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Publisher Taylor & Francis

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Polymer-Plastics Technology and Engineering

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713925971>

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Online publication date: 28 January 2011

To cite this Article Mosavian, M. Hamed , Sahebian, S. and Bakhtiari, A.(2011) 'Non-Isothermal Crystallization of Al₂O₃/HDPE Composite', Polymer-Plastics Technology and Engineering, 50: 3, 225 – 231

To link to this Article: DOI: 10.1080/03602559.2010.531432

URL: <http://dx.doi.org/10.1080/03602559.2010.531432>

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Non-Isothermal Crystallization of Al₂O₃/HDPE Composite

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To clarify the effect of Alumina (Al₂O₃) particles on the crystallization of high density polyethylene (HDPE), HDPE and Al₂O₃/HDPE composite using compression molding in the amount of Alumina 10 wt% was prepared. The non-isothermal crystallization of Al₂O₃/HDPE composite and neat HDPE have been studied by Differential Scanning Calorimetry (DSC) at different cooling rates between 1 and 30°C/min. The crystallization kinetic was evaluated by a direct fitting of the experimental data to Avrami model. The results of this study showed that the crystallization exotherm became wider and shifted toward a lower temperature range, with an increasing cooling rate.

Keywords Alumina; Crystallization kinetic; Non-isothermal crystallization; Polyethylene

INTRODUCTION

The semi-crystalline polyethylene has been introduced as the first selection among thermoplastic materials in the most engineering application. Good properties such as low cost, easy production by almost convenient procedures such as injection, compression molding, extrusion, cause to PE, which can be the first selection for many consumers.

Among the consumer polyethylenes in industry, HDPE with high toughness especially at low temperatures and good chemical and electrical resistivity has received much more attention^[1–2]. But its application has been limited compared to its potential, since thermal (thermal stability, melting temperature) and mechanical properties are not high enough for some industrial applications.

One measure to improve the properties and lessen costs is to reinforce with mineral fillers to form a composite^[3–4]. Mineral fillers can change the physical, mechanical and thermal properties of HDPE due to its nature, shape^[5], size^[6], distribution^[5–7], the loading of

filler content, microstructure and interaction between filler and matrix^[8].

The crystallization behavior of semi-crystalline polymer is a basic problem in the polymer physics. During the cooling step, semi-crystalline polymers develop crystalline regions. The characteristics of the crystalline regions strongly affect the mechanical, physical and thermal properties of polymer^[9]. So, the crystallization kinetics of semi-crystalline polymers has continuously been the subject of intense research for many decades. The crystallization kinetics of composite base polymer is very complicated since the filler in a polymer will affect the crystallization behavior of polymers because the fillers act as the crystal nuclei^[10–13]. The isothermal crystallization with constant external conditions is investigated by many researchers. But isothermal crystallization conditions rarely occur during the practical processing in industry.

To be relevant to industrial processing, it is desirable to study the crystallization of polymers under non-isothermal conditions^[13–20]. For example, studies on non-isothermal crystallization of HDPE/POSS nanocomposite were done by Joshi and Butola. They showed that the value of Avrami exponent *n* for HDPE/POSS nanocomposite decreased with increasing cooling rate. It is postulated that the values of *n* close to 3 are caused by spherulitic crystal growth with heterogeneous nucleation while simultaneous occurrence of spherulitic and lamellar crystal growth with heterogeneous nucleation account for lower values of *n* at higher cooling rates^[15].

Non-isothermal crystallization and subsequent melting behavior of pigmented medium density polyethylene is investigated by Thanankiat et al.^[17]. They showed that the all off pigments investigated were able to shift the crystallization exotherm toward higher temperature rang and diarylide as pigment was the only pigment that was effective in accelerating the crystallization processes of the filled polymer^[17]. The aim of this work is to clarify the effect of Alumina particles on the non-isothermal crystallization of HDPE using differential scanning calorimetry.

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EXPERIMENTAL

Materials

High density polyethylene (HDPE) provided by Tabriz petrochemical complex, Iran, was used in this study. A 99.99% pure Alumina with a mean diameter of about 80.472 μm was obtained from Shimadzu Co., Japan.

Sample Preparation

Alumina particles and HDPE were first mechanically mixed to achieve HDPE/10 wt% of alumina composite. The premixed HDPE and Alumina particles were squeezed between glass sheets, and heated at about 160°C under pressure for 5 min, followed by cooling to room temperature.

Differential Scanning Calorimetry (DSC)

A Shimadzu DSC 60 Differential scanning calorimeter (DSC) was used to evaluate the non-isothermal melt-crystallization of HDPE and its composite. Temperature calibration was carried out using an indium standard ($T_m = 156.6^\circ\text{C}$ and $\Delta H_f = 28.5 \text{ J/g}$). Samples were between 2–3 milligrams in weight. The samples heated from room temperature at a heating rate of 10°C/min to 200°C and held for 10 min to eliminate any previous thermal history. After complete melting, the samples cooled to 30°C at constant cooling rates of 1, 5, 10 and 30°C/min. Afterward, the samples were reheated from room temperature to 200°C at a heating rate of 10°C/min to observe the melting behavior. At least two specimens for each type of material were tested by DSC tests, and the average values were reported.

RESULTS AND DISCUSSION

Figures 1 and 2 showed the non-isothermal crystallization exotherms of HDPE and its composite at 5 cooling rates

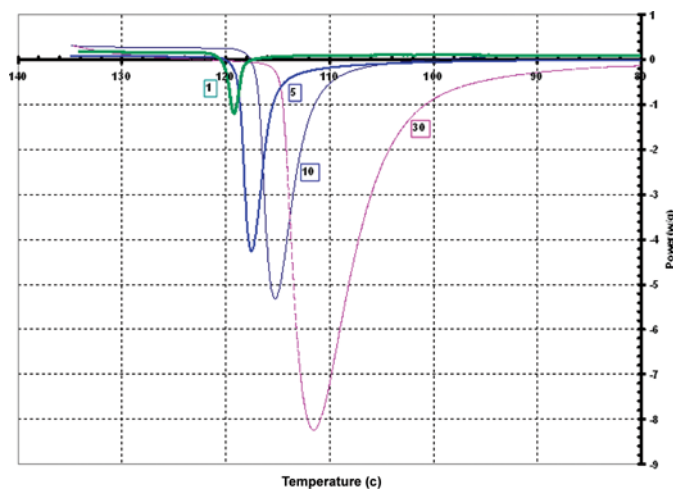


FIG. 1. DSC thermograms of non-isothermal crystallization at different cooling rates for HDPE.

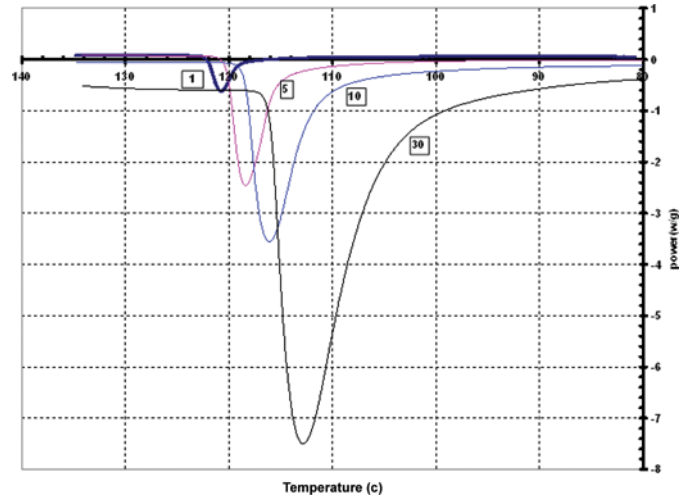


FIG. 2. DSC thermograms of non-isothermal crystallization at different cooling rates for HDPE/10 wt% Alumina particles.

rates, ranging from 1 to 30°C/min. As seen from these figures, the crystallization peaks shifted to a lower temperature and became wider when cooling rate increased. The reason of this effect is related to the crystallization kinetic, which was done in a nucleation-controlled region^[17–21].

The fusion and solidification heat, melting (T_{Pr}) and solidification (T_{PC}) temperature, initial and final temperature of solidification and fusion peaks were obtained from DSC curves and summarized in Table 1. As seen in Table 1 and DSC curves, the crystallization peak shifted to a lower temperature with an increase in cooling rates for HDPE and HDPE/Alumina composite. Also, the presence of Alumina particles caused to increase in initial crystallization temperature. It could be explained that the alumina particles act as nucleation sites^[22].

At low temperatures, the molecular chains have low mobility and only form imperfect crystals, which can be destroyed at lower temperatures; therefore, T_{Ci} , T_{fi} shifts to a lower temperature, and the broader ΔT ($T_{Cr} - T_{Ci}$) might be caused by the larger degree of imperfection of the crystal^[16].

Fusion and solidification heat of HDPE lessened when the cooling rate and weight percent of Alumina particles increased. Imperfect crystals and the situation of Alumina particles in the amorphous structure of polymer^[22] could be expressed as the reason for the reduction of fusion and solidification heat.

Based on Table 1, the duration of HDPE crystallization was affected by the increasing secondary phase and cooling rate. They caused an increase in the crystallization time.

By using the DSC test, nucleation and growth rate of spherulites could be determined. Mareri expressed that the subtraction of crystallization temperature corresponding to

TABLE 1
Characteristic data of non-isothermal crystallization exotherms and melting endotherms for HDPE and its composites

Cooling rate (°C/min)	Enthalpy (j/g)	T _{ci} (°C)	T _{cf} (°C)	T _{cp} (°C)	Enthalpy (j/g)	T _{fi} (°C)	T _{ff} (°C)	T _{fp} (°C)
HDPE								
1	130.56	120.28	118.29	119.2	180.52	123.52	133.78	131
5	148.53	118.92	115.35	117.53	148.05	124.85	133.85	131.08
10	152.50	117	110.94	115.25	161.62	123.9	132.67	130.18
30	166.04	114.66	104.05	111.49	152.15	123.1	132.04	129.5
Composite								
1	103.66	122.18	119.09	120.78	150.32	124.03	135.51	132.62
5	131.26	120.33	115.49	117.42	149.74	124.32	133.25	130.42
10	127.92	118.48	110.73	116.13	135.93	123.03	133.17	129.99
30	136.83	116.02	104.87	112.82	134.85	122.61	131.5	128.77

the maximum of the crystallization peak, and initial crystallization temperatures are ($T_{cp} - T_{ci}$), inversely proportional to spherulite growth rate^[23], and the slope of the peak at the end of solidification has a direct relationship with the nucleation rate of spherulites^[23].

Table 2 demonstrated the nucleation and growth rate of spherulites as a function of cooling rate variation for HDPE and its composite. Apparently, the crystallization peak became wider when cooling rate and weight percent of Alumina increased. So, the growth rate of spherulites decreased. Also, nucleation rate of spherulites lessened when both cooling rate and weight percent of alumina particles increased.

By using the DSC test, the energy released over the non-isothermal crystallization process as a function of temperature could be obtained. As a result, the relative crystallinity index as a function of time and temperature

could be defined as^[15]:

$$X(t) = \frac{\int_{T_0}^T \left(\frac{dH}{dT}\right) \times dT}{\int_{T_0}^{T_\infty} \left(\frac{dH}{dT}\right) \times dT} \quad (1)$$

where $X(t)$, T_0 and T_∞ are the relative crystallinity index, the onset and end crystallization temperature, respectively, and $\left(\frac{dH}{dT}\right)$ is the heat flow rate. T is the crystallization temperature at time t . The relative crystallinity index as a function of temperature for HDPE and its composite at various cooling rates were illustrated in Figures 3 and 4. Based on Figures 3 and 4, the solidification temperature range extended when cooling rate and weight percent of alumina particles increased.

The plots of $X(t)$ versus crystallization time at different cooling rates ranging from 1 to 30°C/min for HDPE and its composite were represented in Figures 5 and 6. They showed that the higher the cooling rate caused to increase the overall crystallization time; therefore, the transformation is controlled by nucleation^[24]. In addition, since the alumina particles delayed the crystallization, the duration of crystallization increased.

To quantify the kinetics of the non-isothermal crystallization process^[17,21,25], crystallization time at an arbitrary relative crystallization could be obtained from the $X(t)$ curves. The $X(t)$ values, for various values of the relative crystallinity (i.e., at the θ value of 0.01, 0.1, 0.3, 0.5, 0.7, 0.9 and 0.99, respectively) for HDPE and HDPE/10wt%Al₂O₃ composite were summarized in Table 3 and were plotted as a function of cooling rate in Figures 7 and 8.

All of the t_θ values generally decreased with increasing cooling rate, so crystallization proceeded faster when cooling rate increased. By comparison of Figures 7 and 8, all of the t_θ values increased when the Alumina particles reinforced in HDPE matrix.

TABLE 2
Nucleation and growth rates of spherulite of HDPE and its composites

	T _p - T _{ci}	Tan(α)
HDPE		
1	1	1.9
5	1.33	2.068
10	1.8	1.519
30	2.86	1.061
HDPE/10wtAl ₂ O ₃		
1	1.62	0.42
5	1.9	0.93
10	2.48	0.83
30	3.31	0.7

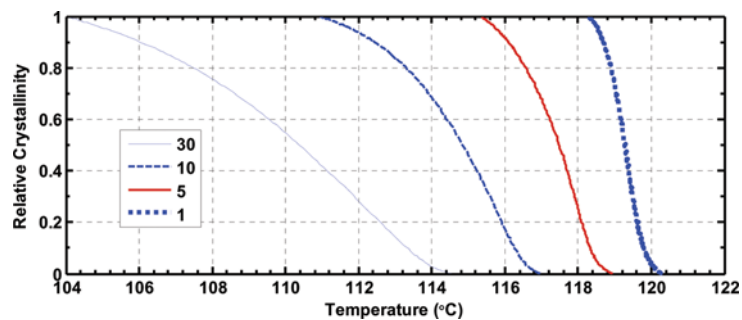


FIG. 3. Relative crystallinity index as a function of temperature of HDPE at four different cooling rates ranging from 1 to 30°C/min.

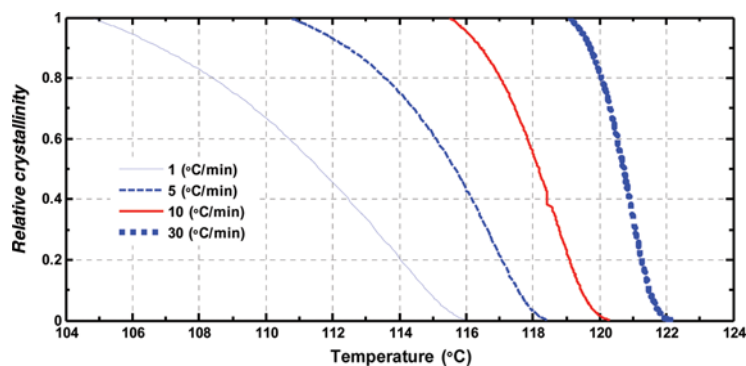


FIG. 4. Plots of relative crystallinity as a function of temperature for HDPE/10wt%Al₂O₃ composite.

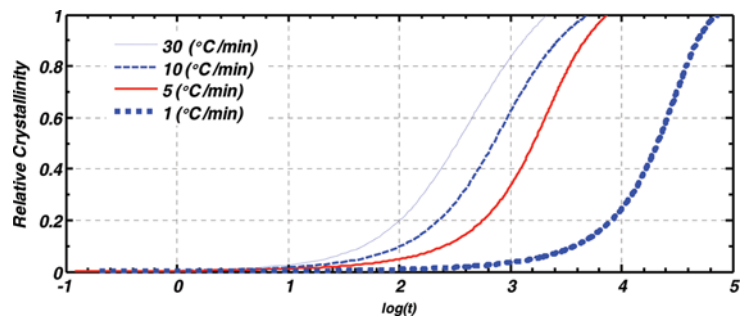


FIG. 5. Plots of relative crystallinity as a function of time for pure HDPE crystallized non-isothermally at various cooling rates.

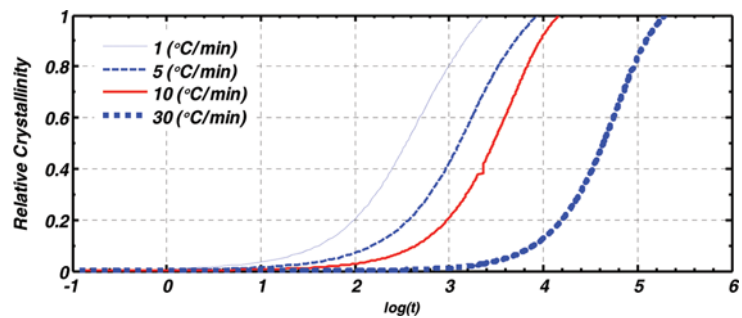


FIG. 6. Relative crystallinity versus time of HDPE/10wt%Al₂O₃ composite at various cooling rates.

TABLE 3
Quantitative analysis of the relative crystallinity as a function of time which were converted from non-isothermal crystallization of pure HDPE and its composites

Φ (°C/min)	$\theta = 0.01$	$\theta = 0.1$	$\theta = 0.3$	$\theta = 0.5$	$\theta = 0.7$	$\theta = 0.9$	$\theta = 0.99$
HDPE							
1	0.4053	3.592	4.093	4.324	4.499	4.687	4.845
5	0.9557	2.416	2.955	3.211	3.421	3.674	3.854
10	0.6932	2.028	2.565	2.856	3.109	3.434	3.664
30	0.4706	1.687	2.219	2.518	2.797	3.118	3.311
HDPE/10%wtAl ₂ O ₃							
1	1.965	3.924	4.394	4.648	4.855	5.097	5.273
5	1.386	2.653	3.186	3.472	3.709	3.963	4.143
10	0.7886	2.197	2.797	3.109	3.374	3.709	3.916
30	0.3	1.61	2.219	2.549	2.833	3.17	3.353

The Avrami model is the most common approach for describing the overall isothermal crystallization kinetics. In this model, the relative crystallinity as a function of time can be expressed as^[26–28]

$$X(t) = 1 - \exp(-(kt)^n) \quad (2)$$

$$\ln[-\ln(1 - X_t)] = n \times \ln(k) + n \ln(t) \quad (3)$$

where K and n are the Avrami rate constant and the Avrami exponent, respectively. The Avrami exponent provides a qualitative indication of the nucleation mechanism and the form of crystallization growth, and k is the constant including nucleation and growth parameter; the constant k increases with the decrease of crystallization

temperature^[19]. The units of k are given as the inverse of time. Although the Avrami equation is often used to describe the isothermal crystallization behavior of semi-crystalline polymers^[26–28].

Applying the Avrami theory, when $\ln[-\ln(1 - X_t)]$ is plotted against $\ln(t)$, a straight line is obtained with the slope as n and the intercept as $\ln(k)$. The plots of $\ln[-\ln(1 - X_t)]$ versus time at various cooling rates for HDPE and its composite were shown in Figures 9 and 10, respectively. Based on these figures, the Avrami kinetic parameters (i.e., k and n) could be obtained and summarized in Table 4 for HDPE and HDPE/10wt%Al₂O₃ composite.

According to values reported in Table 4, k constant increased with increasing cooling rate and weight percent of alumina particles. Also, the Avrami exponent decreased when the cooling rate and weight percent of alumina

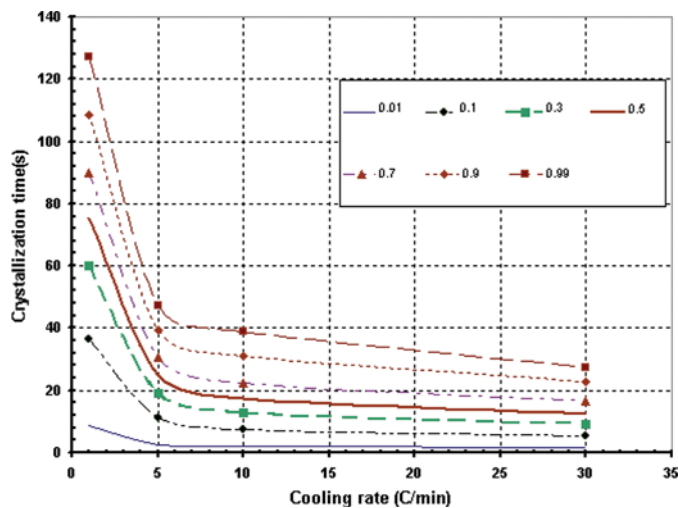


FIG. 7. Crystallization time at various relative crystallinity as a function of cooling rate for HDPE.

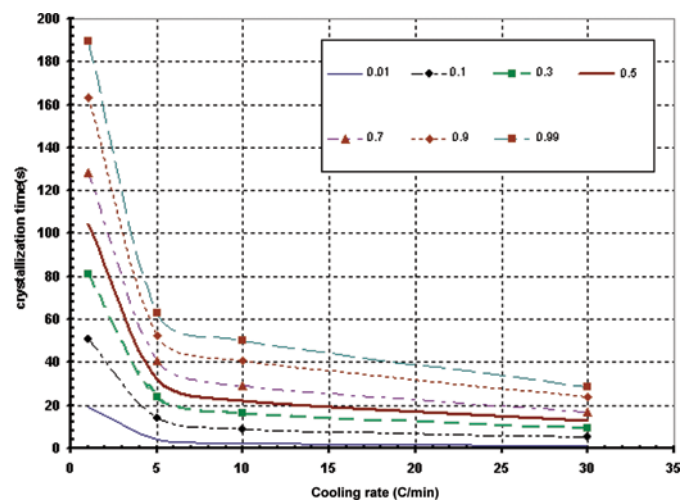


FIG. 8. Crystallization time at various relative crystallinity as a function of cooling rate for HDPE/10%wtAl₂O₃.

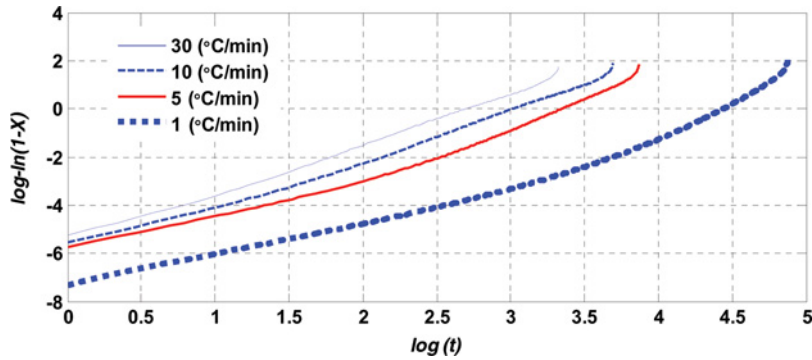


FIG. 9. Plots of the variation of $\ln[-\ln(1 - X_t)]$ versus $\ln(t)$ for HDPE at various cooling rates.

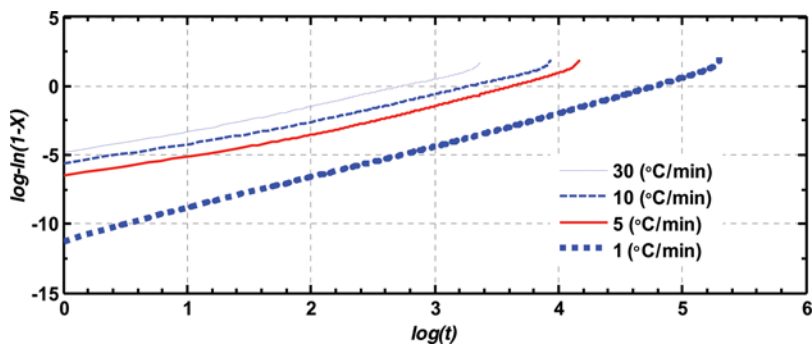


FIG. 10. Plots of the variation of $\ln[-\ln(1 - X_t)]$ versus $\ln(t)$ at various cooling rates ranging from 1 to 30°C/min for HDPE/10wt% alumina particles.

particles increased. Avrami index 3 suggests an instantaneous nucleation with spherulite growth geometry. It seems that the nucleation mechanism and spherulite growth rate of HDPE were changed when the weight percent of Alumina particles and cooling rate increased.

TABLE 4

Values of k and n at various cooling rates for HDPE and its composites

Φ (°C/min)	k	n
HDPE		
1	1.87×10^{-13}	2.863
5	7.12×10^{-9}	2.422
10	2.165×10^{-7}	2.165
30	1.33×10^{-6}	2.179
HDPE/10%wtAl ₂ O ₃		
1	1.39×10^{-12}	2.468
5	5.39×10^{-9}	2.277
10	1.97×10^{-7}	2.0397
30	1.68×10^{-6}	1.986

CONCLUSIONS

Non-isothermal crystallization for HDPE and HDPE/10wt% alumina composite were investigated using differential scanning calorimetry (DSC). The results showed that the crystallization exotherm peaks became wider and shifted toward a lower temperature with an increase in the cooling rate used. The Alumina particles in HDPE matrix caused to change in crystallization similar to increasing cooling rate. Further analysis of the non-isothermal crystallization showed that the apparent incubation period, the crystallization time at different relative crystallinity values, and the apparent total crystallization period were all found to decrease with increasing cooling rate and weight percent of Alumina particles. The Avrami model described the non-isothermal crystallization data of HDPE and its composite. The Avrami exponent and Avrami index increased with an increase in cooling rate and alumina content in HDPE matrix.

ACKNOWLEDGMENTS

The authors wish to thank the Chemical Engineering Research Lab of Ferdowsi University of Mashhad (FUM),

for performing the experiments, and also the office of the Vice President for Research and Technology, FUM, for financing the budget of this project (No. 28341).

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