simpler crystallization mode at the secondary stage. Further, Mo's
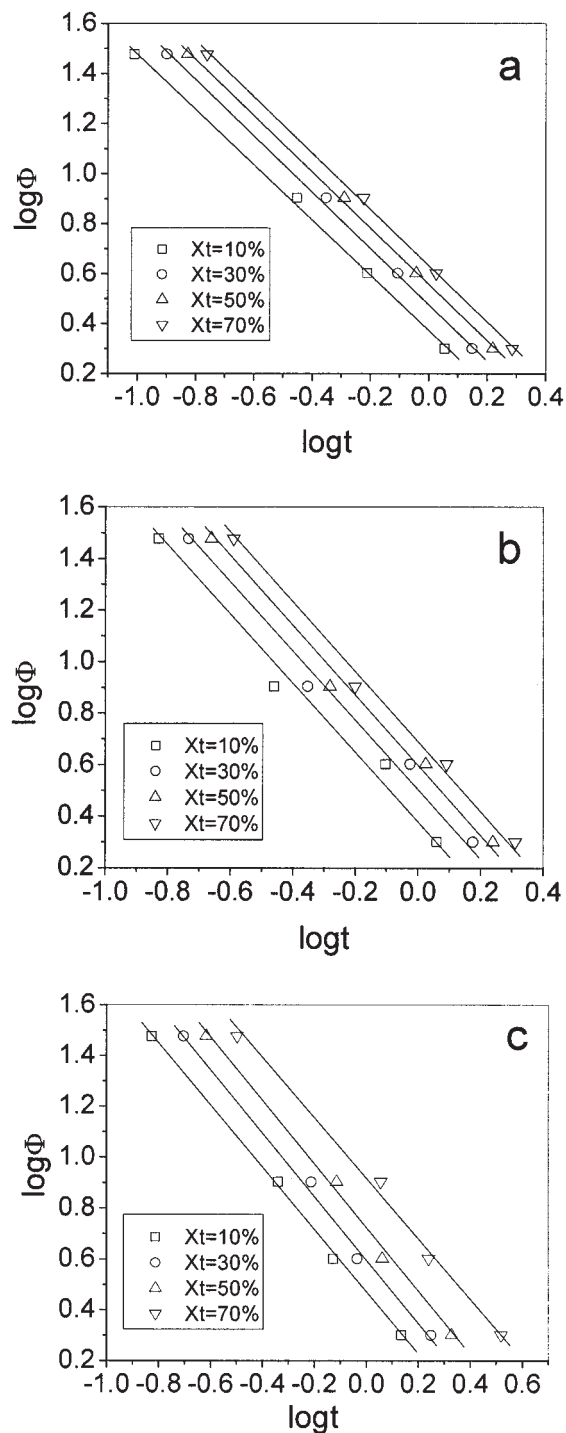

Figure 6 Plots between log Φ vs. log t for UHMWPE and UHMWPE/LP blends from the combined Avrami and Ozawa equation for (a) 10 wt % UHMWPE/LP, (b) 20 wt % UHMWPE/LP, and (c) UHMWPE.

approach can describe the nonisothermal crystallization kinetics of UHMWPE and UHMWPE/LP blends satisfactorily. The value of $F(T)$ increases with increasing relative crystallinity for all polymer systems and also with increasing UHMWPE content in the blends at a given relative crystallinity value. The value of b

TABLE II
The Values of b and $F(T)$ at Various Crystallinity Degree for UHMWPE and UHMPE/LP Blends

$X(t)$ (%)	10	30	50	70
10 wt % UHMWPE/LP				
b	1.088	1.102	1.113	1.119
$F(T)$	2.40	3.05	3.63	4.34
20 wt % UHMWPE/LP				
b	1.308	1.327	1.328	1.349
$F(T)$	2.44	3.33	4.09	5.03
UHMWPE				
b	1.213	1.234	1.244	1.184
$F(T)$	2.92	4.05	5.20	7.95

ranges from 1.088 to 1.349 and slightly increases with increase in relative crystallization.

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