

Isothermal Crystallization Behavior of Nano-Alumina Particles-Filled Poly(ether ether ketone) Composites

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ABSTRACT: The isothermal crystallization behavior of nano-alumina particle-filled poly(ether ether ketone) (PEEK) composites has been investigated using differential scanning calorimeter. The results show that all the neat PEEK and nano-alumina-filled PEEK composites exhibit the double-melting behavior under isothermal crystallization. The peak crystallization times (τ_p) for all the neat PEEK and PEEK/aluminum oxide (Al_2O_3) composites increase with increasing crystallization temperature. Moreover, the crystallinity of the PEEK/ Al_2O_3 composite with 7.5 wt % nano-filler content reached the maximum value of 44.8% at 290°C, higher than that of the neat PEEK polymer. From the lower value in τ_p and higher value in X_c for the PEEK/ Al_2O_3 composites, the inclusion of the nano-alumina into the PEEK matrix favored the occurrence of het-

erogeneous nucleation. The Avrami exponents n of all the neat PEEK and PEEK/ Al_2O_3 composites ranged from 2 to 3, and the n values for PEEK/ Al_2O_3 composites were slightly higher than that of the neat PEEK polymer, indicating that the inclusion of the nano-filler made the crystallization mechanism more complex. However, the growth rate of crystallization was lowered as the nano-filler was introduced, and the decrease in growth rate reduced the grain size of the PEEK spherulites because of the lowering of molecule mobility during isothermal crystallization. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 494–504, 2012

Key words: differential scanning calorimetry; high performance polymers; poly(ether ketones)

INTRODUCTION

The high-performance poly(ether ether ketone) (PEEK) polymer was first prepared by Bonner in 1962.¹ It is a derivative of poly(aryl ether ketones). PEEK is chemically recognized as a linear poly(aryl ether ketone) and is a melt-processable aromatic and semicrystalline polymer with high glass transition and melting temperatures ($T_g = 143^\circ\text{C}$, $T_m = 340^\circ\text{C}$).² It is well known that PEEK polymer is capable of providing numerous unique properties on temperature and solvent resistances. Except for the applications on the field of composites, PEEK can also be applied to the high-performance of microfiltration membranes.^{3,4} Nanoparticle-filled PEEK composites have been successfully fabricated through the compression-molding process.^{5–8} It was reported that the alumina nanoparticles are scattered individually in the PEEK matrix. There are also particles locally

clustering with three to six particles aligned together. Nevertheless, the majority of the nanoparticles were seen to disperse semihomogeneously in the PEEK matrix.⁹

The well-known and most popular approach to investigate the crystallization behavior of polymers is the isothermal crystallization technique. It is proposed that the thermal history of PEEK polymer can be completely eliminated by heating this polymer up to 400°C for 10 min.¹⁰ After this heating procedure, the investigations of the isothermal and nonisothermal crystallizations on PEEK polymer can be followed. Numerous reports on the isothermal^{11–16} and nonisothermal crystallization¹⁷ behaviors of PEEK have been proposed. Hay and Kemmish¹⁸ conducted their investigation on the isothermal crystallization of PEEK and proposed that two crystallization processes would occur during the isothermal crystallization of PEEK polymer. The primary crystallization process with Avrami exponent n value of 3 would contribute approximately 80% in crystallinity of the overall crystallization process, suggesting the heterogeneous nucleation of spherulites. The secondary process with n value of 1 would refer to the interlamellar growth. Velisaris and Seferis¹¹ conducted the study of crystallization kinetics of APC-2

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pregreg-reinforced PEEK 450P composites. They proposed that the first crystallization process would provide an Avrami exponent of 2.5 and an onset crystallization temperature of 320°C under nonisothermal crystallization. The second process exhibits an Avrami exponent of 1.5 and an onset crystallization temperature of 342°C. However, numerous studies have focused on the double-melting behavior of PEEK before two millenniums.^{12–15} Porter and co-workers^{13,14} proposed that the multimelting behavior of PEEK polymer is raised by the crystal reorganization. However, Marand et al.¹⁵ postulated that the high- and low-temperature endothermic regions are associated with the melting of primary and secondary crystals, respectively.

Fornes and Paul¹⁹ have conducted their investigation on the crystallization behavior of nylon 6/clay nanocomposites. It is shown that crystallization kinetics of the nanocomposites with clay contents below 1.6 wt % is dramatically increased when compared with that of the neat nylon 6 polymer. However, high clay loadings would retard the crystallization process. It is also proposed that nanocomposites containing commercially relevant concentrations of clay, that is, approximately 3–5 wt %, would have comparable crystallization times and temperature as the neat polyamide. Conversely, Belfiore and co-workers²⁰ suggested that the nano-sized zinc oxide (30–40 nm) could increase the exothermic enthalpy and crystallization temperature of isotactic polypropylene from the differential scanning calorimeter (DSC) cooling traces, that is, the ZnO nanoparticles could promote the event of heterogeneous nucleation in the polypropylene matrix. They concluded that the higher T_p from the DSC cooling traces could be attributed to the increase in specific surface area provided by zinc oxide nanoparticles, where the polymer chain segments would deposit on and crystallize.

As mentioned previously (in Refs. 10 to 15), numerous studies focused on the crystallization behavior of neat PEEK. However, little investigation was conducted on the micro-sized or even nano-sized particle-filled PEEK composite in the past decades. In our previous studies, the nano-alumina-filled or nano-silica particle-filled PEEK composites were successfully fabricated, and the transmission electron microscopy (TEM) micrographs show that the majority of the nanoparticles disperse semihomogeneously in the PEEK matrix.^{8,9} We have conducted the investigation of nonisothermal crystallization on the nano-alumina-filled PEEK composites.⁹ 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, 10 wt % (weight fraction). In this study, the effects of the

nano-alumina on the nonisothermal crystallization kinetics and behavior of the PEEK/aluminum oxide (Al_2O_3) composites were examined, and it was found that the inclusion of nano-sized alumina particles could enhance the effect of heterogeneous nucleation, but reduce the growth rate because of retarding polymer chain mobility.⁹

As mentioned previously, isothermal crystallization study is the most popular method to investigate the crystallization kinetics behavior of polymers. Hence, it is of basic interesting to explore the isothermal crystallization kinetics and melting behaviors of the nano-alumina particle-filled PEEK composites. In our previous study on the nonisothermal crystallization behavior of alumina nanoparticle-filled PEEK, we found that the onset crystallization temperatures ranged from 311 to 277°C for the cooling rates ranging from 2.5 to 20°C min⁻¹.⁹ As expected, the crystallization process usually proceeds under both isothermal and nonisothermal conditions. With this consideration, we wanted to know what could occur when the PEEK/alumina composites crystallized isothermally between 280 to 310°C. In this study, we investigated the isothermal crystallization behavior between 310 and 280°C on the PEEK/ Al_2O_3 composites using DSC, and our results showed how the alumina nanoparticles affect the isothermal crystallization behavior of PEEK polymer.

EXPERIMENTAL

The PEEK powders (grade Victrex 450G, diameter approximately 2–3 mm, Taiwan, Republic of China) were further grinded into fine powders measuring 50 μm . The density of PEEK polymer is about 1.30 g cm⁻³. The Al_2O_3 nanoparticle with diameter \sim 30 nm and purity \sim 99.9% was purchased from the Plasma-chem GmbH Company, Germany/Russian. The Al_2O_3 powder is basically irregular in shape. The density of Al_2O_3 is 3.98 g cm⁻³. The detailed procedures for the preparation of nano-alumina particles filled PEEK nanocomposites have been described in our previous article.⁸ In this study, the nano-alumina contents in the PEEK matrix are designed to be 2.5, 5.0, and 7.5 wt %.

A JEOL 3010 TEM, operated at 150–200 kV, was used to estimate the nanoparticle dispersion condition in the PEEK matrix. To obtain a clear image during the TEM observation, the PEEK and PEEK/ Al_2O_3 thin foils were cut to approximately 50–70 nm in thickness using the microtome diamond cut. The spherulite morphology of PEEK polymer was observed using a ZEISS Axioskop-40 polarization optical microscope (POM). The PEEK polymer was heated to 400°C and held for 10 min to remove the previous thermal history, and then quenched to 290°C to determine the spherulite dimension.

The effect of the nano-alumina particles on the isothermal crystallization behavior was investigated using Perkin-Elmer DSC (DSC Diamond). The weights of specimens used in the DSC scan are 4–5 mg. The neat PEEK and PEEK/Al₂O₃ composites samples were heated to 400°C at a heating rate of 10°C min⁻¹ under nitrogen atmosphere, and held for 10 min to remove the previous thermal history. Subsequently, these samples were quenched to the predetermined temperatures of 280, 290, 300, and 310°C for 60 min to undergo isothermal crystallization. After isothermal crystallization, the specimens were immediately subjected to a heating scan from the predetermined crystallization temperatures to 380°C at 10°C min⁻¹ to study the melting behavior.

RESULTS AND DISCUSSION

TEM observations

Figure 1 shows the TEM micrographs of 2.5 and 5.0 wt % nano-alumina-filled PEEK composites. The shape of the alumina particle is basically irregular. The domains of most nano-alumina particles in PEEK matrix range from 30 to 180 nm, accordingly, and we described such dispersion as semihomogeneous dispersion. There are particles locally clustering with five to seven particles aligned together; however, the majority of the nanoparticles would cluster with two to four particles in the PEEK matrix, corresponding to the major filler domain being less than 120 nm. Under this condition, we investigated the isothermal crystallization behavior of PEEK/Al₂O₃ composites and explored the difference between neat PEEK and the nano-alumina-filled PEEK composite under isothermal crystallization.

Isothermal crystallization behavior

As mentioned previously, numerous studies have been conducted on the isothermal or nonisothermal crystallization behavior of the neat PEEK polymer. However, few studies have been performed on the microsized or nano-sized particle-filled PEEK composite. We conducted the nonisothermal crystallization investigation on the nano-alumina-filled PEEK composites.⁹ In this study, the isothermal crystallization behavior of these composites was determined. Figure 2 shows the DSC isothermal crystallization traces for neat PEEK and PEEK/Al₂O₃ composites at the predetermined crystallization temperatures of 280, 290, 300, and 310°C. Furthermore, Figure 3 shows the heating traces from 50 to 380°C at 10°C min⁻¹ after isothermal crystallization. According to Figures 2 and 3, the crystallization enthalpies (ΔH_c), peak crystallization times (τ_p), high endotherm melting temperatures (T_m^{high}), and low endotherm melting

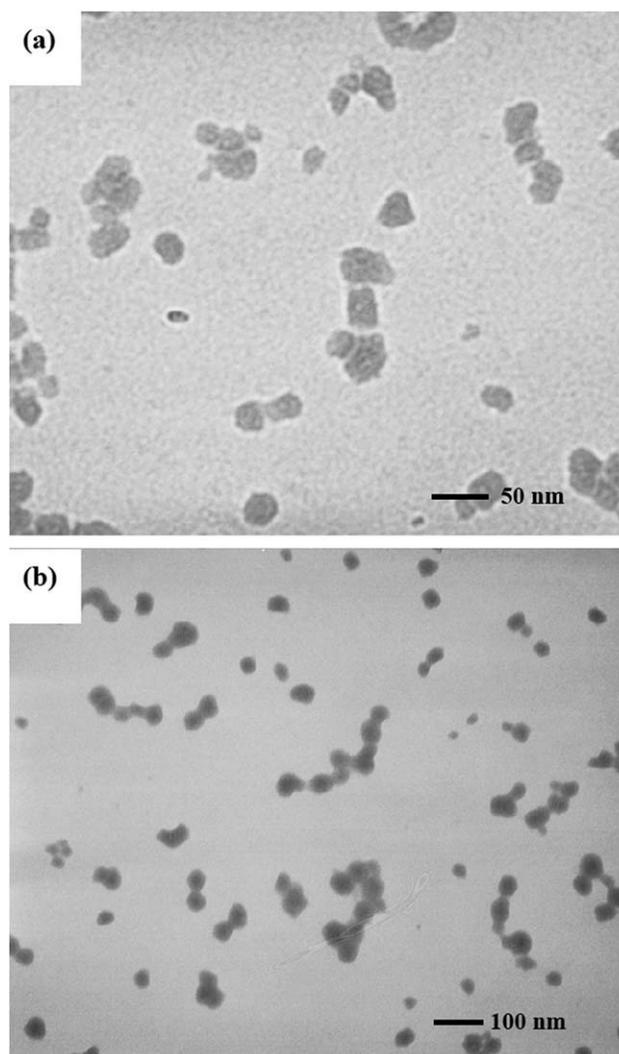


Figure 1 TEM micrograph showing the distribution of the nano-alumina particle in PEEK matrix: (a) alumina content 2.5 wt % (b) alumina content 5.0 wt %.

temperatures (T_m^{low}) of neat PEEK and PEEK/Al₂O₃ composites can be estimated. The absolute crystallinities of neat PEEK and PEEK/Al₂O₃ composites can be also estimated by relating to the heat of fusion of an infinitely thick PEEK crystal, ΔH_f^0 .²¹

$$X_c = \frac{\Delta H_c}{\Delta H_f^0 W_{\text{polymer}}} \times 100, \quad (1)$$

where ΔH_f^0 is $\sim 130 \text{ J g}^{-1}$,²² and W_{polymer} is the weight fraction of the polymer matrix. The isothermal crystallization parameters were tabulated in Table I.

As shown in Table I, the sample crystallized isothermally at a higher temperature would be associated with higher melting temperature and more time to complete the crystallization process because of the highly molecular mobility and more perfect crystals. Polymer crystallized at a lower temperature

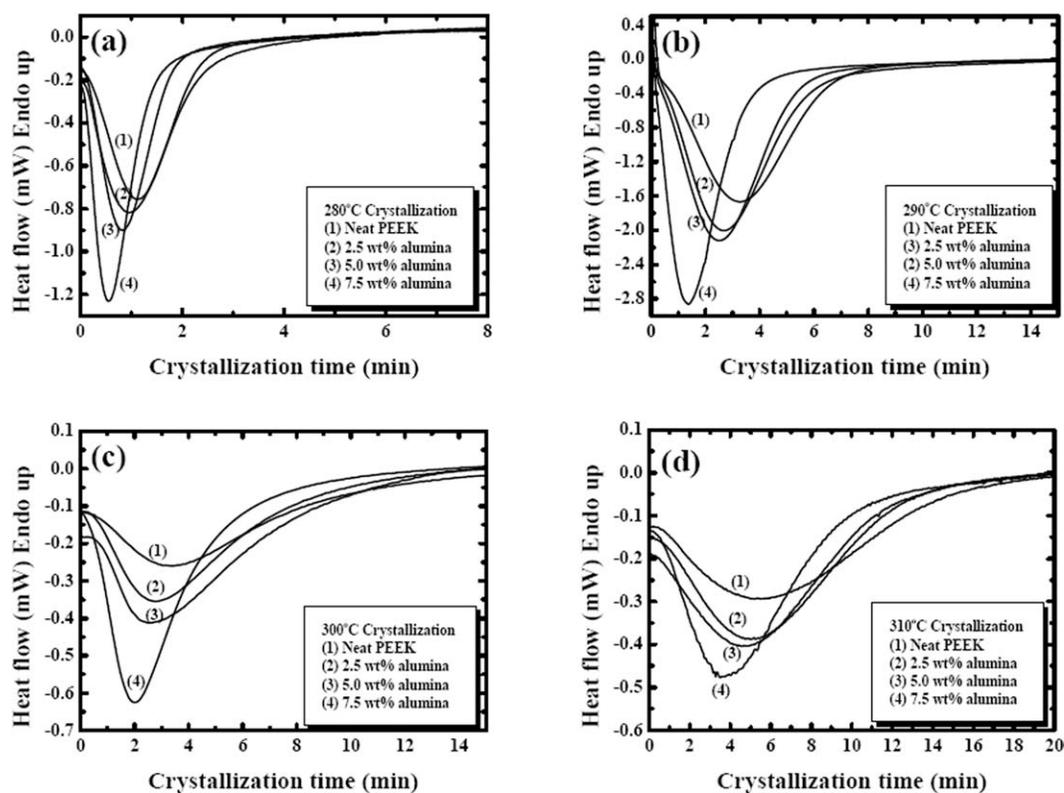


Figure 2 DSC isothermal crystallization traces for neat PEEK and PEEK/ Al_2O_3 composites. All the crystallization times for various specimens under isothermal crystallization are 60 min and (a–d) are neat PEEK and PEEK/ Al_2O_3 isothermally crystallized at 280, 290, 300, and 310°C, respectively.

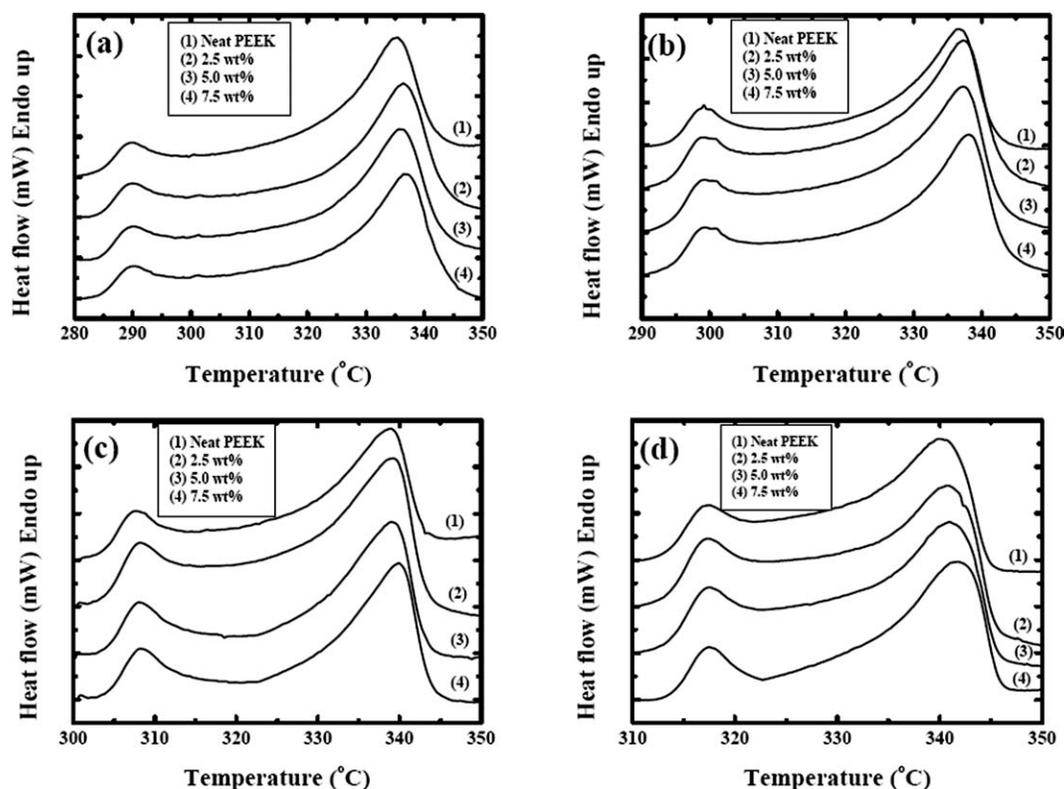


Figure 3 The second DSC heating traces for neat PEEK and PEEK/ Al_2O_3 composites; (a–d) are neat PEEK and PEEK/ Al_2O_3 isothermally crystallized at 280, 290, 300, and 310°C, respectively.

TABLE I
The Low Endotherm Melting Temperatures (T_m^{low}), High Endotherm Melting Temperatures (T_m^{high}), Supercooled Temperature Region (ΔT), Crystallization Enthalpies (ΔH_c), Absolute Crystalinities (X_c), and Peak Crystallization Times (τ_p) of the Neat PEEK and Nano-Alumina Particles Filled PEEK Composites Crystallized Isothermally at 280, 290, 300, and 310°C

Sample	Crystallization temperature (°C)	T_m^{low} (°C)	T_m^{high} (°C)	ΔT (°C)	$-\Delta H_c$ (J g ⁻¹)	X_c (%)	τ_p (min)
Neat PEEK	280	289.7	335.2	55.2	36.66	22.1	1.12
	290	299.1	336.7	46.7	43.29	37.5	3.03
	300	307.7	338.7	38.9	26.65	20.5	3.28
	310	317.4	340.2	30.2	21.45	16.5	5.56
Al ₂ O ₃ , 2.5 wt %	280	289.9	336.2	56.2	29.28	23.1	0.95
	290	299.3	337.3	47.3	44.74	39.7	2.64
	300	308.3	339.2	39.2	26.74	21.1	2.69
	310	317.4	340.8	30.8	23.83	18.8	5.07
Al ₂ O ₃ , 5.0 wt %	280	290.2	336.4	56.4	30.50	24.7	0.84
	290	299.7	337.3	47.3	44.21	40.3	2.41
	300	308.2	339.4	39.4	27.91	22.6	2.54
	310	317.6	341.0	31.0	24.21	19.6	4.62
Al ₂ O ₃ , 7.5 wt %	280	290.2	337.0	57.0	26.09	27.1	0.56
	290	300.0	338.1	48.1	47.86	44.8	1.38
	300	308.3	339.9	39.9	30.66	25.5	2.00
	310	317.7	341.7	31.7	25.13	20.9	3.61

would result in a larger span of a supercooled temperature region ($\Delta T = T_m^{\text{high}} - T_c$, where T_c is the predetermined crystallization temperature) and in less time available to complete crystallization because of the less mobility of polymer chain segments at a lower crystallization temperature. Moreover, PEEK/Al₂O₃ composites with higher nano-alumina contents would be associated with slightly larger span in ΔT , and both T_m^{high} and T_m^{low} would shift to slightly higher values when compared with the neat PEEK. For example, the differences in T_m^{high} between 7.5 wt % PEEK/Al₂O₃ composite and neat PEEK at 280 and 310°C are 1.8 (337 – 335.2) and 1.5 (341.7 – 340.2), respectively. Because of this difference in T_m^{high} , the ΔT of PEEK/Al₂O₃ composites with higher nano-alumina contents would be slightly larger than those of the neat PEEK, suggesting that the larger temperature span is available for PEEK/Al₂O₃ composite. The inclusion of nano-alumina would be responsible for the larger span in ΔT for PEEK/Al₂O₃ composite. It is believed that the mobility lowering and heterogeneous nucleation could work in parallel when the nano-alumina filler was incorporated into the PEEK polymer, that is, this nano-filler could simultaneously enhance the possibility of heterogeneous nucleation and lower the mobility of PEEK molecules.

Double-melting behavior of neat PEEK has been extensively investigated in the past decades. Porter and Lee^{13,14} conducted the investigation on the double-melting behavior of neat PEEK and found that both the T_m^{high} and T_m^{low} temperatures would increase in conjunction with the predetermined crystallization temperature under the melt-crystallization condition,

and they explained the double-melting behavior by the sum of four contributions: melting of most original crystals, their recrystallization, remelting of recrystallized PEEK, and melting of residual crystalline regions. Porter and coworkers^{13,14} proposed that the high-temperature endotherm is the melting of crystals reorganized during a heating scan. However, Marand et al.¹⁵ proposed that the high-temperature and low-temperature endothermic regions are associated with the melting of primary and secondary crystals, respectively, when PEEK polymer crystallized from the melt, and their postulate is different from the suggestion by Porter. According to the postulate of Marand, the T_m^{low} (that is, secondary melting temperature) occurs at or below the T_m^{high} to an extent and decrease with decreasing crystallization temperature. In our study, the nano-alumina-filled PEEK composites also exhibited the double-melting behavior. Moreover, both T_m^{high} and T_m^{low} temperatures increased in conjunction with the crystallization temperature under melt-crystallization condition, which is the same as the suggestion by Porter. As shown in Table I, the incorporation of nano-alumina into the PEEK matrix would slightly enlarge the span between T_m^{high} and T_m^{low} . Moreover, all the T_m^{high} values of the nano-alumina-filled PEEK composites are slightly higher than those of the neat PEEK and increase in conjunction with nano-filler contents. The above two phenomena would relatively favor the occurrence of heterogeneous nucleation for the nano-alumina particle-filled PEEK composites. The thermal conductivities of the PEEK and alumina at room temperature were reported to be 0.2 and 30 W m⁻¹K⁻¹, respectively.²³ Thermal

conductivity of the alumina filler was higher than that of the PEEK polymer, and consequently, the thermal conductivity of the PEEK polymer was enhanced when the inorganic filler was incorporated. With the higher thermal conductivity for the PEEK-based nanocomposites, the temperature of the PEEK polymer could reach the set temperature earlier during DSC quenching. This effect favored the occurrence of nuclei at a slightly earlier stage of crystallization process for PEEK/Al₂O₃ composites when compared with the neat PEEK because the polymer molecules in nano-alumina-filled PEEK composites can be easier and earlier to deposit down. As a result, the PEEK molecules crystallized at slightly earlier stage would be associated with a slightly higher melting temperature.

It is well known that the crystallization half-life time ($t_{1/2}$) can well define the time spent from the onset of crystallization to a point at which crystallization is 50% complete. However, this parameter is difficult to estimate accurately. In this study, we used the peak crystallization time (τ_p) to define the time spent from the onset to a point where the exothermic peak appeared under isothermal crystallization. If the peak profile of crystallization is symmetric, the peak crystallization time would be exactly the same as the crystallization half-life time.²⁴ In Figure 2, the exothermic peaks were found to be more flattened as the crystallization temperature shifted higher. As shown in Table I, the inclusion of the nano-alumina particles significantly reduced the τ_p value, from 1.12 min for neat PEEK to 0.56 min for 7.5 wt % PEEK/Al₂O₃ composite crystallized at 280°C. Moreover, the τ_p value decreased with increasing nano-filler contents for all the predetermined crystallization temperatures, suggesting the occurrence of heterogeneous nucleation.

As for the absolute crystallinities of PEEK/Al₂O₃ composites, as shown in Table I, the X_c values for these composites were all higher than those of the neat PEEK polymer at the predetermined crystallization temperatures. The maximum value for X_c is the 7.5 wt % PEEK/Al₂O₃ composite crystallized at 290°C, reaching 44.8%. Irrespective of the predetermined crystallization temperatures, the X_c values increased in conjunction with the nano-filler contents, and the X_c of the PEEK/Al₂O₃ composites reached the maximum value at 290°C. Under isothermal crystallization of PEEK and PEEK/Al₂O₃ composites, the mobility hindrance and heterogeneous nucleation competed with each other during the crystallization process. Low temperature made the mobility hindrance notable; conversely, high temperature favored the heterogeneous nucleation. Thus, the cooperation resulted in the maximum crystallinity at 290°C.

As mentioned previously, PEEK/Al₂O₃ composite with 7.5 wt % filler content exhibited the maximum crystallinity of 44.8% at 290°C, higher than 41% reported by Jonas et al.²⁵ for neat PEEK 450G and 40% by Chen et al.¹⁶ for PEEK 150P. The inclusion of nano-alumina particles would increase the X_c value for ~ 4% when compared with that of the value reported by Jonas et al. In this study, the samples crystallized isothermally at the predetermined temperatures showed the crystallinities ranging from 17 to 38% and 19 to 45% for the neat PEEK 450G and PEEK/Al₂O₃ composites, respectively. The PEEK/Al₂O₃ composite with 7.5 wt % filler content exhibited an increase in X_c for ~ 7% at 290°C, compared with that of the neat PEEK 450G. As stated previously, the values of T_m^{high} and τ_p for PEEK/Al₂O₃ composite were higher than those of the neat PEEK. As expected, the absolute crystallinities of the PEEK/Al₂O₃ composites were again higher than that of the neat PEEK. These results might favor the occurrence of heterogeneous nucleation. It is believed that the inclusion of inorganic fillers affected the crystallization behavior of the polymer molecules in two ways: increasing the crystallinity because of heterogeneous nucleation or decreasing the crystallinity due to mobility hindrance. As shown in Table I, the inclusion of the nano-alumina particles into the PEEK matrix increased the X_c values from 37.5 to 44.8% at 290°C. In Figure 1, the shape of the nano-alumina particle was basically irregular. Accordingly, these irregular particles offered extraordinary sites for the PEEK molecules to deposit on and nucleate heterogeneously. In this study, the X_c values increased with increasing nano-alumina content, and these values for the PEEK/Al₂O₃ composites were all higher than those of the neat PEEK polymer at all the predetermined crystallization temperatures. In this study, the increases in T_m^{high} temperature, τ_p and X_c values for the PEEK/Al₂O₃ composites followed the result of Belfiore and coworker.²⁰

Our previous study on the crystallization behavior of 15 nm silica-filled PEEK 150P showed that the X_c values of the nano-silica-filled PEEK composites were significantly lower than that of the neat PEEK 150P, and the X_c value decreased in conjunction with the nano-silica content.²⁶ This study seems to be contrary to our previous study. There is one possibility accounting for this disagreement. The main difference between the two nano-fillers is the particle dimension, 30 nm for alumina, and 15 nm for silica. The spatial confinement among the nano-fillers could be estimated according to the following equation²⁷:

$$L = d[(F/V_f) - 1], \quad (2)$$

TABLE II
The Mean Distance L Between Statistically Distributed Nanoparticles

Filler	Weight fraction (%)	Volume fraction (%)	Filler diameter (nm)	Filler spacing (nm)
SiO ₂ (15 nm)	2.5	1.2	15	800
	5.0	2.5	15	369
	7.5	3.7	15	244
Al ₂ O ₃ (30 nm)	2.5	0.8	30	2370
	5.0	1.6	30	1170
	7.5	2.5	30	768

$L = d[(F/V_f) - 1]$, where d , F , and V_f are filler diameter, packing factor (0.64 for spherical fillers), and volume fraction, respectively.²⁴ The densities of silica and alumina are 2.65 and 3.98 g cm⁻³, respectively.

where L , d , F , and V_f are mean distance between statistically distributed nanoparticles, filler diameter, packing factor (0.64 for spherical fillers), and volume fraction, respectively. The densities of silica and alumina are 2.65 and 3.98 g cm⁻³, respectively. As shown in Table II, the inter-filler distance for the 30-nm nano-alumina is approximately three times of the 15-nm nano-silica. The distribution of nano-fillers in the PEEK matrix is not a statistical distribu-

tion but more likely to be local clustering or agglomeration. The real inter-filler distance in the PEEK matrix should be significantly larger than the values in Table II. According to the above discussion, the 30-nm alumina-filled PEEK composite would have more inter-filler spacing than that of the 15-nm silica counterpart, in which the PEEK molecules can move and crystallize.

Isothermal crystallization kinetics

From the DSC isothermal crystallization trace, the relative crystallinity $X_c(t)$ can be estimated as follows:²⁸

$$X_c(t) = \frac{\int_{t_0}^t (dH_c/dt)dt}{\int_{t_0}^{t_\infty} (dH_c/dt)dt} = \frac{A_0}{A_\infty}, \quad (3)$$

where t_0 and t_∞ are the crystallization times at which crystallization starts and ends, and A_0 and A_∞ are areas under the normalized DSC crystallization traces, respectively. Figure 4 shows the plots of $X_c(t)$ versus crystallization time t . The PEEK polymer filled by nano-alumina particles would have less time available to induce the nucleation of crystallization, compared with those of the neat PEEK at

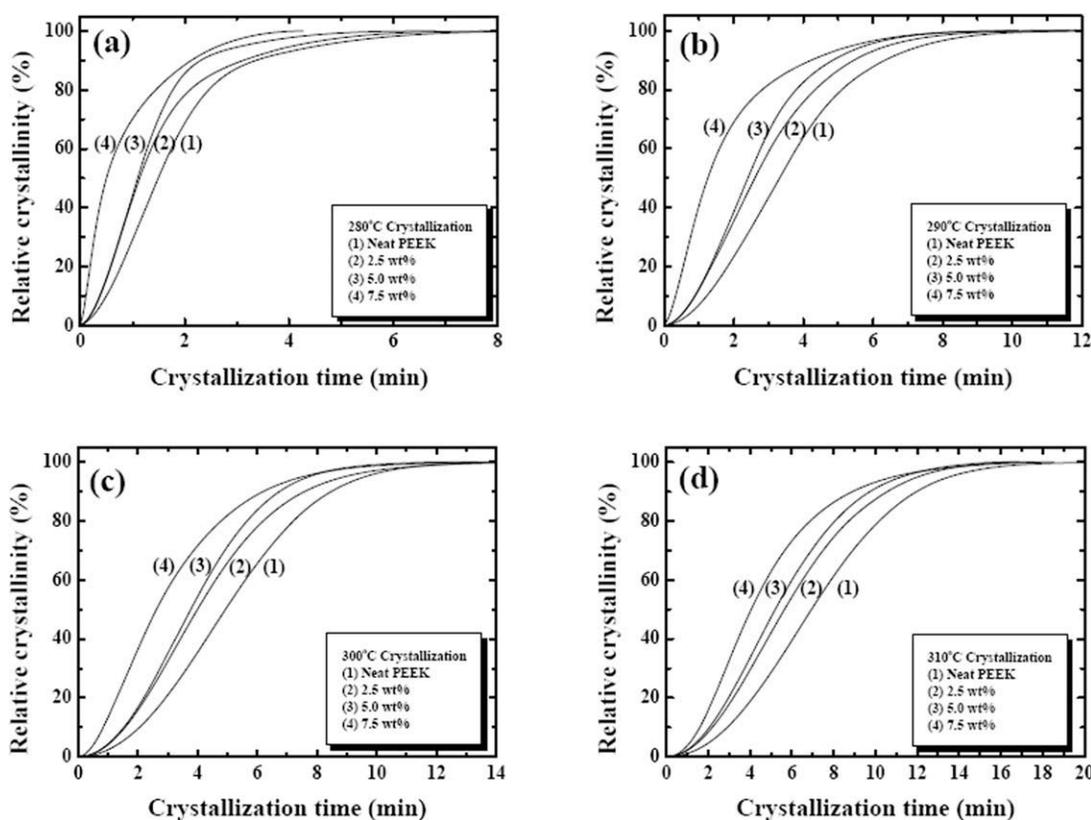


Figure 4 The relative crystallinity of neat PEEK and PEEK/Al₂O₃ composites at various crystallization times; (a–d) are neat PEEK and PEEK/Al₂O₃ isothermally crystallized at 280, 290, 300, and 310°C, respectively.

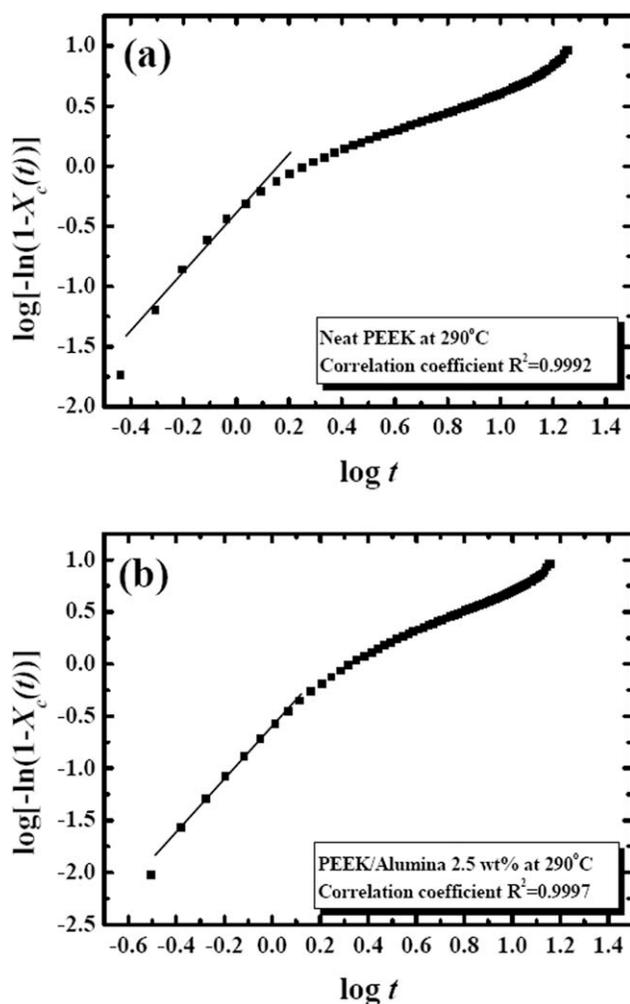


Figure 5 The Avrami plots of PEEK composites crystallized isothermally at 290°C: (a) neat PEEK and (b) 2.5 wt % nano-alumina filled PEEK composite.

various predetermined temperatures, and this result is consistent with the τ_p values in Table I.

The Avrami equation can well describe the isothermal crystallization behavior, as followed:²⁸

$$1 - X_c(t) = \exp(-Kt^n), \quad (4)$$

$$\log[-\ln(1 - X_c(t))] = n \log t + \log K. \quad (5)$$

A plot of $\log[-\ln(1 - X_c(t))]$ versus $\log t$ yields the slope n , the Avrami exponent, and the intercept $\log K$, as shown in Figure 5. Both the parameters of K and n are diagnostic of the crystallization mechanism.²⁸ To make an insight into the primary stage of the crystallization behavior, the linear fits for all the plots were conducted for region with the relative crystallinities X_c between 6 and 63.2%, for which the corresponding values of $\log[-\ln(1 - X_c(t))]$ were -1.25 and 0 , respectively. In other words, the analysis was aimed for the initial crystallization stage with no complex impingement effect. In this primary

crystallization stage, all the correlation coefficients (R^2) were up to 0.998, indicating that the fitting was well linear. As expected, because the crystallinity was more than 75%, the spherulites of PEEK polymer impinged together, and this range was associated with the secondary crystallization stage.¹⁸ Table III shows the kinetics parameters of neat PEEK and PEEK/ Al_2O_3 composites. For neat PEEK 450G, the n values, ranging from 2.16 to 2.61, increase in conjunction with crystallization temperatures. It has been suggested that the crystallization behavior of neat PEEK 150P is a diffusion-controlled growth with a geometrical dimension of 3.¹⁶ The higher crystallization temperature would favor the diffusion rate of polymer segments and result in higher value of Avrami exponent n . In this study, the nano-alumina-filled PEEK composites showed higher n but lower K values when compared with those of the neat PEEK 450G at different temperatures, as shown in Table III. In addition, the increase filler contents resulted in slightly higher n but lower K values. The n values for the PEEK/ Al_2O_3 composites ranged from 2.23 to 2.96, and these values were significantly higher than those of the neat PEEK 450G at different crystallization temperatures. It was proposed that the n values for homogeneous and heterogeneous nucleations are 4, that is, $(n + 1)$ and 3, respectively, for the three-dimensional (3D) sphere-like crystallites, and 3 and 2, respectively, for two-dimensional (2D) disc-like crystallites.²⁸ However, during the measurement of the DSC run, the thickness of the DSC specimen (sample weight is approximately 4–5 mg in the aluminum pan) was ~ 0.2 mm.²⁹ As expected, the dimensions of polymer spherulites are often larger than 200 μm . With this consideration,

TABLE III
Kinetics Parameters of the Neat PEEK and Alumina Particles Filled PEEK Composites Crystallized Isothermally at 280, 290, 300, and 310°C

Sample	Crystallization temperature (°C)	n	$K \times 10^3$ ($\text{min}^{1/n}$)
Neat PEEK	280	2.16	220
	290	2.39	30
	300	2.49	5.01
	310	2.61	0.58
Al_2O_3 , 2.5 wt %	280	2.23	70
	290	2.44	6.87
	300	2.63	1.40
	310	2.71	0.31
Al_2O_3 , 5.0 wt %	280	2.51	47
	290	2.68	5.67
	300	2.74	1.20
	310	2.79	0.27
Al_2O_3 , 7.5 wt %	280	2.71	38
	290	2.73	4.01
	300	2.84	0.81
	310	2.96	0.22

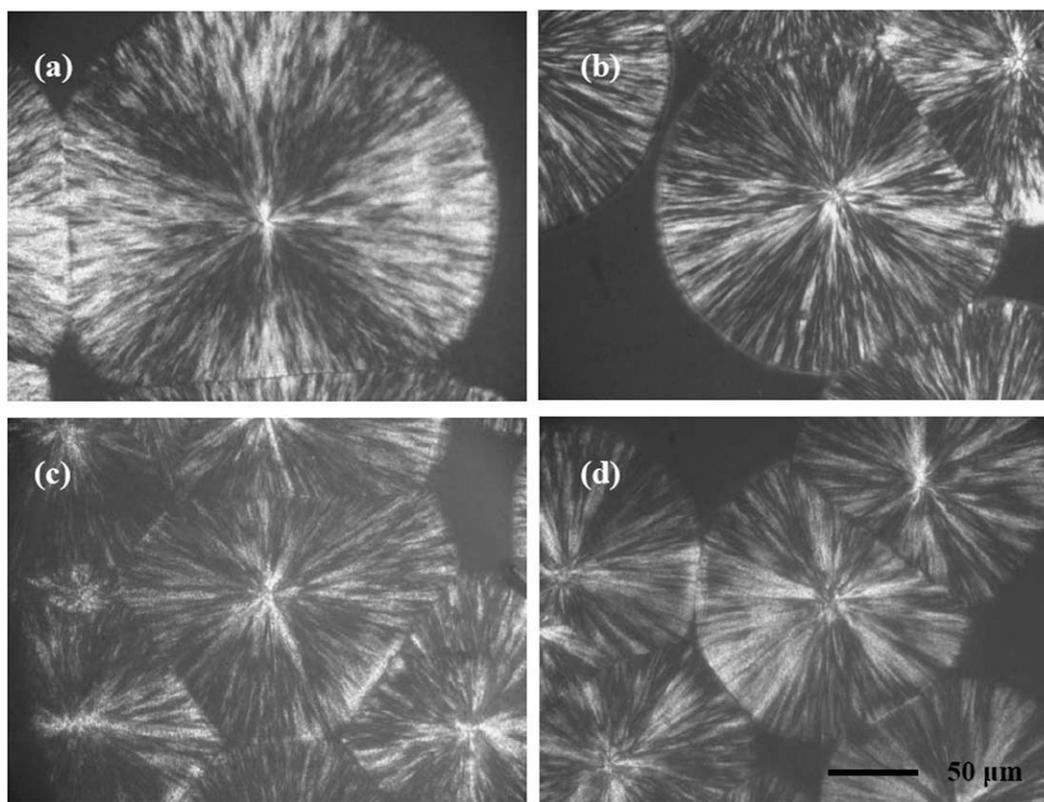


Figure 6 The spherulite morphologies of neat PEEK and PEEK/ Al_2O_3 composites isothermally crystallized at 290°C . (a–d) are neat PEEK, 2.5, 5.0, and 7.5 wt % nano-alumina filled PEEK composites, respectively. The spherulite diameters for (a), (b), (c), and (d) are approximately 240, 190, 160, and 140 μm , respectively.

the crystallite growth along the thick direction in the aluminum pan was not completely 3D, but rather in a mixed manner of 3D and 2D, indicating that the n value would be in the range between 3 and 4 for homogeneous nucleation and between 2 and 3 for heterogeneous nucleation. In this study, the n values for neat PEEK range from 2.16 to 2.61, indicating that the PEEK polymer could crystallize in homogeneous nucleation with 2D discs or in heterogeneous nucleation with 3D sphere-like crystallites.²⁸ The heterogeneous nucleation behavior of neat PEEK might be because of the existence of nucleation agent in the as-received neat PEEK polymer. As for the PEEK/ Al_2O_3 composites, the n values range from 2.23 to 2.96, suggesting that geometry of the spherulites in the PEEK matrix might crystallize in heterogeneous nucleation and that the spherulite growth of PEEK/ Al_2O_3 composites might probably crystallize in a 3D manner, compared with neat PEEK. The inclusion of nano-alumina particles into the PEEK polymer might favor the occurrence of heterogeneous nucleation and complicate the crystallization dimension of PEEK polymer.

To unveil the dilemma on the Avrami exponent n , we used POM to determine the spherulite dimensions of neat PEEK and PEEK/ Al_2O_3 composites. Figure 6 shows the spherulite morphologies of the

neat PEEK and nano-alumina-filled PEEK composites isothermally crystallized at 290°C . The spherulite diameters for neat PEEK, 2.5, 5.0, and 7.5 wt % PEEK/ Al_2O_3 composites were approximately 240, 190, 160, and 140 μm , respectively. The inclusion of nano-alumina particles increased the crystallinity of the PEEK matrix, but decreased the grain size of the PEEK polymer. As stated previously, the thickness of the samples for DSC studies was ~ 0.2 mm.²⁹ The spherulite diameter for neat PEEK was ~ 240 μm and larger than those of the PEEK/ Al_2O_3 composites, indicating that the n values for PEEK/ Al_2O_3 composites would be higher than those of the neat PEEK. Accordingly, the spherulite growth of PEEK/ Al_2O_3 composites would probably crystallize in a 3D manner, compared with neat PEEK during the DSC measurement. The results from the POM observations are consistent with the results from the crystallization kinetics. As for the growth rate, K , the inclusion of nano-alumina significantly lowered the K value, compared with that of the neat PEEK polymer, indicating the increase in mobility hindrance for the diffusion of PEEK molecules.

Crystallization activation energy (ΔE)

Based on the Arrhenius model, the crystallization rate parameter K can be approximately described by the following equation:³⁰

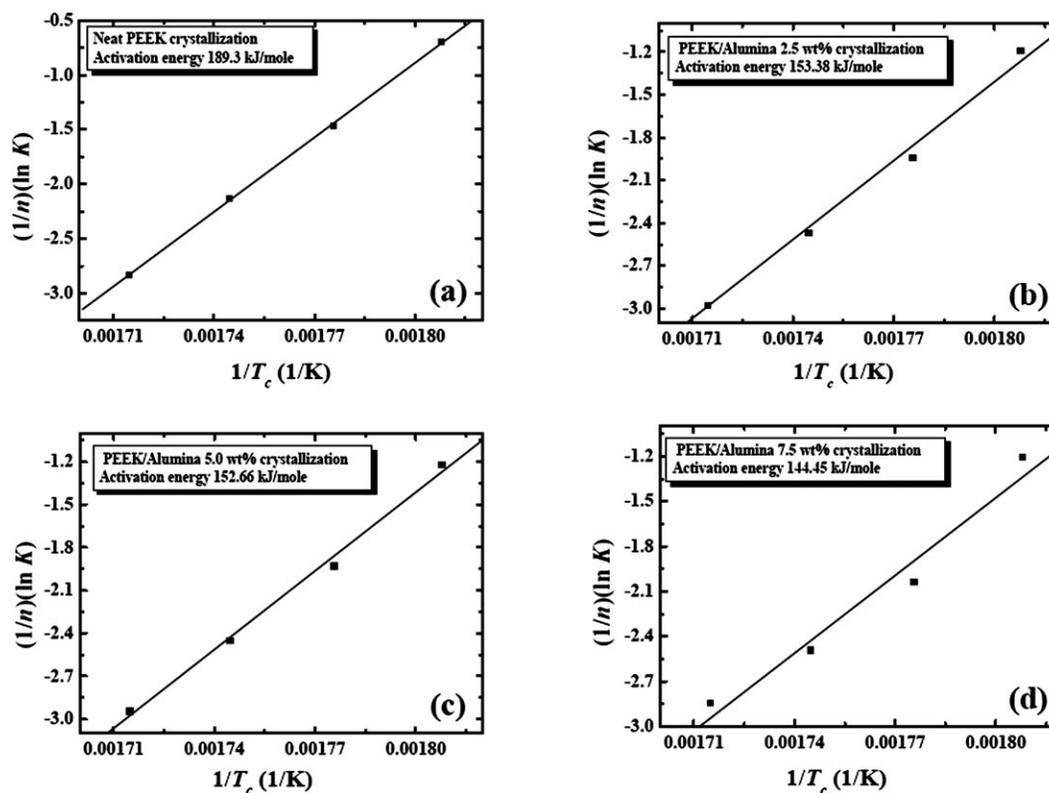


Figure 7 Plots of $(1/n) \ln K$ versus $1/T_c$ for determining the activation energy under isothermal crystallization. The crystallization activation energy for neat PEEK, 2.5, 5.0, and 7.5 wt % PEEK/ Al_2O_3 composites are determined to be 189.3, 153.4, 152.7, and 144.5 kJ mol^{-1} , respectively.

$$K^{1/n} = k_0 \exp(-\Delta E/RT_c), \quad (6)$$

$$\frac{1}{n} \ln K = \ln k_0 - \frac{\Delta E}{RT_c}. \quad (7)$$

where k_0 is a temperature-independent preexponential factor, R is the universal gas constant, and $(-\Delta E)$ is the activation energy for isothermal crystallization. Accordingly, a plot of $(1/n) \ln K$ versus $1/T_c$ yields the activation energy for primary crystallization stage, as shown in Figure 7. The crystallization activation energies for neat PEEK, 2.5, 5.0, and 7.5 wt % PEEK/ Al_2O_3 composites were estimated to be 189.3, 153.4, 152.7, and 144.5 kJ mol^{-1} , respectively. The inclusion of nano-alumina decreased the activation energy of PEEK under isothermal crystallization, and the value of $(-\Delta E)$ decreased with increasing nano-alumina content, indicating that the inclusion of nano-alumina would facilitate the crystallization of molecular chains of PEEK.

Liu et al.³⁰ determined the activation energy of Nylon 11 under isothermal crystallization using eq. (5) and reported that the value of $(-\Delta E)$ is $\sim 394.6 \text{ kJ mol}^{-1}$. Kim et al.²¹ conducted the investigation of crystallization kinetics on the silica nanoparticle-filled poly(ethylene 2,6-naphthalate) (PEN), and they estimated the activation energies during nonisothermal crystallization for neat PEN, 0.3, 0.5, 0.7, and 0.9

wt % PEN/silica composites are 105, 91, 86, 79, and 75 kJ mol^{-1} , respectively.

The inclusion of nano-alumina decreased the activation energy and increased the crystallinity, but lowered the growth rate of PEEK matrix under isothermal crystallization. There is one possibility that the inclusion of nano-alumina particles might impart the smaller grain size to the PEEK matrix, and POM results, as shown in Figure 6, on neat PEEK and PEEK/ Al_2O_3 composites could this possibility.

It is plausible that the inclusion of nano-alumina particles could make the PEEK molecules easier to deposition and nucleation, but lower the growth rate because of the mobility hindrance. As stated previously, two factors affected the crystallization behavior: segment mobility and heterogeneous nucleation. In this study, these two factors worked in parallel and resulted in smaller grain size in the PEEK/ Al_2O_3 composite during the isothermal crystallization process.

CONCLUSIONS

The inclusion of the nano-alumina into the PEEK matrix increased both the T_m^{high} and T_m^{low} temperatures and the span of the super cooled region compared with those of the neat PEEK. The X_c values for the PEEK/ Al_2O_3 composites were higher than

those of the neat PEEK at all the predetermined crystallization temperatures. Moreover, the τ_p values for the PEEK composites were lowered when the nano-alumina particles were incorporated. The isothermal crystallization parameters favored the occurrence of heterogeneous nucleation for the nano-alumina-filled PEEK composites.

According to the study of isothermal crystallization kinetics on these PEEK/ Al_2O_3 composites, the inclusion of the nano-filler increased the Avrami exponent, suggesting an increase in the dimension of crystallization for the PEEK/ Al_2O_3 composites. However, it also retarded the growth rate of crystallization for these PEEK composites, and the inclusion of the nano-alumina particles resulted in smaller grain size for the PEEK/ Al_2O_3 composites.

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