Non-isothermal Crystallization of Poly(ethylene-co-glycidyl methacrylate)/Silica Nanocomposites

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ABSTRACT: Nano-sized silica particles were modified by γ -aminopropyltriethoxysilane and the modified and unmodified silica particles were then respectively compounded with poly(ethylene-co-glycidyl methacrylate) (PEGMA) in a twin-screw extruder. Non-isothermal crystallization behaviors of neat PEGMA, PEGMA/unmodified silica (Silica), and PEGMA/modified silica (A-Silica) were studied by differential scanning calorimeter at various cooling rates. Modified Avrami model, Ozawa model, and Liu model all successfully described the non-isothermal crystallization processes of the samples. All these models predicted correctly that the crystallization rate follows the order: PEGMA/Silica > PEGMA/A-Silica > PEGMA. Calculated activation energies for the non-isothermal crystallization processes also indicated that the addition of silica accelerated the crystallization process of PEGMA, whereas the silica particles also retarded the crystallization process if well dispersed. [DOI 10.1295/polymj.37.418]

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The incorporation of an inorganic network into a polymer matrix has been extensively studied because it exhibits a wide range of multifunctional properties. Organic–inorganic nanocomposites could dramatically improve material properties because they frequently exhibit unexpected hybrid properties that are synergistically derived from the two components.^{1–5}

In comparison with neat polymers and microparticle composites, these improvements are achieved at low concentrations of the inorganic components (1–10 wt %); this contrasts strongly with conventional filled polymers, which generally require high loadings within the range of 25–40 wt %. The control of morphology and phase separation is critical in the preparation and application of organic/inorganic hybrid composites. The introduction of well-dispersed and nanoscale size inorganic domains into a polymer matrix and the control of compatibility between organic and inorganic interphases will result in the maximum effectiveness in a given hybrid composite. The tendency of nanoparticles to agglomerate makes the preparation of polymer-based nanocomposites difficult with the processing techniques common to conventional plastics. Researchers have attempted many specific routes to break down nanoparticle agglomerates and to produce nanostructured composites.^{6–12}

The properties of nanocomposites strongly depend on the organic matrix, nanoparticles, and the way in

which they were prepared. Chemical surface modification is widely used to obtain a high wettability for a solid surface, a good dispersion of particles, and adhesion of fillers in composite materials.¹³

In crystalline thermoplastics, the crystalline morphology and the degree of crystallinity are the most important variables in determining mechanical and physical properties of the final products. The crystallization of these polymers is often influenced not only by processing conditions, but also by the presence of the reinforcing phases.

Research on the polymer crystallization process is limited to idealized conditions such as isothermal crystallization with constant external conditions; therefore, the theoretical analysis is relatively easy, and the problems concerning cooling rates and thermal gradients within the specimens can be avoided. Practically, however, the crystallization in a continuously varying environment is of great interest because industrial processes generally proceed under non-isothermal conditions. In our previous work,¹⁴ γ -aminopropyltriethoxysilane (APTS) was used to modify the nano-sized silica particles (A-Silica) and poly(ethylene-co-glycidyl methacrylate) (PEGMA)/A-silica nanocomposite (PEGMA/A-Silica) *via* melt-direct intercalation was successfully prepared. The dispersion, morphology and isothermal crystallization kinetics had been also studied. In this article, non-isother-

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mal crystallization of PEGMA, PEGMA/Silica and PEGMA/A-Silica nanocomposite were studied by DSC and several nonisothermal crystallization models were used to describe the crystallization process. In addition, the activation energies of crystallization were also estimated by Augis–Bennett model, Kissinger model and Takhor model.

EXPERIMENTAL

Materials

Commercial grade PEGMA (trade name: CG5004) was supplied by Sumitomo Chemical Co., Ltd., containing 81 wt % ethylene and 19 wt % glycidyl methacrylate. Nano-silica (trade name: A-200) and γ -aminopropyltriethoxysilane (APTS) were purchased from Degussa. Tetrahydrofuran (THF) and triethylamine (TEA) were supplied from Aldrich. All materials were used as received without purification.

Preparation of PEGMA/Nano-Silica Composites

Detailed experimental process and characterizations have been described in our previous articles¹⁴ and are only briefly outlined as follows: To 10 g nano-sized silica and 0.5 g TEA diluted in 2 g water were stirred in 100 g THF for 1 h and then 1 g APTS was added. The mixture was sonicated for 2 h. The modified silica (A-Silica) was separated using a centrifuge and dried at 50 °C under vacuum for 6 h.¹⁵

PEGMA was compounded respectively with 3 wt % unmodified and modified silica (A-Silica) in a twin-screw extruder (Continent Machinery Company, Model CM-MTE) at 150 °C and 300 rpm to prepare nanocomposites PEGMA/Silica and PEGMA/A-Silica. All materials were dried in a vacuum oven at room temperature for six hours before compounding.

The modified silica was identified by solid-state ¹³C and ²⁹Si MAS NMR, and the dispersion of unmodified and modified silica in PEGMA were observed by transmission electron microscope. A-Silica particles were well dispersed in PEGMA (PEGMA/A-Silica) with particles size *ca.* 25 nm, but unmodified silica particles exhibited aggregation in the matrix (PEGMA/Silica).

Characterizations

Non-isothermal Crystallization. The non-isothermal crystallization behaviors of polymer blends were investigated with a differential scanning calorimeter, PerkinElmer DSC-1. The differential scanning calorimeter was calibrated using indium with samples weights of 8–10 mg. All operations were carried out in a nitrogen atmosphere. Before the data gathering, the samples were heated to 120 °C and held in the molten state for five minutes to eliminate the influence

of thermal history. The sample melts were then subsequently cooled to 35 °C at a cooling rate of 4, 5, 8, 10, 12 and 14 K/min.

RESULTS AND DISCUSSION

The crystallization processes of PEGMA, PEGMA/Silica and PEGMA/A-Silica nanocomposite were measured at a range of cooling rates from 4 to 14 K/min. The DSC curves of the samples were compared in Figures 1a, b and c. The cooling rate dependence of the onset (T_o) and peak (T_p) of the crystallization exotherms were shown in Table I. In all samples, the T_o and T_p shifted to lower temperature with increasing cooling rate; the shifting indicated the slower the cooling rate, the earlier the crystallization started. For a given cooling rate, T_o and T_p for both PEGMA/Silica and PEGMA/A-Silica were higher than those of neat PEGMA because silica acted as nucleating agent and PEGMA/silica systems started to crystallize earlier. The T_o of PEGMA/A-Silica was slightly higher than that of PEGMA/Silica due to the fact that the modified silica (A-Silica) were better dispersed in the PEGMA matrix¹⁴ resulting in more abundant nuclei than the silica without modification.

Relative crystallinity (X_T) as a function of temperature was calculated as the ratio of the exothermic peak areas.^{15–17}

$$X_T = \frac{\int_{T_o}^T \left[\frac{dH_c}{dT} \right] dT}{\int_{T_o}^{T_\infty} \left[\frac{dH_c}{dT} \right] dT} \quad (1)$$

where T is an arbitrary temperature, dH_c is the enthalpy of crystallization released during an infinitesimal temperature interval dT . Figures 2a, b and c present the relative crystallinity (X_T) as a function of temperature for PEGMA, PEGMA/Silica and PEGMA/A-Silica nanocomposites. During the non-isothermal crystallization process, the time (t) and temperature exhibit the following relationship:

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

where Φ is cooling rate. The abscissa of temperature in Figures 2a, b and c could be transformed into a timescale. The relative crystallinity of PEGMA, PEGMA/Silica and PEGMA/A-Silica as a function of time were illustrated in Figures 3a, b and c. At higher cooling rate, less time was available to complete the crystallization.

Half-time ($t_{1/2}$) of the non-isothermal crystallization can be obtained with the following relationship:

(a)

(b)

(c)

Figure 1. DSC nonisothermal measurement curves for PEGMA, PEGMA/Silica and PEGMA/A-Silica nanocomposite: (a) PEGMA, (b) PEGMA/Silica, and (c) PEGMA/A-Silica.

$$t_{1/2} = |T_0 - T_{1/2}|/\Phi \quad (3)$$

where $T_{1/2}$ is the temperature at which $X_t = 50\%$ and Φ is the cooling rate. Table I also shows the $t_{1/2}$ for PEGMA, PEGMA/Silica and PEGMA/A-Silica. The

(a)

(b)

(c)

Figure 2. Experimental relative crystallinity as a function of temperature at different cooling rate: (a) PEGMA, (b) PEGMA/Silica, and (c) PEGMA/A-Silica.

inverse value of $t_{1/2}$ (*i.e.*, $1/t_{1/2}$) signifies the bulk crystallization rate and a higher $t_{1/2}$ value (*i.e.*, lower $1/t_{1/2}$ value) indicates slower crystallization. The $t_{1/2}$ value decreased with increasing cooling rate indicating the polymer crystallized faster when the cooling

Table I. Characteristic data of non-isothermal melt crystallization exotherms for PEGMA and PEGMA/Silica and PEGMA/A-Silica

Cooling Rate, Φ (K/min)	PEGMA			PEGMA/Silica			PEGMA/A-Silica		
	T_o (K)	T_p (K)	$t_{1/2}$ (min)	T_o (K)	T_p (K)	$t_{1/2}$ (min)	T_o (K)	T_p (K)	$t_{1/2}$ (min)
4	350.9	345.9	1.16	355.4	351.0	1.01	356.6	351.8	1.11
5	349.6	345.1	0.87	355.0	350.4	0.84	355.8	351.3	0.84
8	348.5	343.2	0.63	353.3	349.5	0.46	354.8	350.6	0.52
10	347.7	342.0	0.53	352.9	348.6	0.40	354.3	349.9	0.42
12	346.7	341.4	0.44	352.2	348.1	0.34	353.7	349.4	0.36
14	345.6	340.8	0.34	351.8	347.3	0.28	353.2	348.8	0.32

rate was increased. At a given cooling rate, the value of $t_{1/2}$ for neat PEGMA was higher than those for PEGMA/Silica and PEGMA/A-Silica suggesting that the addition of silica increased the overall crystallization process. The $t_{1/2}$ for PEGMA/A-Silica was higher than that for PEGMA/Silica. The overall crystallization rate is governed by nucleation and diffusion.¹⁸ Nano-sized silica particles acted as nucleating agent to increase the nucleation rate, onset and peak temperature as mentioned earlier; however, the silica also hindered the crystallization under non-isothermal conditions by slowing down the diffusion of PEGMA chains.^{19–22} Comparing with PEGMA/Silica, the PEGMA/A-Silica had better dispersed A-Silica¹⁴ to act as nucleating agent to increase crystallization rate; at the same time, the well-dispersed A-Silica also reduced the diffusion process and decreased the crystallization rate.

A crystallization rate parameter (CRP), determined from the slope of a line drawn through a plot of $1/t_{1/2}$ versus the cooling rate has been proposed to quantitatively compare non-isothermal crystallization rate.^{23,24} A higher slope indicates faster rate. Figure 4 shows plots of $1/t_{1/2}$ as a function of cooling rate. The CRP values for neat PEGMA, PEGMA/Silica and PEGMA/A-Silica were respectively 0.15, 0.26 and 0.23 K⁻¹ leading to the same conclusion that crystallization ability of the samples followed the order: PEGMA/Silica > PEGMA/A-Silica > PEGMA.

Avrami Model

Based on the assumption that the crystallization temperature is constant and the thermal lag between the sample and the furnace is kept minimal. Avrami equation^{24–34} can be used to describe the primary stage of nonisothermal crystallization. The Avrami equation is expressed as:

$$X_t = 1 - \exp(-(K_a t)^{n_a}) \quad (4)$$

where X_t is the relative crystallinity, t is crystallization time, K_a is the Avrami crystallization rate constant and n_a is the Avrami exponent. X_t can be calculated

as the ratio between the area of the exothermic peak at time t and the total measured area of crystallization. Values of K_a and n_a were found by fitting experimental data of X_t to eq 4 and the results were shown in Table II.

Avrami equation is usually written as following:

$$X_t = 1 - \exp(-k_a^* t^{n_a^*}) \quad (5a)$$

or

$$\ln[-\ln(1 - X_t)] = \ln k_a^* + n_a^* \ln t \quad (5b)$$

Values of n_a^* and k_a^* could be determined from the slope ($X_t = 0.1$ to 0.8) and intercept with the y axis by plotting $\ln[-\ln(1 - X_t)]$ versus $\ln(t)$ as shown in Figure 5 and the results were also shown in Table II for comparison. K_a is more preferable than k_a^* because it is independent of Avrami exponent and its dimension is given in (time⁻¹).^{35–37}

In nonisothermal crystallization K_a and n_a do not have the same physical significance as in the isothermal crystallization because temperature changes constantly under non-isothermal condition. This temperature changes affect the rate of both nuclei formation and spherulite growth. However, eq 4 provided a good fit to experimental data based on regression coefficient (R^2) as can be seen in Figure 3.

To meet requirement of Avrami model, Jeziorny³⁸ assumed constant or approximately constant cooling rate and proposed the final form of the parameter characterizing the kinetics of nonisothermal crystallization:

$$\ln K_J = \frac{\ln K_a}{\Phi} \quad (6)$$

The values of K_J were listed in Table II. K_J increased with increasing cooling rate for all samples. At same cooling rate, the K_J values of three samples followed the order: PEGMA/Silica > PEGMA/A-Silica > PEGMA indicating that nano-sized silica acted as nucleating agent to increase crystallization rate, but it also hindered the crystallization under non-isothermal conditions by slowing down the diffusion process as discussed earlier.

Figure 3. Experimental relative crystallinity as a function of time at different cooling rate: (a) PEGMA, (b) PEGMA/Silica, and (c) PEGMA/A-Silica.

Ozawa Model

Ozawa extended the Avrami theory from isothermal crystallization to the nonisothermal crystallization by assuming that crystallization occurs at a constant cooling rate and the model as following:^{39,40}

Figure 4. Plots of reciprocal half-time of crystallization as a function of cooling rate for PEGMA, PEGMA/Silica and PEGMA/A-Silica nanocomposite.

$$X_T = 1 - \exp \left[- \left(\frac{K_o}{\Phi} \right)^{n_o} \right] \quad (7)$$

Where K_o and n_o are Ozawa crystallization rate constant and Ozawa exponent, respectively. Figure 6 illustrates the plots of $\ln[-\ln(1 - X_t)]$ as a function of $\ln \Phi$ for a fixed temperature. The K_o and n_o could be estimated from the y-intercept [$(K_o = \exp(\text{y-intercept}/n_o))$] and slope. The Ozawa kinetic parameters as well as regression coefficient (R^2) were listed in Table III. Figure 6 and regression coefficient (R^2) listed in Table III showed that Ozawa model provided a satisfactory fit to the experimental data of both samples studied. Ozawa exponent n_o was found to range from 3.12 to 3.63 for neat PEGMA within 340–346 K, from 1.86 to 3.38 for PEGMA/Silica within 346–358 K and from 1.61 to 2.84 for PEGMA/A-Silica within 346–358 K. n_o increased with increasing crystallization temperature indicating the change of nucleation during the crystallization process.^{41,42} The Ozawa crystallization rate constant K_o was found to decrease with increasing temperature suggesting that PEGMA, PEGMA/Silica and PEGMA/A-Silica crystallized slower with increasing temperature.

Liu Model

Liu *et al.*⁴³ combined Avrami and Ozwa models to deal with the nonisothermal crystallization behavior and its form is given as follow:

$$\ln \Phi = \ln \left[\frac{K_o^{n_o}}{K_a^{n_a}} \right]^{1/n_o} - \frac{n_a}{n_o} \ln t \quad (8a)$$

$$F(T) = \left[\frac{K_o^{n_o}}{K_a^{n_a}} \right]^{1/n_o} \quad (8b)$$

$$a = \frac{n_a}{n_o} \quad (8c)$$

Table II. Avrami kinetics parameters

Sample	Cooling Rate, Φ (K/min)	n_a	K_a	K_J	$R^{2\ddagger}$	n_a^*	k_a^*	R^2
PEGMA	4	3.83	0.7901	0.9428	0.9993	3.55	0.4159	0.9972
	5	3.45	1.0535	1.0105	0.9994	3.21	0.8811	0.9974
	8	3.71	1.4436	1.0470	0.9995	3.47	3.4452	0.9974
	10	3.73	1.7254	1.0561	0.9995	3.50	6.5339	0.9974
	12	3.66	2.0923	1.0635	0.9996	3.47	12.6038	0.9977
	14	3.40	2.6100	1.0709	0.9997	3.27	22.6011	0.9983
PEGMA/Silica	4	3.16	0.8955	0.9728	0.9994	2.94	0.6975	0.9982
	5	3.26	1.0721	1.0140	0.9996	3.06	1.1975	0.9985
	8	2.92	1.9220	1.0851	0.9997	2.77	5.9807	0.9988
	10	3.06	2.2100	1.0825	0.9998	2.98	10.0779	0.9990
	12	3.08	2.6614	1.0850	0.9997	2.96	17.7770	0.9990
	14	3.26	3.1913	1.0864	0.9995	3.12	36.6801	0.9986
PEGMA/A-Silica	4	3.02	0.8004	0.9459	0.9997	2.89	0.5137	0.9995
	5	2.97	1.0551	1.0108	0.9997	2.83	1.1375	0.9995
	8	2.83	1.7037	1.0689	0.9999	2.77	4.3235	0.9997
	10	2.99	2.0961	1.0768	0.9998	2.91	8.4921	0.9997
	12	2.93	2.4468	1.0774	0.9999	2.89	13.4464	0.9998
	14	3.02	2.7593	1.0752	0.9999	2.98	26.4849	0.9999

$\ddagger R^2 = \frac{\sum (\hat{y}_i - \bar{y})^2}{\sum (y_i - \bar{y})^2}$; $\hat{y}_i$: predicted value, y_i : experimental value, $\bar{y}$: mean value R^2 is a measure of the proportion of variability explained by a sample of paired data. It is a number between zero and one and a value close to one suggests a good model.

Table III. Ozawa kinetics parameters

Sample	Temperature (K)	n_o	K_O	R^2
PEGMA	340	3.12	15.9822	0.9861
	342	3.19	9.8623	0.9928
	344	3.58	6.1812	0.9908
	346	3.62	3.8066	0.9984
PEGMA/Silica	346	1.86	22.1384	0.9704
	348	2.08	10.8706	0.9881
	350	2.63	5.4449	0.9663
	352	3.38	3.1920	0.9961
PEGMA/A-Silica	348	1.61	16.2938	0.9931
	350	1.82	6.7257	0.9411
	352	2.32	3.5703	0.9519
	354	2.84	1.9826	0.9848

Table IV. Value of $F(T)$ and a for PEGMA and PEGMA/Silica and PEGMA/A-Silica

Sample	X_t	$F(T)$	a	R^2
PEGMA	0.2	2.94	1.20	0.9794
	0.4	3.99	1.18	0.9819
	0.6	4.84	1.19	0.9857
	0.8	5.74	1.19	0.9991
PEGMA/Silica	0.2	2.42	0.96	0.9898
	0.4	3.61	0.96	0.9931
	0.6	4.45	0.97	0.9948
	0.8	5.26	0.98	0.9960
PEGMA/A-Silica	0.2	2.72	0.93	0.9976
	0.4	3.71	0.93	0.9981
	0.6	4.67	0.93	0.9984
	0.8	5.58	0.94	0.9985

Where the kinetic parameter, $F(T)$, refers to the value of the cooling rate chosen at the unit crystallization time when the measured system amounts to a certain degree of crystallinity; a is the ratio of Avrami exponent (n_a) to the Ozawa exponent (n_o). At a given degree of crystallinity, plotting $\ln \Phi$ versus $\ln t$ (Figure 7) yielded a linear relationship between $\ln \Phi$ and $\ln t$ and the values of $F(T)$ and a (Table IV) could be obtained from the slopes and intercepts of these lines respectively. The value of a varied from 1.18 to 1.19 for neat PEGMA, 0.96 to 0.98 for PEGMA/Silica and 0.93 to 0.94 for PEGMA/A-Silica. The value of $F(T)$ increased with increasing degree of crystallinity indi-

cating that at unit crystallization time, a higher cooling rate was required to reach a higher degree of crystallinity. At the same relative degree of crystallinity, the value of $F(T)$ for PEGMA was higher than those for PEGMA/Silica and PEGMA/A-Silica; that is, to reach the same relative degree of crystallinity, PEGMA required higher cooling rate, which indicated that PEGMA/Silica and PEGMA/A-Silica crystallized faster than neat PEGMA. According to the values of $F(T)$, the crystallization ability of samples also followed the order: PEGMA/Silica > PEGMA/A-Silica > PEGMA.

Figure 5. Avrami analysis from eq 5b for PEGMA, PEGMA/Silica and PEGMA/A-Silica nanocomposite: (a) PEGMA, (b) PEGMA/Silica, and (c) PEGMA/A-Silica.

Ziabicki Analysis

Ziabicki^{44–46} suggested that the kinetics of polymer phase transform can be described by a first-order kinetic equation:

$$\frac{dX_t}{dt} = K_z(1 - X_t) \quad (9)$$

Figure 6. Ozawa analysis based on the nonisothermal crystallization of PEGMA, PEGMA/Silica and PEGMA/A-Silica nanocomposite: (a) PEGMA, (b) PEGMA/Silica, and (c) PEGMA/A-Silica.

where X_t is the relative degree of crystallinity as a function of time and K_z is a temperature-dependent crystallization rate function. Ziabicki suggested a concept of kinetic crystallinity as follows:

Figure 7. Plots of $\ln \Phi$ vs. $\ln t$ for different relative degree of crystallinity for PEGMA, PEGMA/Silica and PEGMA/A-Silica nanocomposite: (a) PEGMA, (b) PEGMA/Silica, and (c) PEGMA/A-Silica.

$$G = \int_{T_g}^{T_m} K_z dT \quad (10)$$

The kinetic crystallizability, G , characterizes the de-

gree of crystallinity obtained when the polymer is cooled at unit cooling rate from the melting temperature (T_m) to the glass transition temperature (T_g). Jeziorny⁴⁷ derived a simple equation to calculate the kinetic crystallizability, G :

$$G = \int_{T_g}^{T_m} K_z dT = \left(\frac{\pi}{\ln 2} \right)^{1/2} K_{z,\max} \frac{D}{2} \quad (11)$$

where $K_{z,\max}$ is the value of K_z at the maximum crystallization rate, and D is the half-width of the crystallization curve.

In nonisothermal crystallization, crystallization rate function K_z is replaced with a derivation function of the relative crystallinity, $(dX/dT)_\Phi$, specific for each cooling rate. eq 10 is replaced by^{36,38}

$$G_\Phi = \int_{T_g}^{T_m} (dX/dT)_\Phi dT = \left(\frac{\pi}{\ln 2} \right)^{1/2} (dX/dT)_{\Phi,\max} \frac{D_\Phi}{2} \quad (12)$$

where $(dX/dT)_{\Phi,\max}$ is the maximum crystallization rate, and D_Φ is the half-width of the derivative relative crystallinity as a function of temperature. G_Φ is the kinetic crystallizability at an arbitrary cooling rate, Φ . Because of the effect of cooling rate, G_Φ must be corrected properly as follows:

$$G_c = \frac{G_\Phi}{\Phi} \quad (13)$$

After normalizing the effect of the cooling rate, the values of kinetic crystallizability at the unit cooling rate G_c are shown in Table V. Since the physical meaning of the G_c parameter is to characterize the ability of a polymer to crystallize when it is cooled from the melting temperature to the glass transition temperature at unit cooling rate, A higher G_c value indicated a more readily crystallized polymer. As shown in Table V, PEGMA had a lower G_c value indicating the neat PEGMA had lower crystallize rate. The results were similar to the other models discussed above.

Comparison of Kinetic Models

All these four models (Avrami, Ozawa, Liu, and Ziabicki) provided good fit to experimental data and the kinetic parameters from these models (K_j , K_o , $F(T)$ and G_c) predicted correctly that the crystallization rate followed the order: PEGMA/Silica > PEGMA/A-Silica > PEGMA at a given cooling rate. It is difficult, however, for Ozawa, Liu, and Ziabicki models to reconstruct the nonisothermal crystallization process with those kinetic parameters (*e.g.* Figure 3). Avrami model, on the other hand, has provided a simple method to describe a nonisothermal crystallization process although the physical meanings of its

Table V. Characteristic data of non-isothermal melt crystallization exotherms for PEGMA and PEGMA/Silica and PEGMA/A-Silica

Cooling Rate (K/min)	4	5	8	10	12	14
PEGMA						
D_{Φ} (K)	3.28	3.41	3.67	3.77	3.81	3.95
$(dX/dT)_{\Phi, \max}$	1.26	1.75	2.77	3.1	3.47	3.95
G_{Φ}	4.40	6.35	10.82	12.43	14.07	16.60
G_c	1.10	1.27	1.35	1.24	1.17	1.19
$T_{\max}$	345.96	345.05	343.09	342.02	341.32	340.65
PEGMA/Silica						
D_{Φ} (K)	3.65	3.64	3.58	3.67	3.67	3.50
$(dX/dT)_{\Phi, \max}$	1.68	2.09	3.39	4.10	4.94	6.13
G_{Φ}	6.53	8.07	12.93	16.01	19.31	22.86
G_c	1.63	1.61	1.62	1.60	1.61	1.63
$T_{\max}$	351.12	350.49	349.39	348.62	347.95	347.59
PEGMA/A-Silica						
D_{Φ} (K)	4.03	4.15	4.14	4.06	4.12	4.17
$(dX/dT)_{\Phi, \max}$	1.29	1.67	2.63	3.37	3.95	4.54
G_{Φ}	5.52	7.37	11.59	14.57	17.32	20.14
G_c	1.38	1.47	1.45	1.46	1.44	1.44
$T_{\max}$	352.02	351.43	350.67	349.99	349.32	348.80

kinetic parameters (K_a and n_a) are not yet clear. To be able to simulate a nonisothermal process is of great interest because industrial operations involve mostly nonisothermal crystallization. Avrami model, with the highest R^2 value, also provided the best fit among the four models.

Ozawa has extended the Avrami theory to a nonisothermal case by assuming a constant cooling rate when the sample is cooled from the molten state. Similar to the Avrami exponent, the Ozawa exponent depends on the nucleation and growth mechanisms. Ozawa treatment is essentially quasi-isothermal in nature. The X_T chosen at a given temperature include the values on the earliest stage as well as the values from the end stage of crystallization due to variation in the cooling rates. When the cooling rates vary in a wide range, the selected X_T values may have included secondary crystallization. Furthermore, nonisothermal crystallization is a dynamic process in which the crystallization rate is no longer constant but a function of time and cooling rate. Also, nucleation may be more complicated than that of isothermal crystallization. These factors have made the quasi-isothermal nature of Ozawa treatment somewhat questionable.

The practical meaning of the kinetic crystallizability G_c in Ziabicki treatment is to characterize the ability of a polymer to crystallize when it is cooled from the melting temperature to the glass transition temperature at a unit cooling rate. A higher G_c value indicates the polymer crystallizes more readily. It was found that kinetic crystallinities are different when they are calculated from different cooling rate. When

normalized with the cooling rate, however, the values of the kinetic crystallizability G_c at the unit cooling rate are comparable and are related only to the intrinsic composition of the samples. In the present study, the average G_c values were 1.22, 1.61 and 1.44 for PEGMA, PEGMA/Silica, and PEGMA/A-Silica, respectively.

Liu model combines Avrami and Ozawa models, where the physical meaning of the rate parameter $F(T)$ refers to the necessary value of cooling rate to reach a defined degree of crystallinity at unit crystallization time. The good linearity of the plots ($\ln R$ against $\ln t$) verifies the advantage of the combined approach applied.

Crystallization Activation Energy

In order to estimate the effective energy barrier (ΔE) for nonisothermal melt crystallization process, many models^{48–50} were proposed to estimate the crystallization activation energy from nonisothermal thermoanalytical investigations. Considering the variation of cooling rates and the peak temperatures (T_p) in the nonisothermal crystallization, the activation energy ΔE could be determined as following:

(1) Augis–Bennett model⁴⁸

$$\frac{d\{\ln[\Phi/(T_0 - T_p)]\}}{d(1/T_p)} = -\frac{\Delta E}{R} \quad (14)$$

(2) Kissinger model⁴⁹

$$\frac{d[\ln(\Phi/T_p^2)]}{d(1/T_p)} = -\frac{\Delta E}{R} \quad (15)$$

Figure 8. Determination of the crystallization activation energy for PEGMA, PEGMA/Silica and PEGMA/A-Silica nanocomposite: (a) PEGMA, (b) PEGMA/Silica, and (c) PEGMA/A-Silica.

(3) Takhor model⁵⁰

$$\frac{d[\ln(\Phi)]}{d(1/T_p)} = -\frac{\Delta E}{R} \quad (16)$$

Table VI. Crystallization activation energy ΔE (kJ/mole) calculated from Augis–Bennett, Kissinger and Takhor models

Samples	X_t	Augis–Bennett	Kissinger	Takhor
PEGMA	ΔE	−199.57	−254.57	−248.84
	R^2	0.8996	0.9979	0.9984
PEGMA/Silica	ΔE	−389.71	−377.36	−371.53
	R^2	0.9700	0.9819	0.9863
PEGMA/A-Silica	ΔE	−507.44	−471.13	−465.29
	R^2	0.9711	0.9731	0.9783

where R is the universal gas constant. Figure 8a, b and c show the plot of Augis–Bennett model, Kissinger model and Takhor model, respectively. The activation energy ΔE can be calculated from the slopes ($-\Delta E/R$) of these plots and the results are listed in Table VI. ΔE is the activation energy required to transport molecular segments to the crystallization surface. The activation energy of PEGMA/Silica and PEGMA/A-Silica were higher than that of neat PEGMA because the silica particles increased the viscosity of PEGMA, which prevents the PEGMA macromolecular chains from rearranging, and as a result, increased the activation energy. The value of ΔE for PEGMA/A-Silica was larger than that of PEGMA/Silica which indicated the well dispersed silica particles highly retarded the crystallization though they could be used as nucleating agent.⁵¹

CONCLUSIONS

The investigation of nonisothermal crystallization kinetics of neat PEGMA, PEGMA/Silica and PEGMA/A-Silica nanocomposite had been carried out by DSC. Results from the analyses of $t_{1/2}$, CRP, modified Avrami model by Jeziorny, Ozawa mode, Liu model, and Ziabicki's model all showed that the crystallization rate followed the order: PEGMA/Silica > PEGMA/A-Silica > PEGMA at a given cooling rate. The energy barrier governing the nonisothermal melt-crystallization calculated from Augis–Bennett model, Kissinger model, and Takhor model showed that A-Silica acted as nucleating agent to increase crystallization rate; at the same time, the well-dispersed A-Silica also reduced the diffusion process and decreased the crystallization rate.

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