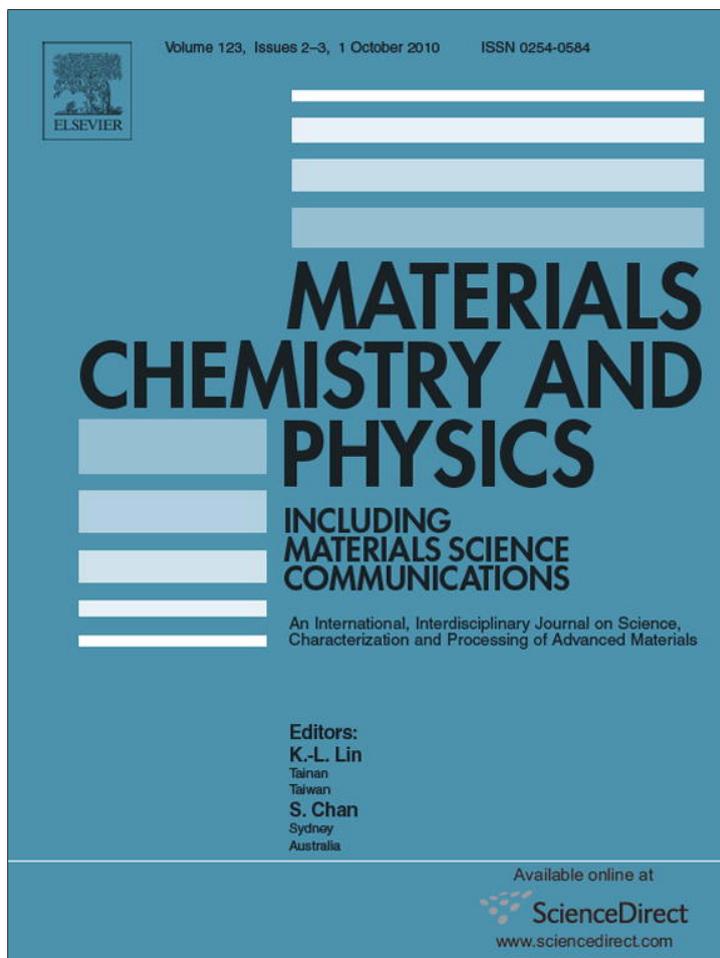


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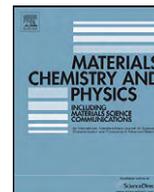
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On the crystallization behavior of the nano-silica filled PEEK composites

M.C. Kuo^{a,*}, J.S. Kuo^a, M.H. Yang^a, J.C. Huang^b^a Department of Polymer Materials, Kun Shan University, Tainan 700, Taiwan, ROC^b Institute of Materials Science and Engineering, Center for Nanoscience and Nanotechnology, National Sun Yat-Sen University, Kaohsiung 804, Taiwan, ROC

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ABSTRACT

Differential scanning calorimetry (DSC) was applied to investigate the isothermal and non-isothermal crystallization behaviors of the nano-silica filled PEEK composites. The inclusion of the 15 nm silica particles would significantly decrease the crystallinity of the PEEK matrix by about 15% under isothermal crystallization. The nano-silica filled PEEK composites show the higher values of Avrami exponent n as compared to those of the neat PEEK at various temperatures, and the n value will increase with increasing silica content. Under non-isothermal crystallization, the crystallization peak temperature of the nano-silica filled PEEK composites will be lowered by 2–4 °C as compared with that of the neat PEEK. The crystallinity of the PEEK/SiO₂ nanocomposite will exhibit slightly lowered value with increasing nano-silica content, indicating that the inclusion of the nano-silica particles would decrease the mobility of the PEEK molecules. The Avrami exponent n will show a lower value as the cooling rate increases, but exhibit a higher value with increasing nano-silica content, suggesting that the smaller grain size in the PEEK matrix could be resulted in. The combined Avrami and Ozawa equation can well describe the crystallization behavior of the nano-silica filled PEEK composites under non-isothermal crystallization.

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1. Introduction

It is well known that the polymer composites can be fabricated by the incorporating of the inorganic reinforcements into the polymer matrices. During the past 20 years, there were many techniques proposed on the fabrication of the polymer nanocomposites, including melting processing with a twin screw extruder [1–4], compression molding [5–8], and in situ polymerization [9–12]. Through these processing methods, a tailor-made polymer nanocomposite could be successfully prepared.

Poly(ether ether ketone) (PEEK) is a semi-crystalline and high-performance engineering plastics with high glass transition and melting temperatures ($T_g = 143$ °C, $T_m = 340$ °C) [13]. Rae et al. proposed the detailed experimental results of PEEK 450G on the mechanical properties [14]. Hay and Kimmish conducted investigation on the isothermal crystallization of PEEK, and proposed that there are two crystallization processes occurrence during the isothermal crystallization of PEEK polymer [15]. The primary crystallization process with n value of 3 will contribute about 80% of the overall crystallization process, suggesting the heterogeneous nucleation of spherulites. The secondary process with n value of 1 will refer to the interlamellar growth. Furthermore, Jonas and

Legras reported the n value of the primary crystallization would range from 2 to 3.8 for PEEK [16]. Chen and coworkers conducted a clear-cut study on the origin of double melting peaks in PEEK 150P by using DSC and temperature-modulated DSC (TMDSC) [17]. From the TMDSC results, the exothermic behavior in the non-reversing curves supports the mechanism of melting–recrystallization when the crystallization temperature, T_c , is below 310 °C. Moreover, many studies were also performed on the neat PEEK about both isothermal and non-isothermal crystallization kinetics [18–21]. On the other hand, the studies on the isothermal [22–24] and non-isothermal [25] crystallizations of PEEK polymer filled by micro-scale reinforcements have been also proposed.

As mentioned above, there have been some research reports during the last two decades on the preparation and crystallization behavior of polymer nanocomposites, including isothermal and non-isothermal crystallization. Fornes and Paul have performed their investigations on the crystallization behavior of nylon 6/clay nanocomposites, and proposed that the relevant concentrations of clay are 3–5 wt% [26]. Clay loading below 1.6 wt% will dramatically increase the crystallization kinetics of the resulting nylon 6/clay nanocomposites. However, high clay contents would retard the crystallization behavior. Weng et al. carried out their investigations on the isothermal crystallization behavior of the nylon/foliated graphite nanocomposite with filler content of 1.5 wt%. It is found that the Avrami exponents n for the neat nylon 6 samples and the nylon/foliated graphite nanocomposites at the primary stage are centered about 3.2 and 1.2, respectively [27]. However, the n values

* Corresponding author. Tel.: +886 6 2050346; fax: +886 6 2050493.

E-mail addresses: muchen@mail.ksu.edu.tw, moochen@ms37.hinet.net (M.C. Kuo).

extracted from the non-isothermal DSC runs would reach 5.81 and 5.56 for the neat and the resulting nanocomposites, respectively, at a cooling rate of $5\text{ }^{\circ}\text{C min}^{-1}$. Moreover, a combined Avrami and Ozawa equation could properly describe the crystallization behavior of the two samples under non-isothermal crystallization.

Nanoparticle-filled PEEK composites have been successfully fabricated by means of compression molding process [5–8]. It is suggested that the majority of the nano-sized silica particles disperse semi-homogeneously in the PEEK matrix [8]. Accordingly, it is feasible to investigate the effect of nano-silica on the crystallization kinetic behavior of PEEK matrix. As stated above, there have been many studies conducted on the fabrication, physical properties, and the crystallization behavior of organic/inorganic polymeric hybrid composites. However, there is little research on the crystallization behavior of inorganic nano-filler reinforced PEEK composites.

We have conducted the investigations of the non-isothermal crystallization on the nano-alumina filled PEEK composites [28]. The contents of nano-alumina in the PEEK matrix were designated to be 0, 0.8, 1.6, 2.5, and 3.3 vol% (volume fraction), corresponding to 0, 2.5, 5.0, 7.5, and 10 wt% (weight fraction). In this previous paper, the effects of the nano-alumina on the non-isothermal crystallization kinetics and behavior of the PEEK/alumina composites are examined. It was found that inclusion of the nano-alumina could accelerate the nucleation rate due to heterogeneous nucleation but reduce the growth rate due to the retardation of polymer chain mobility. The higher values of Avrami exponent n and smaller grain size would be resulted in for the PEEK/alumina composites as compared to the neat PEEK polymer.

It is well known that the isothermal study is the most popular method to investigate the polymer crystallization kinetics. However, during practical industry polymer processing, the crystallization process of the polymer could proceed under both isothermal and non-isothermal conditions. Moreover, most of commercial polymer nanocomposites contain organic fillers less than 5 wt%. Therefore, in the present study, it is intentional to explore the effects of nano-silica, the most commonly used nanoparticles, on both the isothermal and non-isothermal crystallizations of the PEEK polymer with the filler content below 5 wt%. Also, the crystallization characteristics in the current PEEK/nano-silica and previous PEEK/nano-alumina composites under the non-isothermal or isothermal crystallization are compared.

2. Experimental

The PEEK powder (grade Victrex 150P, diameter $\sim 2\text{--}3\text{ mm}$) was purchased from the ICI Company, USA, and was further grinded into fine powders measuring $50\text{ }\mu\text{m}$. The density of PEEK polymer is 1.30 g cm^{-3} . The SiO_2 nanoparticles with diameter $\sim 15\text{ nm}$ and purity $\sim 99.9\%$ were purchased from the Plasmachem GmbH Company, Germany/Russian. The density of SiO_2 is 2.65 g cm^{-3} . The detailed procedures for the preparation of nano-silica filled PEEK composites have been described in the preceding paper [8]. The contents of the nano-silica in the PEEK matrix are designated as 0, 2.5, and 5.0 wt%.

A JEOL 3010 transmission electron microscope (TEM), operated at 150–200 kV, was used to estimate the nanoparticle dispersion condition in the PEEK matrix. In order to obtain a clear image during the TEM observation, the PEEK and PEEK/ SiO_2 thin foils were cut to about 50–70 nm in thickness by using the microtome diamond cut. The spherulite morphology of the PEEK polymer was observed using a ZEISS Axioskop-40 polarization optical microscope (POM). The PEEK polymer was heated to $410\text{ }^{\circ}\text{C}$ and held for 5 min to remove the previous thermal history, and then quenched to $290\text{ }^{\circ}\text{C}$ to determine the spherulite dimension.

The effects of the nano-silica particles on the crystallization behavior, both isothermal and non-isothermal crystallization, were investigated by a PerkinElmer differential scanning calorimeter (DSC Diamond). On the isothermal crystallization study, the neat PEEK and PEEK/ SiO_2 samples were heated to $410\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under nitrogen atmosphere, and held for 5 min to remove the previous thermal history. Subsequently, these samples were quenched to the designated temperatures of 260, 270, 280, 290, 300, and $310\text{ }^{\circ}\text{C}$ for 20 min to undergo isothermal crystallization. After isothermal crystallization, the samples were directly heated to $400\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ to undergo second heating run.

On non-isothermal crystallization investigation, the neat PEEK and PEEK/ SiO_2 samples were heated to $410\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ and held for 5 min.



Fig. 1. TEM micrographs showing the dispersion of the 15 nm silica particles in the PEEK matrix. The silica content in the PEEK matrix is 5.0 wt%.

Then, these samples were cooled from 410 to $50\text{ }^{\circ}\text{C}$ at various cooling rates of 2.5, 5, 10, 15, and $20\text{ }^{\circ}\text{C min}^{-1}$. After non-isothermal crystallization, the samples were directly heated to $400\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ to undergo second heating run.

3. Results and discussion

3.1. TEM observations

As shown in Fig. 1, the nano-silica particles are nearly spherical in shape. There are minor agglomerations of nano-silica with 8–12 particles aligned and clustering. However, most of the nano-silica particles in the PEEK matrix seem to disperse semi-homogeneously, showing 2–6 particles clustering and corresponding to the dispersive domains of 30–80 nm. Owing to this homogeneous dispersion and the nano-sized dispersion domains, it is feasible to investigate the crystallization kinetics under isothermal and non-isothermal conditions.

3.2. Isothermal crystallization

3.2.1. Isothermal crystallization behavior

It is well known that the isothermal crystallization investigation is the most popular method to explore the crystallization behavior of polymers. In the present study, the contents of nano-silica in the PEEK polymer are designated as 0, 2.5, and 5.0 wt%. The resulting PEEK/ SiO_2 composites were isothermally crystallized at the predetermined temperatures of 260, 270, 280, 290, 300, and $310\text{ }^{\circ}\text{C}$. Fig. 2 shows the DSC traces for samples crystallized isothermally at these temperatures. Furthermore, Fig. 3 shows the second heating melting thermograms. From Figs. 2 and 3, the crystallization enthalpies (ΔH_c), melting temperatures (T_m), melting enthalpies (ΔH_m), and peak crystallization times (τ_p) of neat PEEK and PEEK/ SiO_2 composites can be estimated. The absolute crystallinities (X_c) can also be estimated by relating to the heat of fusion of an infinitely thick

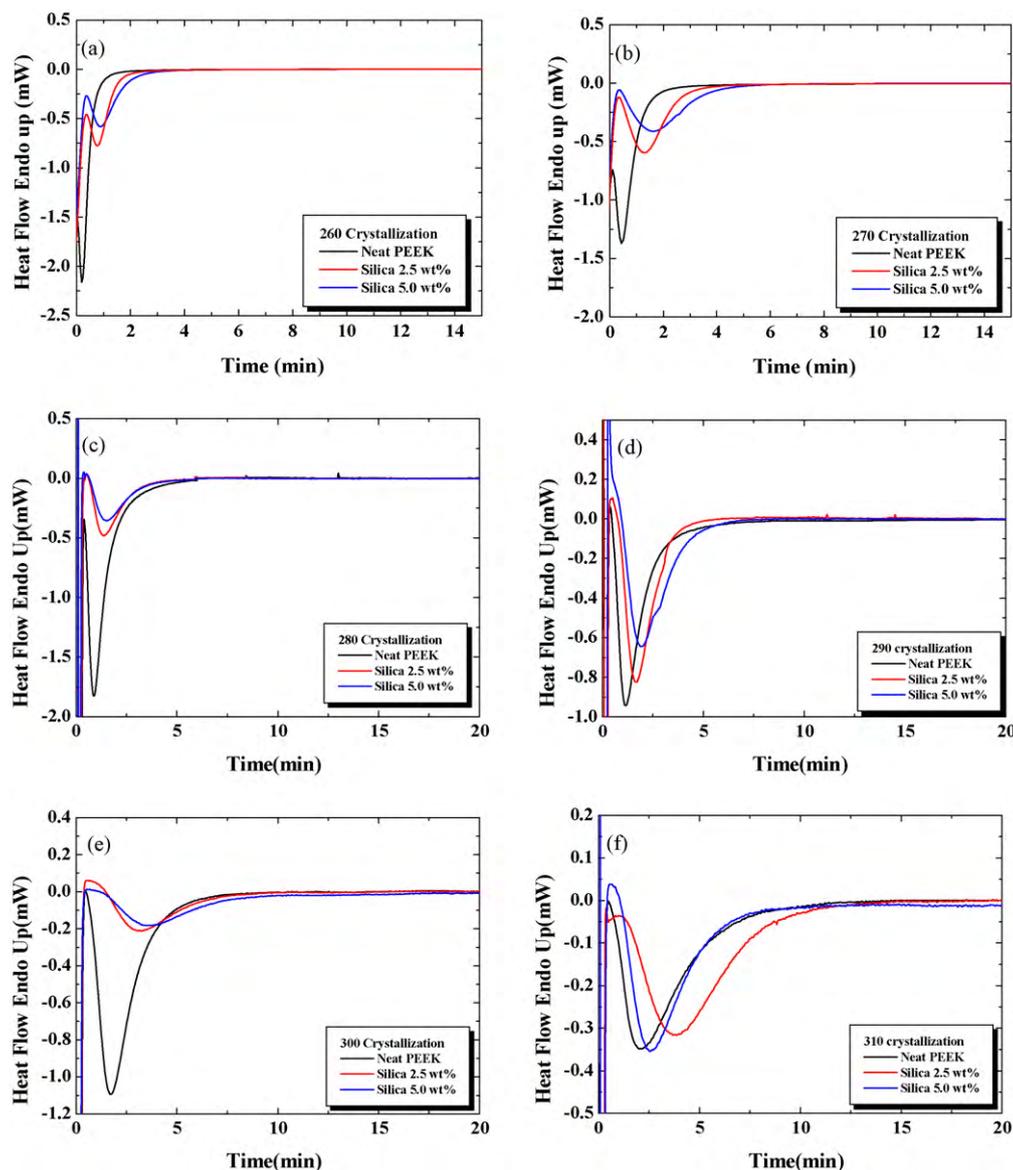


Fig. 2. Isothermal crystallization scans for neat PEEK and PEEK/SiO₂ composites. The isothermal crystallization time is 20 min, and (a)–(f) are neat PEEK and PEEK/SiO₂ isothermally crystallized at 260, 270, 280, 290, 300, and 310 °C, respectively.

PEEK crystal, ΔH_f° [29]:

$$X_c = \frac{\Delta H_c}{\Delta H_f^\circ W_{polymer}} \times 100, \quad (1)$$

where ΔH_f° is $\sim 130 \text{ J g}^{-1}$ [30] and $W_{polymer}$ is the weight fraction of the polymer matrix. And the isothermal crystallization parameters were tabulated in Table 1.

As shown in Fig. 3 and Table 1, the sample crystallized isothermally at higher temperature would be accompanied by higher melting temperature and more time to complete the crystallization process. Polymer crystallized at lower temperature would result in larger span of supercooled temperature ($\Delta T = T_m - T_c$). T_c is the designated temperature of crystallization and in less time available to complete crystallization. Also, the exothermic peaks are found to be more flattened as the crystallization temperature shifts to higher. However, the exothermic peaks resulted from the nano-silica filled samples appear to be smaller than those of the neat PEEK polymer, reflecting the less crystallinity for the nano-silica filled PEEK composite. In Table 1, the neat PEEK exhibits the maximum crys-

tallinity of 37.8% at 290 °C, slightly lower than 41% reported by Jonas et al. for the PEEK 450G [31]. However, Chen and coworkers suggested that the absolute crystallinity of PEEK 150P would be about 37% [17]. In the present study, the samples crystallized isothermally at the predetermined temperatures show the crystallinities ranging from 14 to 38% and 9 to 23% for the neat PEEK 150P and the nano-silica filled PEEK composites, respectively. There is less investigation conducted for the isothermal crystallization of PEEK at temperatures below 280 °C. In the present study, the isothermal crystallization temperatures were designed to be 260, 270, 280, 290, 300, and 310 °C. The crystallinity from the total curve of DSC traces is between 8.6 and 37.5% for the specimens crystallized isothermally between 260 and 310 °C for 20 min. The maximum crystallinity is 37.5% for the neat PEEK crystallized at 290 °C, and the temperatures below or above 290 °C would bring into lower crystallinities. As shown in Table 1, the crystallinities resulted from crystallization temperatures below 290 °C are significantly lower than those of the specimens crystallized above 290 °C for both the neat and PEEK/Silica composites. Furthermore, the crystallinities for PEEK/Silica composites isothermally crystallized below 280 °C

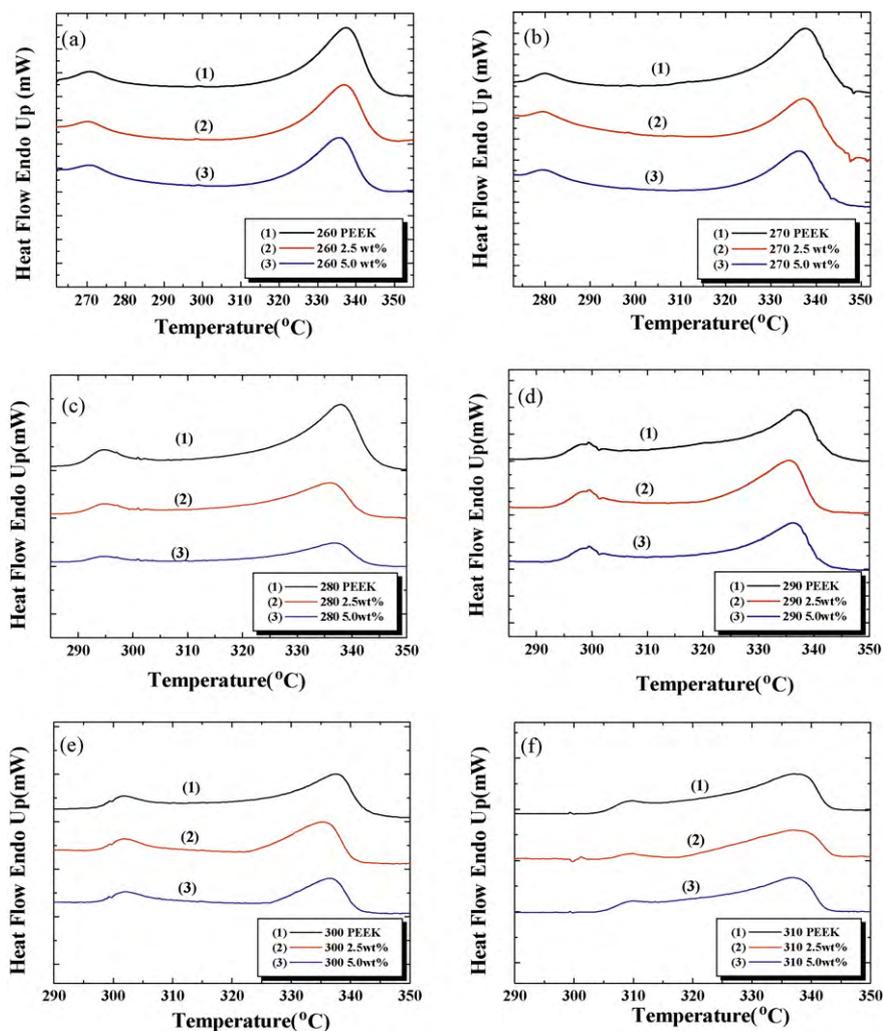


Fig. 3. The second heating scans for neat PEEK and PEEK/SiO₂ composites. (a)–(f) Neat PEEK and PEEK/SiO₂ isothermally crystallized at 260, 270, 280, 290, 300, and 310 °C, respectively.

range from 8.6 to 14.1%, as compared with the crystallinities ranging from 16 to 23% for PEEK/Silica composites crystallized above 280 °C. It is believed that the lower the crystallization temperature will greatly retard the mobility of the polymer molecules to

undergo crystallization process. It is obvious that the inclusion of the 15 nm silica particles would significantly decrease the crystallinity of the PEEK matrix. The inclusion of inorganic fillers would affect the crystallization behavior of the polymer molecules in two

Table 1
The lower melting temperatures (T_{m1}), upper melting temperatures (T_{m2}), crystallization enthalpies (ΔH_c), absolute crystallinities (X_c), and peak crystallization times (τ_p) of the neat PEEK and the 15 nm silica particles filled PEEK composites crystallized isothermally at 260, 270, 280, 290, 300, and 310 °C.

Sample	Crystallization temperature (°C)	T_{m1} (°C)	T_{m2} (°C)	$-\Delta H_c$ (J g ⁻¹)	X_c (%)	τ_p (min)
Neat PEEK	260	270.8	337.3	18.59	14.3	0.24
	270	280.1	337.7	23.53	18.1	0.44
	280	294.5	338.0	39.32	30.2	0.85
	290	299.4	337.5	48.72	37.5	1.18
	300	305.7	340.5	38.54	29.7	1.73
	310	315.0	342.7	36.71	28.2	2.10
SiO ₂ 2.5 wt%	260	270.0	336.8	13.31	10.5	0.79
	270	280.1	337.3	18.80	14.1	1.31
	280	294.5	336.2	26.79	21.1	1.4
	290	299.5	335.5	28.86	22.8	1.68
	300	305.7	337.8	26.10	20.6	3.17
	310	315.0	340.5	24.51	19.3	2.57
SiO ₂ 5.0 wt%	260	270.7	335.3	11.77	8.6	0.89
	270	279.3	336.5	15.60	11.4	1.47
	280	294.5	337.0	20.96	17.0	1.53
	290	299.5	336.0	24.57	19.9	1.93
	300	305.8	339.3	22.66	18.3	3.67
	310	315.0	340.5	19.10	15.5	3.85

ways: increases the crystallinity due to heterogeneous nucleation, or decreases the crystallinity due to mobility hindrance. The silica nanoparticles in the PEEK 150P might play the role of decreasing mobility of PEEK chain segments. As shown in Table 1, the incorporation of 15 nm silica particles apparently lowers the values of crystallinity by about 15%, as compared with those of the neat PEEK. PEEK/SiO₂ with nano-silica content of 5 wt% appears to be more mobility hindrance as compared with silica content 2.5 wt% because of the lower values of crystallinity for the former composite. Belfiore and coworkers suggested that the nano-sized zinc oxide (30–40 nm) could increase the exothermic enthalpy and crystallization temperature of isotactic polypropylene from the DSC cooling traces, i.e. the ZnO nanoparticles could promote the event of heterogeneous nucleation in the PP matrix [32]. It seems to be still dilemma that should the inorganic nanoparticles in the polymers promote or retard the process of crystallization. The peak crystallization times (τ_p) in Table 1 might convince that the more the nano-silica contents would, in turn, result in more times required to complete the crystallization process for the PEEK/SiO₂ nanocomposites. The mobility hindrance of the PEEK molecules during crystallization might be responsible for the increases in τ_p . In other words, the increase in mobility hindrance when silica nanoparticles incorporated into the PEEK polymer would be dominated during crystallization process.

Also shown in Table 1 are the lower and upper melting temperatures of neat PEEK and PEEK/SiO₂ nanocomposites. Both neat PEEK and nano-silica filled PEEK composites show double melting behavior. This phenomenon has been widely discussed [33–36]. In present study, the double melting behavior shows no change when the silica nanoparticles were incorporated. Note that the upper melting temperatures for the PEEK/SiO₂ nanocomposites are slightly lower than those of the neat PEEK. It is well known that the polymer crystallizing in the way of heterogeneous nucleation would impart the polymer matrix higher values of T_m and crystallinity [29,32]. The present study shows the opposite trend, and this opposite trend would convince that the incorporation of 15 nm silica particles might significantly and greatly lower the mobility of the PEEK molecules. On the other hand, because of less mobility hindrance, the neat PEEK could result in more perfect crystallites than those of the nano-silica filled PEEK composites, resulting in higher value of T_m .

3.2.2. Isothermal crystallization kinetics

The Avrami equation can well describe the isothermal crystallization behavior, as followed [37]:

$$1 - X_c(t) = \exp(-Kt^n), \quad (2)$$

$$\log[-\ln(1 - X_c(t))] = n \log t + \log K, \quad (3)$$

where $X_c(t)$ is the relative degree of crystallinity at time t . A plot of $\log[-\ln(1 - X_c(t))]$ versus $\log t$ will give the slope n , the Avrami exponent, and the intercept $\log K$, as shown in Fig. 4. Both the parameters of K and n are diagnostic of the crystallization mechanism [37]. Table 2 shows the kinetics parameters of neat PEEK and PEEK/SiO₂ nanocomposites. For neat PEEK 150P, the n values, ranging from 1.13 to 2.39, increase with the increasing of crystallization temperatures. It has been suggested that the crystallization behavior of neat PEEK 150P is a diffusion-controlled growth with a geometrical dimension of three [17]. The higher the crystallization temperatures would favor the rate of diffusion and result in higher value of Avrami exponent. The nano-silica filled PEEK composites show higher n values and lower K values as compared to those of the neat PEEK at different temperatures. Also, the increasing in filler content would result in slightly higher n values and in lower K values. The inclusion of nano-silica seems to make the crystallization dimension of PEEK polymer more complex because

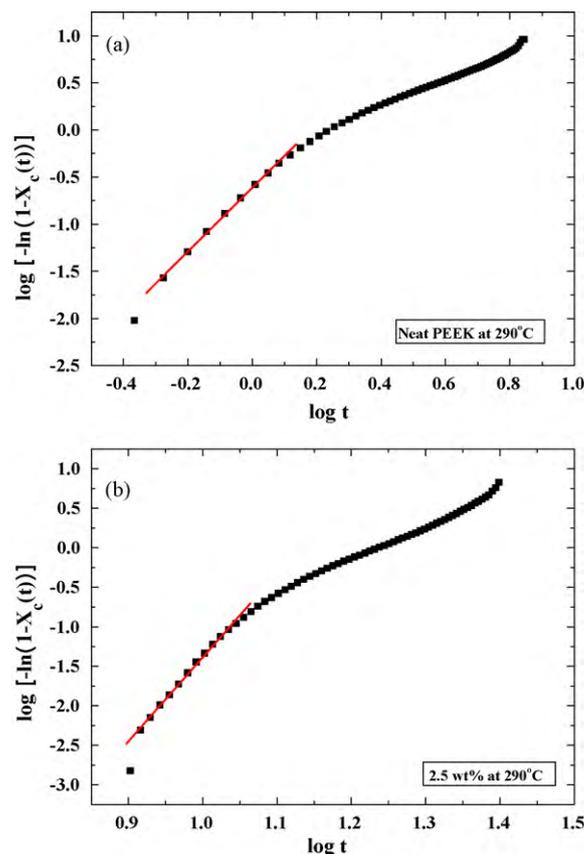


Fig. 4. The Avrami plots of PEEK composites crystallized isothermally at 290 °C: (a) neat PEEK and (b) 15 nm silica particles filled PEEK composite.

of the increasing of the n values. There is one possibility that the inclusion of 15 nm silica particles might impart the smaller grain size to the PEEK matrix. Fig. 5 shows the spherulite morphologies of the neat PEEK and 15 nm silica filled PEEK composites isothermally crystallized at 290 °C. The spherulite diameters for neat PEEK, 2.5 wt%, and 5.0 wt% PEEK/Silica composites are about 190, 140, and 100 μm , respectively. The inclusion of 15 nm silica particles would not only lower the crystallinity of the PEEK matrix, but also decrease the grain size of the PEEK polymer. It is plausible that the inclusion

Table 2

Kinetics parameters of the neat PEEK and the 15 nm silica particles filled PEEK composites crystallized isothermally at 260, 270, 280, 290, 300, and 310 °C.

Sample	Crystallization Temperature (°C)	n	$K \times 10^3$ (min ^{1/n})
Neat PEEK	260	1.13	522
	270	1.32	479
	280	1.99	408
	290	2.16	33
	300	2.31	0.77
	310	2.39	0.58
SiO ₂ 2.5 wt%	260	1.21	76
	270	1.69	54
	280	2.31	30
	290	2.40	6.69
	300	2.53	0.53
	310	2.70	0.33
SiO ₂ 5.0 wt%	260	1.43	58
	270	1.88	37
	280	2.55	23
	290	2.68	3.38
	300	2.76	0.33
	310	2.79	0.26

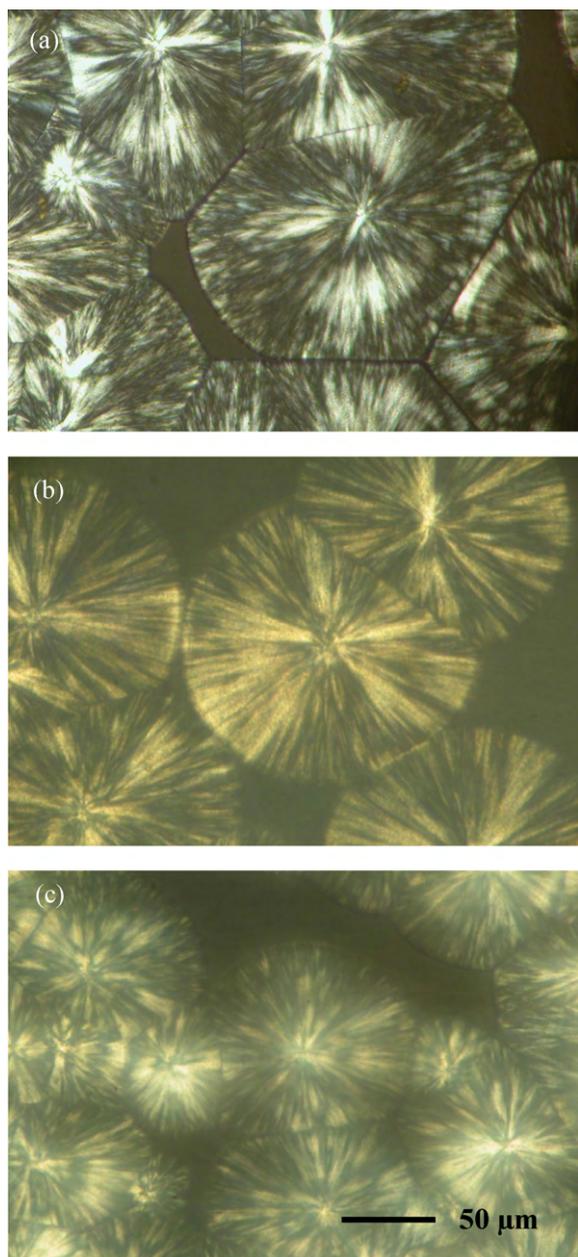


Fig. 5. The spherulite morphologies of neat PEEK and PEEK/SiO₂ composites isothermally crystallized at 290 °C. (a)–(c) Neat PEEK, 2.5 and 5.0 wt% nano-silica filled PEEK composites, respectively. The spherulite diameters for (a), (b), and (c) are about 190, 140, and 100 μm, respectively.

of 15 nm silica nanoparticles could make the PEEK molecules easier to nucleation but lower the grain size during the isothermal crystallization process.

3.3. Non-isothermal crystallization

3.3.1. Non-isothermal crystallization behavior

The crystallization onset, peak, and end temperatures, T_s , T_p , and T_e , for the neat PEEK and the nano-silica filled PEEK composites at various cooling rates are shown in Fig. 6 and Table 3. All the T_s , T_p , and T_e , shift to lower temperatures with increasing cooling rates for neat PEEK and nano-silica filled PEEK composites, indicating that the more supercooled region ($\Delta T = T_m - T_p$) is needed to activate the crystallization process as the cooling rate increases [29]. In addition, T_p shifts to lower temperature by about 2–4 °C with increasing

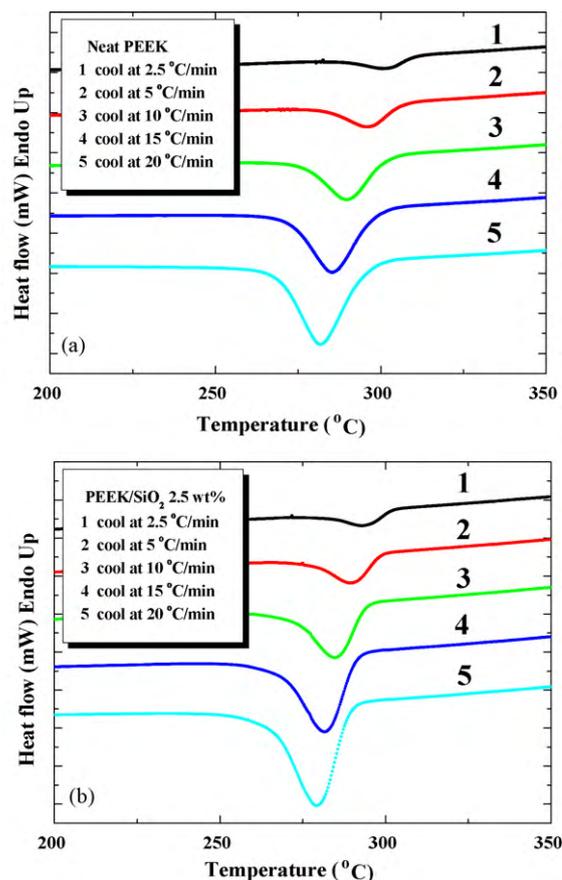


Fig. 6. Non-isothermal crystallization thermograms of the neat PEEK and the 15 nm silica particles filled PEEK composites at various cooling rates: (a) neat PEEK (b) 2.5 wt% 15 nm silica filled PEEK.

nano-silica content, as compared to that of the neat PEEK. Kim et al. reported that the T_p of the neat poly(ethylene 2,6-naphthalate) (PEN) would be higher than that of the nano-silica filled PEN composites for about 2–7 °C under non-isothermal crystallization [29]. They proposed that the PEN polymer should crystallize in way of heterogeneous nucleation. Anand et al. investigated the crystallization characteristics of melt compounded nanocomposites of poly(ethylene terephthalate) (PET) and single walled carbon nanotubes (SWNTs) [38]. It is indicated that at filler content of 3.0 wt% the crystallization temperature would be higher than that of the neat PET polymer by 10 °C under non-isothermal crystallization. However, Fornes and Paul suggested that the nylon 6/organoclay composites would exhibit a lowered T_p value as compared to that of the neat nylon 6 [26]. The current study seems to follow the Fornes' result.

As stated above, there are two major factors simultaneously affecting the crystallization behavior, i.e. the heterogeneous nucleation and mobility of the chain segments. If heterogeneous nucleation is the dominated during crystallization, T_p will shift to a higher value. Otherwise, polymer will crystallize at lower temperature due to the hindrance mobility of chain segments. The mobility of the chain segments seems to be the dominated in the present study. The inclusion of the nano-silica particles into the PEEK polymer would retard significantly the mobility of the polymer chains. Moreover, the polymer molecules crystallized at lower temperatures would result in more defects and smaller crystallites, and, in return, lower the melting temperature, T_m . As shown in Table 3, the melting temperature of the resulting PEEK nanocomposites is lower than that of neat PEEK by 2–4 °C, reflecting the more defects and smaller crystallites in the nano-silica filled PEEK matrix.

Table 3

Non-isothermal crystallization parameters of the neat PEEK and the 15 nm silica particles filled PEEK composites, obtained from the cooling DSC runs. T_m and T_p are measured from the second heating and first cooling runs, respectively. All the filler contents are in terms of wt%.

Sample	Cooling rate ($^{\circ}\text{C min}^{-1}$)	T_m ($^{\circ}\text{C}$)	T_s ($^{\circ}\text{C}$)	T_p ($^{\circ}\text{C}$)	T_e ($^{\circ}\text{C}$)	t_c (min)	$-\Delta H_c$ (J g^{-1})	X_c (%)
Neat PEEK	2.5	341	311	300	283	11.2	50.77	39.1
	5	340	306	296	279	5.4	49.30	37.9
	10	340	302	290	276	2.6	45.89	35.3
	15	340	298	288	272	1.7	44.43	34.2
	20	340	296	286	268	1.4	43.34	33.3
SiO ₂ 2.5%	2.5	340	304	298	286	7.2	49.31	38.9
	5	340	303	292	276	5.4	47.15	37.2
	10	340	298	287	271	2.7	43.98	34.7
	15	340	295	285	267	1.9	43.22	34.1
	20	339	292	282	264	1.4	42.33	33.4
SiO ₂ 5.0%	2.5	338	303	296	287	6.4	47.91	38.8
	5	338	301	290	277	4.8	45.81	37.1
	10	338	296	286	275	2.1	42.62	34.5
	15	338	290	283	271	1.3	41.37	33.5
	20	338	288	280	268	1.0	40.63	32.9

Under non-isothermal crystallization, the overall crystallization time, t_c , of the nano-silica filled PEEK polymer can be estimated as followed [29]:

$$t_c = \frac{T_s - T_e}{a}, \quad (4)$$

where a is the cooling rate. As shown in Table 3, the crystallization time will significantly decrease with increasing cooling rate, suggesting that there is less time available to develop the perfect crystallites as the cooling rate increases, that is, the inclusion of the nano-silica particles would make the crystallites of PEEK matrix becoming smaller and more defects. Moreover, the overall crystallization time of the PEEK matrix will also decrease as the nano-silica particles were introduced, indicating that the heterogeneous nucleation is still in work, but behaves minor effect.

According to Eq. (1), the absolute crystallinity fraction X_c at different cooling rates can be estimated, as shown in Table 3. The values of X_c decrease as the cooling rate increases, suggesting that the less available crystallization time could significantly inhibit the growth of the PEEK crystallites. As stated above, the less crystallization time would also result in smaller and more defects crystallites. Furthermore, the crystallinity, X_c , of the nano-silica filled PEEK matrix will be slightly less than that of the neat PEEK at the same cooling rate. It is obvious that inclusion of the nanoparticles would reduce the mobility of the PEEK chain segments, which would surpass the effect of heterogeneous nucleation. As for this major effect of mobility lowering, the values of T_m , T_p , and X_c reveal the opposite trend to the statement proposed by Kim et al., in which the effect of heterogeneous nucleation is dominated [29].

The nano-silica filled PEEK composites show the slightly higher values in crystallinity, as compared to those of the nano-alumina filled counterparts [28]. From the TEM photographs, the nano-silica particles are nearly spherical in shape, but the nano-alumina particles are irregular. It is reasonable that the spherical shape of the nano-silica is easier to climb and less mobility hindrance for the PEEK molecules during crystallization process. Accordingly, the higher values of T_m , T_p , and X_c might be resulted in for the nano-silica filled PEEK composites.

3.3.2. Non-isothermal crystallization kinetics

It was proposed that the values of the relative crystallinity at different cooling rates under non-isothermal crystallization could be estimated by the following equation [29],

$$X_c(T) = \frac{\int_{T_0}^T (dH_c/dT)dT}{\int_{T_0}^{T_\infty} (dH_c/dT)dT} = \frac{A_0}{A_\infty}, \quad (5)$$

where T_0 and T_∞ are the temperatures at which the crystallization starts ($X_c(T)=0$) and ends ($X_c(T)=1.0$). A_0 and A_∞ are areas under the normalized DSC curves. Under non-isothermal circumstance, the crystallization time, t , can be estimated from the corresponding temperatures by the following equation [29],

$$t = \frac{|T_0 - T|}{a}. \quad (6)$$

Using Eq. (6), the relative crystallinity, $X_c(T)$, can be expressed in terms of crystallization time, $X_c(t)$.

3.3.2.1. Modified Avrami equation. Under non-isothermal crystallization, Eqs. (2) and (3) should be modified to fit into the originally isothermal assumption of Avrami model, as follows [27]:

$$1 - X_c(t) = \exp(-Z_t t^n), \quad (7)$$

$$\log[-\ln(1 - X_c(t))] = n \log t + \log Z_t, \quad (8)$$

where Z_t is the rate constant under non-isothermal crystallization. By using Eq. (8), a plot of $\log[-\ln(1 - X_c(t))]$ versus $\log t$ will give the slope n , the Avrami exponent, and the intercept $\log Z_t$, as shown in Fig. 7. However, under non-isothermal condition, the value of the crystallization rate Z_c can be obtained from the following equation [29],

$$\log Z_c = \frac{\log Z_t}{a}. \quad (9)$$

Table 4 shows the Avrami parameters n and Z_c of neat PEEK and nano-silica filled PEEK composites under non-isothermal crystallization.

In Table 4, the n value decrease with increasing cooling rate, indicating that the less available in crystallization time will limit the growth of polymer spherulites and result in simpler geometry of spherulites, which will in turn result in the lower value of Avrami exponent. At the same cooling rate, the nano-silica filled PEEK shows a higher n value as compared with that of the neat PEEK polymer, accounting for that the dimension of the PEEK spherulite would be more complex when the nano-silica particles were introduced. According to Avrami isothermal crystallization theory, the polymer molecules crystallizing in sporadic manner will result in lower n value, as compared with that of the predetermined (heterogeneous nucleation) ones [37]. In present study, the n value of the nano-silica filled PEEK is higher than the neat PEEK polymer, suggesting the occurrence of the heterogeneous nucleation in the PEEK/SiO₂ composites. However, Kim et al. proposed that the n values will decrease from 4.0 to 3.0 when the nano-silica (7 nm) contents in PEN increase from null to 0.9 wt% at a cooling rate of

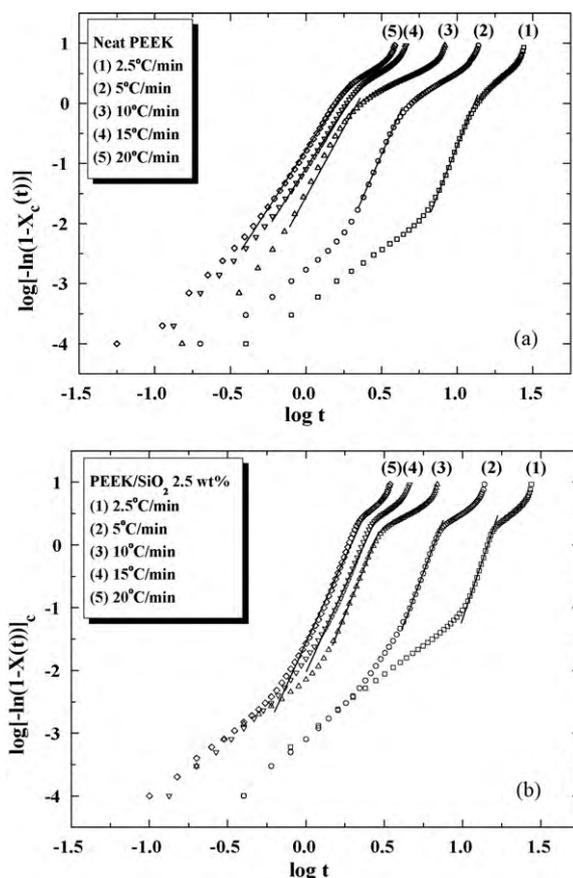


Fig. 7. Avrami plots of $\log[-\ln(1-X_c(t))]$ versus $\log t$ at various cooling rates under non-isothermal crystallization: (a) neat PEEK and (b) 2.5 wt% 15 nm silica filled PEEK.

2.5 °C min⁻¹ [29]. Kim has proposed that the melt viscosities of the PEN/SiO₂ composites were reduced by the incorporation of nano-silica, that is, the nano-silica particles would play a role of lubricant in the PEN matrix. Our current results indicate the opposite trend. Moreover, the inclusion of nano-silica shows the lowering effect on the growth rate constant Z_c of crystallization. The mobility hindrance of PEEK chain segments could be responsible for the Z_c lowering. However, the Z_c value would increase gradually with the increasing of the silica content, suggesting that the effect of heterogeneous nucleation could become predominant in higher silica

Table 4
Avrami exponent n and growth rate constant Z_c of the neat PEEK and the 15 nm silica particles filled PEEK composites under non-isothermal crystallization process.

Sample	Cooling rate (°C min ⁻¹)	n	$Z_c \times 10^3$
Neat PEEK	2.5	6.28	2.07
	5	5.75	229
	10	4.59	737
	15	4.00	849
	20	3.84	909
SiO ₂ 2.5%	2.5	7.08	0.28
	5	6.70	80
	10	5.79	500
	15	5.45	697
	20	4.92	813
SiO ₂ 5.0%	2.5	7.20	1.90
	5	6.92	171
	10	5.96	633
	15	5.54	711
	20	4.96	826

content. From the n and Z_c values, as shown in Table 4, it appears that the inclusion of 15 nm nano-silica into the PEEK matrix might decrease the mobility of PEEK chain segments due to less Z_c value, and in turn make the effect of heterogeneous nucleation in the PEEK matrix becoming less predominance due to higher n value but less crystallinity and smaller grain size.

As for the effect of the filler content on the Avrami parameters, the PEEK matrix with higher nano-silica content shows the higher n but lower Z_c values. The Z_c value hits a lowest value at silica content of 2.5 wt%, and then increases at 5.0 wt%. As stated above, the higher n value would imply the predominance of mobility hindrance during the process of crystallization. Accordingly, it would be accompanied with lower Z_c value. In the present study shows the higher n but lower Z_c values at nano-silica content of 2.5 wt% as compared with those of the neat PEEK. It seems to be contrary to the results proposed by Kim et al. in the consistency of n and Z_c values [29]. It seems to be impossible that a polymer crystallizes in higher mobility hindrance but fast rate for the comparison of 2.5 with 5.0 wt% on the n and Z_c values. The only possibility is that, as mentioned above, the PEEK chain segments crystallize in the manner of smaller grain size, as shown in Fig. 5. The increase in n value with the increasing of filler content would result in more nucleation sites but smaller grain size, and in turn brings into less value in the crystallinity.

The nano-silica filled PEEK composites show the lower values about 0.3–0.4 for the Avrami exponent n , as compared to those of the nano-alumina filled counterparts [28]. It is expected that the nano-alumina particles having the irregular shape would impart the more complexity in crystallization dimension during crystallization process as compared to the nano-silica filled counterparts. On the other hand, all the Z_c values of the nano-silica or nano-alumina [28] filled PEEK composites are less than that of the neat PEEK, indicating that no matter what the nano-fillers are introduced the net effect of the nano-filler inclusion would retard the mobility of the PEEK molecules.

3.3.2.2. Combined Avrami/Ozawa equation. Liu et al. [39] proposed a combined Avrami and Ozawa equation to describe the dynamic crystallization kinetics of polymers, as follows:

$$\log K + n \log t = \log K(T) - m \log a, \tag{10}$$

$$\log a = \log F(T) - b \log t, \tag{11}$$

where the parameters of $F(T)$ and b are equal to $[K(T)/Z_c]^{1/m}$ and n/m , respectively. The combined Avrami and Ozawa equation describes the relationship between the cooling rate a and the crystallization time t for a given crystallinity under dynamic crystallization. Theoretically, the physical meaning of $F(T)$ is the necessary value of cooling rate approaching to a given crystallinity at unit crystallization time [27]. A plot of $\log a$ against $\log t$ will give the slope and intercept of $-b$ and $\log F(T)$, respectively. In Fig. 8, all the plots show linear relationship between $\log a$ and $\log t$, suggesting that the combined Avrami and Ozawa equation could well define the non-isothermal crystallization behaviors of neat PEEK and nano-silica filled PEEK composites. It was proposed that the combined Avrami/Ozawa equation could successfully describe the non-isothermal crystallization kinetics for graphite-filled nylon 6 nanocomposites [27], silica nanoparticle-filled PEN [29], polypropylene/montmorillonite nanocomposites [40], nylon 11 [41] and polyoxymethylene/montmorillonite nanocomposites [42].

As shown in Table 5, the $\log F(T)$ values will increase with increasing relative crystallinities, indicating that the larger temperature gradient is needed as the relative crystallinity is increased. As for the inclusion of nano-silica on the $\log F(T)$ value, it is shown that the $\log F(T)$ value will decrease when the nano-silica parti-

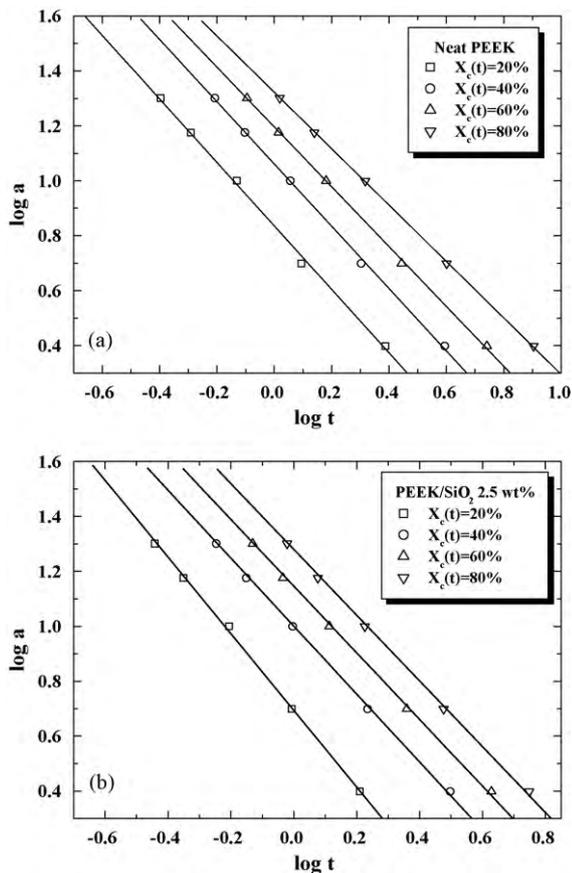


Fig. 8. Avrami–Ozawa plots of $\log a$ versus $\log t$ at various cooling rates under non-isothermal crystallization: (a) neat PEEK and (b) 2.5 wt% 15 nm silica filled PEEK.

cles were introduced. As described above, the physical meaning of $\log F(T)$ is the necessary cooling rate approaching to a given crystallinity at unit crystallization time. Accordingly, the higher value in $\log F(T)$ means the larger temperature span being needed for a given crystallinity at unit crystallization time. As shown in Table 3, the temperature span ($T_s - T_e$) for neat PEEK and nano-silica filled PEEK composites are 26–28 and 13–24 °C, respectively. There is one possibility for the difference of the temperature span: the larger span in temperature would be favor for the crystallization in larger grain size at given relative crystallinity. This effect is consistent with the previous statements, i.e. the inclusion of the nano-silica particles would reduce the grain size of the PEEK polymer. As for the effect of the filler content on the $\log F(T)$ value, it is obvious that there is no significant difference for the higher filler contents. The nano-sized silica possessing huge specific surface area would greatly retard the mobility at a filler of 2.5 wt%, so at higher filler content, such as 5.0 wt%, would do no significant reduction in crystallinity under non-isothermal crystallization.

Table 5
Avrami–Ozawa parameters of the neat PEEK and the 15 nm silica particles filled PEEK composites. All the filler contents are in terms of wt%.

Sample	Avrami–Ozawa parameter							
	$X_c(t)$ 20%		$X_c(t)$ 40%		$X_c(t)$ 60%		$X_c(t)$ 80%	
	b	$\log F(T)$	b	$\log F(T)$	b	$\log F(T)$	b	$\log F(T)$
Neat PEEK	1.160.84	1.13	1.06	1.08	1.20	1.02	1.32	
SiO ₂ 2.5%	1.400.69	1.24	1.00	1.21	1.15	1.20	1.28	
SiO ₂ 5.0%	0.980.82	0.96	1.00	0.91	1.15	0.92	1.29	

The $\log F(T)$ values of the nano-silica filled PEEK composites are higher than those of the nano-alumina counterparts [28]. As stated above, the physical meaning of $F(T)$ is the necessary value of cooling rate approaching to a given crystallinity at unit crystallization time. Accordingly, the higher values in $\log F(T)$ might account for the larger supercooled region ($\Delta T = T_m - T_p$) during non-isothermal crystallization process. The ΔT for the nano-silica and nano-alumina filled PEEK composites are 42–57 and 53–73 °C [28], respectively. The higher ΔT might be necessary for the more hindrance of mobility for the nano-alumina filled PEEK composites, as compared with that of the nano-silica filled counterparts.

4. Conclusions

In this paper, the crystallization behavior and kinetics under both isothermal and non-isothermal conditions of the 15 nm silica filled PEEK composites were investigated using DSC. The following conclusions are reached.

1. Most of the nano-silica particles in the PEEK matrix show 2–6 particles clustering, corresponding to the dispersion domains of 30–80 nm.
2. The inclusion of the 15 nm silica particles would significantly decrease the crystallinity of the PEEK matrix by about 15% under isothermal crystallization due to the mobility hindrance.
3. The peak crystallization times (τ_p) will increase with increasing the contents of nano-silica particles in the PEEK matrix.
4. The nano-silica filled PEEK composites show higher n values as compared to those of the neat PEEK at various temperatures, and the n value will increase with the increasing of silica content. The inclusion of nano-silica seems to make the crystallization dimension of PEEK polymer more complex.
5. The inclusion the nano-silica particles would result in smaller grain size of PEEK matrix as compared to that of the neat PEEK.
6. The crystallization onset, peak, and end temperatures, T_s , T_p , and T_e , will shift to lower temperatures as the cooling rates increase under non-isothermal crystallization. The T_p of the nano-silica filled PEEK composites will be lowered by 2–4 °C as compared with that of the neat PEEK, and the increase of the silica content will slightly decrease the T_p value.
7. The overall crystallization time, t_c , and the absolute crystallinity, X_c , of the PEEK/SiO₂ nanocomposite will be decreased as the cooling rate increases, as compared with those of the neat PEEK. The overall crystallization time will shift to a lower value as the silica content increases, implying that the higher silica content in the PEEK matrix will be easier to induce the occurrence of heterogeneous nucleation. On the other hand, the X_c value of the PEEK/SiO₂ nanocomposite will exhibit slightly lowered value with increasing nano-silica content, indicating that the inclusion of the nano-silica particles would lower the mobility of the PEEK molecules.
8. The Avrami exponent n will show a lower value as the cooling rate increases, but exhibit a higher value with increasing nano-silica content, suggesting that the smaller grain size in the PEEK matrix could be resulted in.
9. The combined Avrami and Ozawa equation can well describe the crystallization behavior of the nano-silica filled PEEK composites under non-isothermal crystallization.
10. As for the comparison of the non-isothermal crystallization behavior between the nano-silica and nano-alumina filled PEEK composites, the former seems to be less hindrance during non-isothermal crystallization process.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.matchemphys.2010.04.043.

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