Isothermal Crystallization Behavior of Polyoxymethylene with and without Nucleating Agents

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ABSTRACT: Nucleation effects of two silicate nucleating agents, attapulgite and diatomite, on the crystallization of polyoxymethylene (POM), were studied by means of differential scanning calorimetry and polarized optical microscopy. The crystallization kinetics of POM with and without nucleating agents was analyzed by means of two isothermal crystallization kinetic equations through the crystallization thermograms. Compared with virgin POM, POM with nucleating agents of attapulgite and diatomite decreased the spherulitic size of POM and interfacial free energies per unit area perpendicular σ_e. The crystallization growth rate was accelerated because of nucleating agents as well. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 304–310, 2001

Key words: attapulgite; diatomite; polyoxymethylene; nucleating agent; crystallization kinetics

INTRODUCTION

The addition of nucleating agents into polymers with a medium crystal growth rate has been widely practiced in the plastics fabrication not only for improving impact properties and optical clarity,[1] but also for shortening the cycle period in injection molding processes.[2] However, most of nucleating agents commercially available were found empirically and the relationship between the chemical or physical properties of the nucleating agents and their nucleation activities was poorly understood. Polyoxymethylene (POM) is a linear polymer with high crystallinity, self-lubrication, and is widely used in the industry field, but its application is restrained by its poor size stability, and the study on the crystallization process of POM is important to meet the requirement of fine injection molding.

Many scientists have concentrated on crystallization of POM. Geil[3] established the basic morphological peculiarities of the supermolecular structure—single crystals, dendrites, hedrites, ovals, and spherulites formed in the crystallization of POM. Pelzbauer and Galeski[4] reported that the crystallization occurred in the spherulite form below 158°C; above this temperature, hedrites and, sporadically, ovoids were obtained for POM. Balik and Hopfinger[5] investigated epitaxial crystallization of POM from concentrated (1.0 wt %) iodobenzene solutions onto the (001) cleavage face of mica and observed two distinct morphologies. Mutsumi and Mimoru[6] reported plastic parts in pens from POM with talc as nucleating agent in order to enhance the size stability. Xu et al.[7] investigated the isothermal crystallization of POM/additive P (an acetal crosslinking polymer) via optical depolarization method. The nonisothermal crystallization process of POM has been investigated by Plummer and Kausch,[8,9]

a) Virgin POM   b) POM with attapulgite   c) POM with diatomite
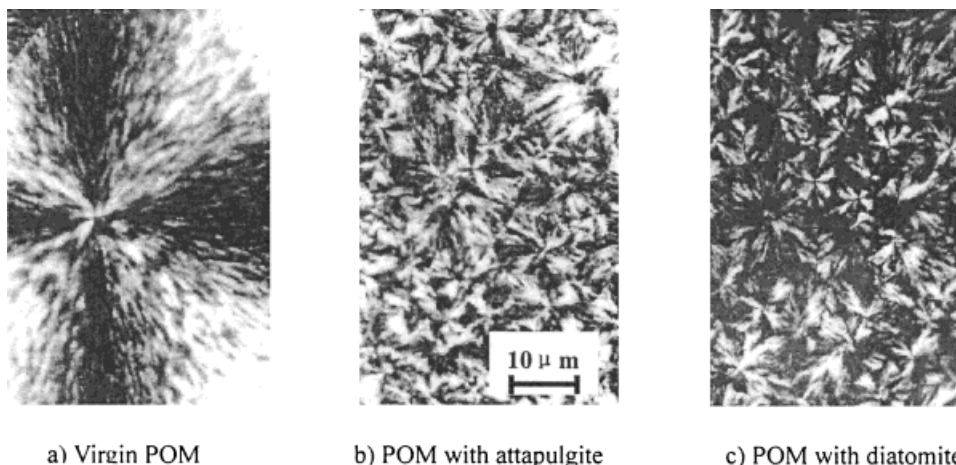
Figure 1   Polarized optical micrographs of POM. (a) without nucleating agent; (b) with attapulgite; (c) with diatomite.

Phillips and Manson,[10] and Martins and Cruz-Pinto[11,12] using differential scanning calorimetry (DSC). It should be noted that the material they used was neat POM without any nucleating agent. Herein, we report the crystallization kinetics of POM with attapulgite and diatomite as nucleating agents. They are low-cost inorganic silicate powders with good thermal stability and dispersity and could be widely used in the process of melt fabrication of POM.

EXPERIMENTAL

Specimens

The POM used was a commercial grade powder (M90) without any additives and supplied by Shanghai Solvent Factory (China). The nucleating agents were two silicate substances: attapulgite powder with average mesh 325 from Jiashan Chemical Factory (China) and diatomite powder from Shanghai Chemical Corp. (China) without any pretreatment. Nucleated POM was prepared by the following procedure: after air-dried at 80°C for 4 h, POM and nucleating agent were mixed mechanically and extruded by a screw extruder at a rotational speed of 30 rpm. The temperature profiles of the barrel were 160, 180, 200, and 190°C from hopper to die. The extrudate containing 1% nucleating agent was palletized and dried.

DSC Measurements

Isothermal crystallization was performed in the sample pan of a Perkin-Elmer 2C Calorimeter in our laboratory with ca. 10 mg of patch cut from nucleated POM pellet in nitrogen gas. The temperature scale of DSC was calibrated with indium. The sample was kept at more than 200°C for 5 min before crystallization to eliminate the effect of the previous thermal history, and quenched to a desired crystallization temperature. The isothermal crystallization process was monitored by the DSC at various temperatures.

Morphology Measurements

The morphology of POM crystallized with and without nucleating agent was performed with an Olympus PM 10M polarized light microscope. A film sample with the thickness of ~0.1 mm obtained by solution casting method was used. POM solution in N,N-dimethylformamide with the concentration of 1% (by weight) was poured onto a glass plate; the solvent was allowed to be evaporated for 30 min at 130°C. The film obtained was melted in the air at 200°C for 5 min before crystallization, and then crystallized at a given temperature of 130°C for 4 h.

RESULTS AND DISCUSSION

Effect of the Nucleating Agents

Figure 1 shows polarized optical micrographs of the nucleated POM, where fine-grain spherulitic structure of nucleated POM is remarkable. Compared with the spherulites of virgin POM, nucleated POM with attapulgite (or diatomite) has more spherulites with less size, as seen in Figure
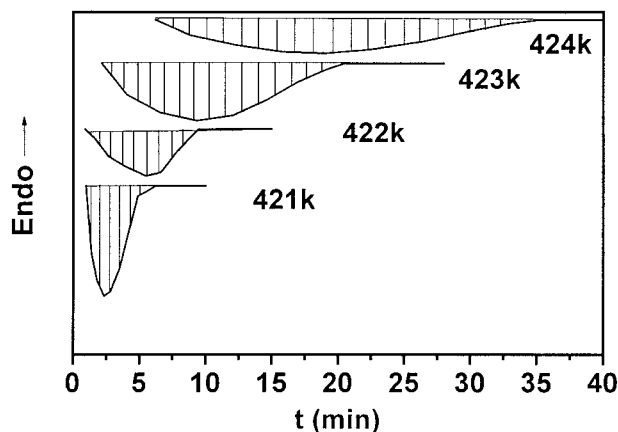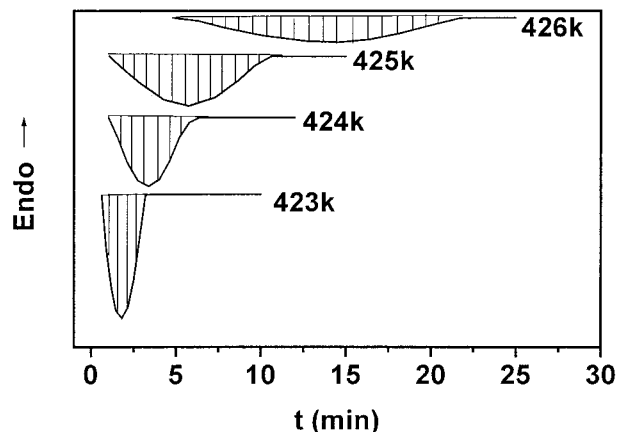
Figure 2 DSC isothermal thermograms obtained during the crystallization of virgin POM at four different temperatures.

Figure 3 DSC isothermal thermograms obtained during the crystallization of POM with attapulgite at four different temperatures.

1. The nucleating agent attapulgite (and diatomite) is a kind of silicate substance with a number of grooves and microvoids on the surface, and the bond Si—O existing in the nucleating agent attapulgite (and diatomite) can well be compatible with the bond C—O in POM. Therefore, a number of the grooves and microvoids, as centers of heterogeneous nuclei, may absorb the chain or segment of POM and the fine-grain spherulitic structures of nucleated POM could be formed. A similar fine-grain spherulitic structure has been observed in isotactic polypropylene with the nucleating agent EC-4 [(p-chloro, p'-methyl)dibenzylidene sorbitol] by Kim and Kim.[13]

The isothermal DSC thermograms of virgin POM, POM with attapulgite and diatomite at four temperatures are shown in Figures 2, 3, and 4, respectively. The times corresponding to peak maximum (t_p) and relative crystalline parameters are listed in Table I. The delay in the DSC signal is representative of the induction time associated with crystal nucleation. The shorter t_p, the faster the crystallization rate.

The relative crystalline degree X_t at a given time t could be estimated from DSC thermograms. The relative crystalline degree X_t of virgin POM, POM with attapulgite and diatomite as a function of time are shown in Figures 5, 6, and 7, respectively. By a comparison of the X_t for three samples at the temperature of 424 K, the crystalline time of POM with attapulgite (and diatomite) would be much shorter than that of unnucleated virgin POM, indicating that adding nucleating agent attapulgite or diatomite accelerates the whole crystallization process because of grooves

or microvoids on the surface of attapulgite (and diatomite) which offer the nucleation sites for POM. The same comparison, but at 426 K, revealed that the diatomite has more effective nucleation capacity for POM than attapulgite.

Isothermal Crystallization Kinetics

The isothermal crystallization kinetics for most polymers, of course for POM as well, could be described by the Avrami equation $X_t = 1 - \exp(-kt^n)$, where X_t is the relative crystalline degree at a given time; t the time; n the Avrami exponent, and k a temperature dependent kinetic constant. Having taken logarithms twice, the following expression of the Avrami equation could be obtained:

$$\lg[-\ln(1 - X_t)] = n \lg(t) + \lg(k) \qquad (1)$$
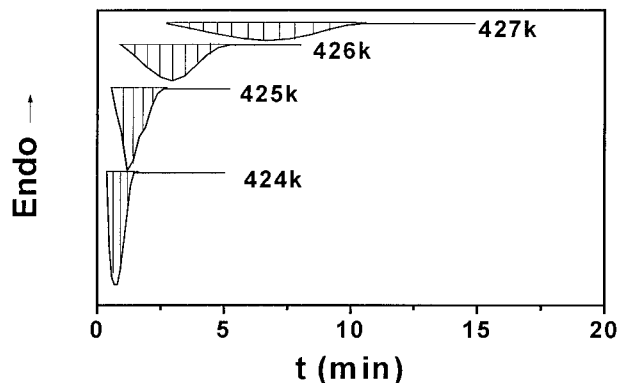
Figure 4 DSC isothermal thermograms obtained during the crystallization of POM with diatomite at four different temperatures.

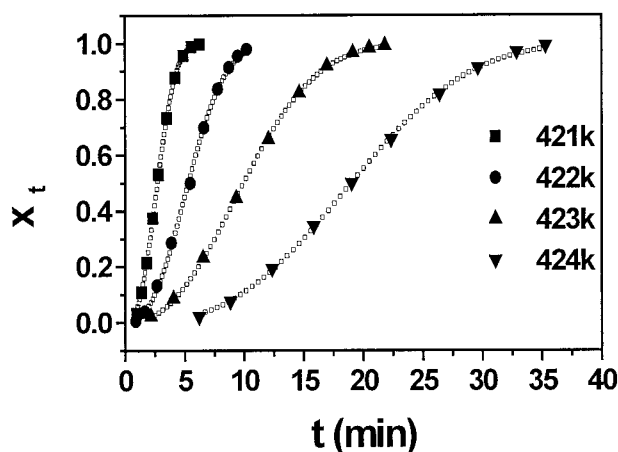**Table I   Values of Isothermal Crystallization of POM and Nucleated POM**

Sample	T_c (K)	n	k	$t_{1/2}$ (min)	t_p (min)	t_p (min, calcd.)
Virgin POM	421	2.67	4.16×10^{-2}	2.72	2.52	2.52
	422	2.59	9.48×10^{-2}	5.27	4.93	5.00
	423	2.36	3.17×10^{-3}	10.13	9.79	9.08
	424	2.98	1.08×10^{-4}	19.02	18.92	19.02
POM with attapulgite	423	3.04	9.57×10^{-2}	1.88	1.79	1.89
	424	3.08	1.52×10^{-2}	3.44	3.44	3.43
	425	2.83	4.99×10^{-3}	5.75	5.75	4.48
	426	3.95	2.06×10^{-5}	13.72	13.76	14.26
POM with diatomite	424	3.14	1.327	0.79	0.72	0.80
	425	3.79	1.50×10^{-1}	1.38	1.32	1.67
	426	3.39	1.75×10^{-2}	2.92	2.93	2.97
	427	3.96	4.12×10^{-4}	6.56	6.75	6.65

If plotting $\lg[-\ln(1 - X_t)]$ versus $\lg(t)$, a linear line could be obtained for the polymer system obeying the Avrami equation, and parameters of n and k could be estimated from the plot. These plots of virgin POM, POM with attapulgite and diatomite are shown in Figures 8, 9, and 10 respectively. The n and k obtained from the slope and intercept of the line are listed in Table I.

The Avrami exponent of virgin POM was in a range of 2.3 and 2.9, whereas POM with attapulgite and diatomite have the values of 2.8–3.9 and 3.1–3.9, respectively. The Avrami exponent value of 3–4 means that the spherulitic growing of POM

with nucleating agents (both attapulgite and diatomite) is in three directions. There was confusion of Avrami exponent values of virgin POM in the literature because of the complication of POM crystallization. For example, it is 2 obtained by Plummer and Kausch[9] and 3–4 reported by Phillips and Manson.[10] However, the Avrami exponent value of POM with nucleating agents (both attapulgite and diatomite) is always larger than that of virgin POM. The same conclusion is available for polypropylene, reported by Lim and Lloyd.[14]
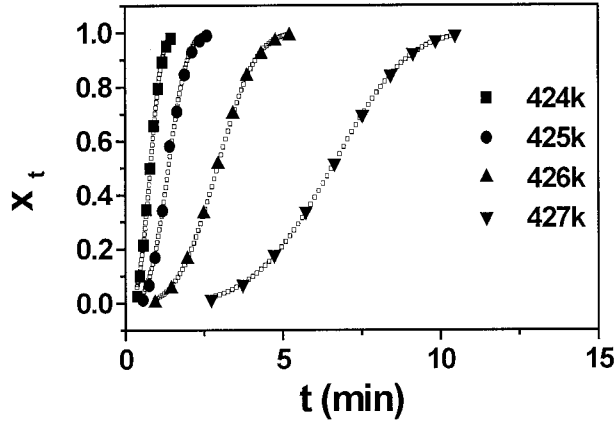
For temperature dependence of kinetic constant k, virgin POM and POM with nucleating

Figure 5 Volume fraction crystallinity of virgin POM is a function of time during the isothermal crystallization. Solid points are experimental data and hollow square points are the value predicted from the Avrami equation model.
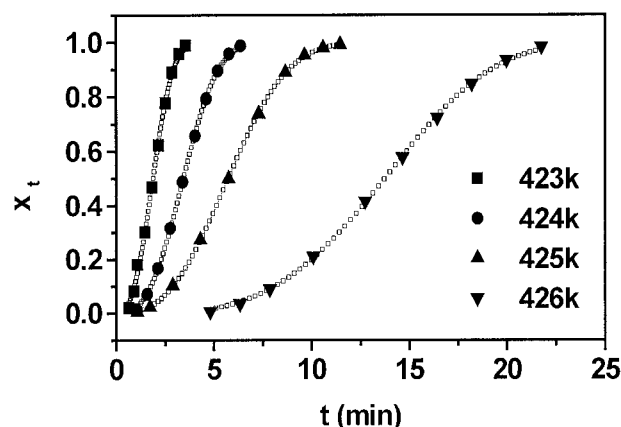
Figure 6 Volume fraction crystallinity of POM with attapulgite is a function of time during the isothermal crystallization. Solid points are experimental data and the hollow square points are predicted from the Avrami equation model.

Figure 7 Volume fraction crystallinity of POM with diatomite is a function of time during the isothermal crystallization. Solid points are experimental data and the hollow square points are predicted from the Avrami equation model.

agents (both attapulgite and diatomite) have the same trend, i.e., k decreases with increasing of crystallization temperature because the experimental temperature here is well above the temperature corresponding to the maximum crystallization rate. The addition of nucleating agent increased the value of kinetic constant k and shortened the half time of crystallization, $t_{1/2}$.

An empirical approach can be used to describe the temperature dependence of the kinetic constant k. Assuming that k is thermally activated[15]:
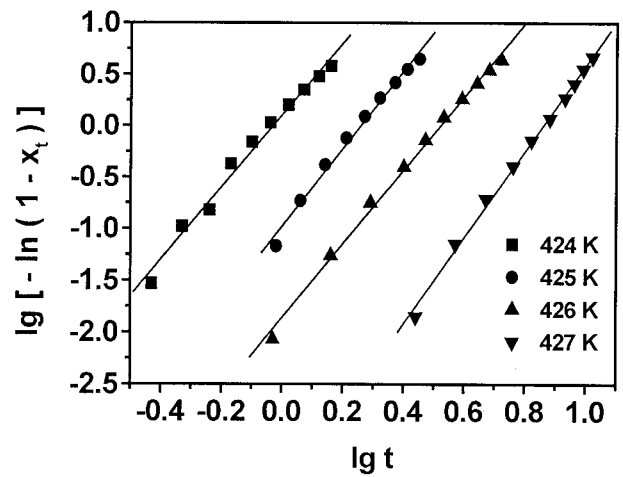
$$k^{1/n} = k_0\exp(-\Delta E/RT_c) \qquad (2)$$
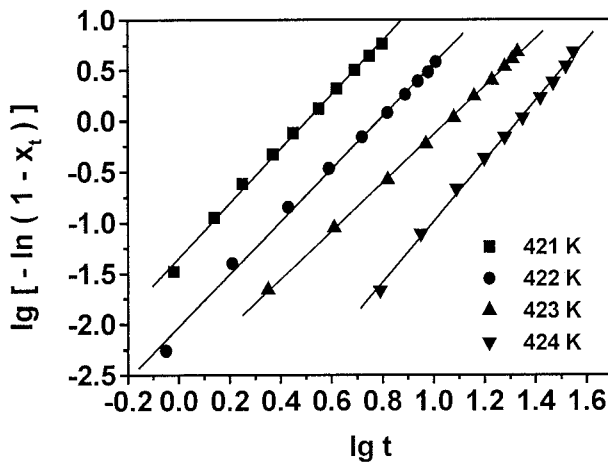
**Figure 8** Avrami plots of the isothermal crystallization data of virgin POM.
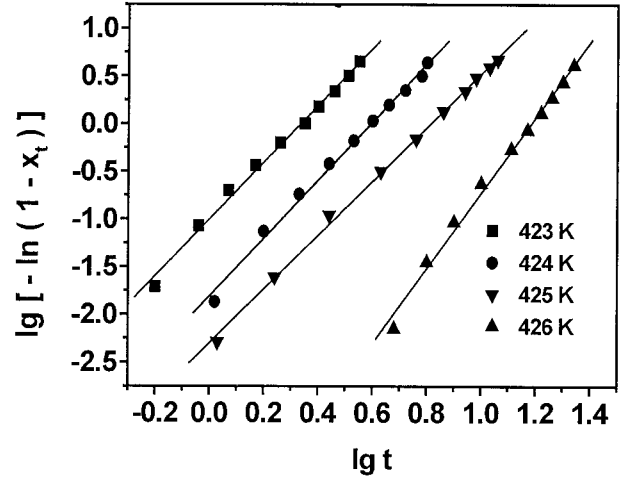
Figure 9 Avrami plots of the isothermal crystallization data of POM with attapulgite.

where ΔE is an activation energy associated with the crystallization process and k_0 is a pre-exponential constant, the logarithmic plots of $(1/n)\ln k$ as a function of $1/T$ are showed in Figure 11 for both POM without and with nucleating agent. The good fitting linear straight lines allow estimation of the activation energy and pre-exponential constant and they are: $\Delta E = -971.7$ kJ/mol, $\ln k_0 = -280.4$; $\Delta E = -895.8$ kJ/mol, $\ln k_0 = -256.9$; and $\Delta E = -977.4$ kJ/mol, $\ln k_0 = -278.8$ for the virgin POM, POM with attapulgite, and POM with diatomite, respectively. These results show that the addition of attapulgite or diatomite affects the crystallization process of POM, and the different surface characteristic of

Figure 10 Avrami plots of the isothermal crystallization data of POM with diatomite.
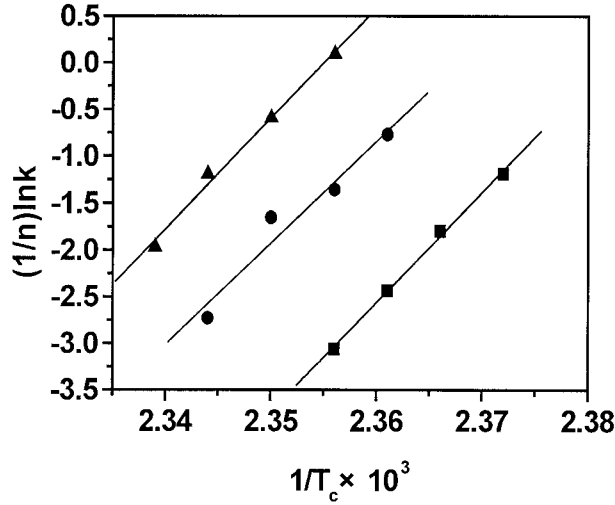
Figure 11   Plots of $(1/n)\ln k$ versus $1/T_c$ for POM. ■, virgin POM; ●, POM with attapulgite; ▲, POM with diatomite.

nucleating agent, attapulgite with groove structure, and diatomite with microvoid, leads to different ΔE values.

The parameter of t_p, the time corresponding to the maximum rate of crystallization, could be estimated from $t_p = [(n - 1)/nk]^{1/n}$ due to $d^2X_t/dt^2 = 0$ and read from thermograms directly. The t_p values of virgin POM, POM with nucleating agents of attapulgite and diatomite are also listed in Table I. The good agreement between the values calculated theoretically and the values obtained experimentally suggested that the crystalline behavior of either virgin POM or POM with nucleating agents of attapulgite and diatomite could be described by the Avrami equation quite well.

Crystallization Rate

The Avrami equation describes the whole crystallization behavior of polymers. To describe the growth rate of spherulites it would be better to use the Hoffman equation. As an extension of the Turnbull-Fisher expression for nucleation,[16] the growth rate of polymers:

$$G = G_0\exp\left\{-\frac{\Delta F_{WLF}}{RT_c}\right\}\exp\left\{-\frac{4b_0\sigma\sigma_e T_m^0}{k\Delta HT_c\Delta T}\right\} \quad (3)$$

where G is the growth rate, G_0 a constant, $\Delta F_{WLF} = C_1T_c/C_2 + (T_c - T_g)$, and $C_1 = 17.22$ kJ/mol, $C_2 = 51.6$ K, T_c crystallization temperature, k Boltzmann constant, b_0 the thickness of the surface

layer defined by the crystalline lattice parameters, σ and σ_e are interfacial free energies per unit area parallel and perpendicular, respectively, to the molecular chain direction, ΔH is the heat of fusion, T_m^0 the equilibrium melting point, and $\Delta T = T_m^0 - T_c$ is the undercooling.

Equation (3) describes the growth rate of the lamellar spherulites. The rate of overall crystallization would be expressed by the generalized eq. (4):

$$\frac{1}{n}\lg k(T) + \frac{\Delta F_{WLF}}{2.3RT_c} = A_n - \frac{K_gT_m^0}{2.3T_c\Delta T} \quad (4)$$

where $k(T)$ is the rate constant in the Avrami equation, $K_g = 4b_0\sigma\sigma_e/k\Delta H$, R the gas constant, A_n the constant which is the characteristic of the concentrations of heterogeneous nuclei.

Having used literature values, i.e., $T_g = 223$ K,[4] $T_m^0 = 456$ K,[7] $\Delta H = 3.55 \times 10^8$ J/m^3,[17] $\sigma = 0.0147$ J/m^2, $b_0 = 4.46 \times 10^{-10}$ m,[17] the experimental temperature dependence of the crystallization rate, plots of $[(1/n)\lg k(T) + \Delta F_{WLF}/2.3RT_c]$ vs $T_m^0/T_c\Delta T$, the results are shown in Figure 12. The straight lines were obtained and K_g could be estimated from the slope of the lines, therefore, σ_e were found to be 0.139 J/m^2, 0.121 J/m^2, and 0.123 J/m^2 for the virgin POM, POM with attapulgite, and POM with diatomite, respectively.

The σ_e value for virgin POM is 0.0955 J/m^2 reported by Pelzbauer and Galeski[4] and 0.205 J/m^2 determined by Rybnikař[18] from the dependence of the melting temperature of POM on the period of
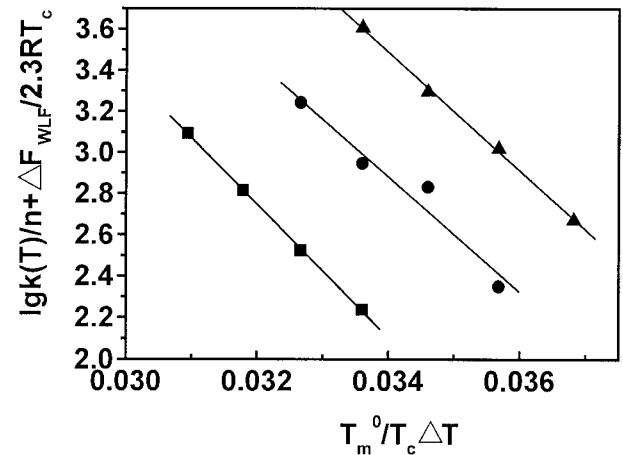
Figure 12   Plots of $\frac{1}{n}\lg k(T) + \frac{\Delta F_{WLF}}{2.3RT_c}$ against $\frac{T_m^0}{T_c\Delta T}$ for POM. ■, Virgin POM; ●, POM with attapulgite; ▲, POM with diatomite.

the small angle X-ray diffraction. The decrease in σ_e value for POM with nucleating agents suggests that the addition of attapulgite or diatomite increases the crystallization growth rate of POM.

CONCLUSION

The additives of attapulgite and diatomite with low cost and facileness could change the crystallization behavior of POM: increasing the crystalline rate k, decreasing the half-time of crystallization $t_{1/2}$ and interfacial free energies per unit area perpendicular σ_e, accelerating the crystallization rate. The POM with attapulgite or diatomite may meet the requirement of fine injection molding.

The Avrami and Hoffman equations are quite able to describe the crystallization of POM with additives of attapulgite and diatomite. This report presents, for the first time, some crystallization parameters of the POM-attapulgite and POM-diatomite systems.

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