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Crystallization kinetics and nucleation activity of silica nanoparticle-filled poly(ethylene 2,6-naphthalate)

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Abstract

Silica nanoparticle-filled poly(ethylene 2,6-naphthalate) (PEN) composites were melt-blended to improve the mechanical and rheological properties of PEN. The melt viscosity and total torque values of the composites were reduced by the silica content. The crystallization exothermic peak shifted to a higher temperature, and the overall crystallization time was reduced by increasing the silica content. Non-isothermal crystallization kinetics was analyzed using the Ozawa and Avrami theories, and a combined method. The combined method was successful in describing the non-isothermal crystallization of these composites. The crystallization activation energy calculated using Kissinger's method was reduced, and the spherulite growth rate increased, with increasing silica content.

A study of the nucleation activity, which indicated the influence of the filler on the polymer matrix, revealed that the fumed silica nanoparticles had a good nucleation effect on PEN.

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Keywords: Silica nanoparticle; Non-isothermal crystallization kinetics; Nucleation activity

1. Introduction

Poly(ethylene 2,6-naphthalate) (PEN) has been used as a high-performance engineering plastic in fibers, films, and packaging, because of its excellent physical properties and outstanding gas barrier characteristics [1-3]. However, the application of PEN is limited because PEN exhibits a relatively high melt viscosity, which makes fiber spinning and injection molding difficult [4]. Recently, there has been much research on creating organic/inorganic composites by adding nanoparticles to the polymer matrix [5], and the nanoparticles have contributed to greatly improved mechanical and rheological properties [6,7].

Fumed silica nanoparticles manufactured by hightemperature hydrolysis of silicon tetrachloride in a flame have extremely large surface areas and smooth non-porous surfaces [8], which could promote strong physical contact between the filler and the polymer matrix. Sumita et al. [9] pointed out earlier, the benefits of replacing silica microparticles by nanoparticles. Silica nanoparticles provide high rigidity, which has actually been demonstrated for almost all composite systems, and increased the yield strength and elongation at break of the nanoparticle-filled polymers compared to the values for pristine nylon 6 [10,11], polyethylene terephthalate [12], polypropylene [13], and polyimide [14]. The yield strength of the silica nanoparticlefilled composites increased with filler content and decreased with filler size [9]. Silica nanoparticles have a prominent reinforcing effect on the elastic properties of the polymers when uniaxially oriented by cold drawing, because the diameters of the silica nanoparticles are comparable to the sizes of crystalline regions in a polymer [15]. These improvements in mechanical properties are related to the crystallization behaviors of the polymer. Furthermore, the crystallization behavior of thermoplastic polymers during non-isothermal processing has technological importance, because these conditions are closely related to the industrial processing conditions. However, there has been little research related to the non-isothermal crystallization behaviors of silica nanoparticle-filled PEN composites.

In this work, the non-isothermal crystallization kinetics and spherulite growth of silica nanoparticle-filled PEN composites, which were prepared by melt-compounding at various silica contents, have been investigated, and the non-isothermal crystallization process was adopted to

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investigate the effect of silica nanoparticles in the PEN matrix for actual processing conditions. The study of nonisothermal crystallization kinetics, from differential scanning calorimetry measurements, was performed using the modified Avrami equation, the Ozawa equation, and methods combining the theories. The spherulite growth rate, nucleation activity, and crystallization activation energy were also investigated.

2. Experimental

2.1. Materials and sample preparation

PEN (I.V. = 0.93 dL/g) was supplied by Hyosung Co., and hydrophilic fumed silica (primary particle size 7 nm) was purchased from Sigma Aldrich Co. All the specimens were dried for 24 h at 100 °C in vacuo to ensure low moisture levels. Silica nanoparticle-filled composites were prepared using a Haake rheomix 600 internal mixer at various silica contents (0.3-0.9 wt%). The melt compounding was performed at 275 °C for 5 min; the rotor speed was 60 rpm, and the total mixing weight per batch was 50 g. Melt viscosity was investigated using Advanced rheological expansion system (ARES, Rheometric Scientific Co.) with parallel plate-type geometry at 275 °C under a nitrogen atmosphere, and the frequency ranged from 0.05 to 300 rad/s. The morphology of the fractured surface which prepared under liquid N₂ were observed using Field Emission Scanning Electron Microscope (FE-SEM, JEOL, JSM-6330F) to investigate on the dispersion states of the silica nanoparticles in the PEN matrix, and all samples were coated with Pt for 5 min prior to perform.

2.2. Differential scanning calorimetry

Non-isothermal crystallization behaviors of the silica nanoparticle-filled composites were studied using a Perkin– Elmer DSC-7 and the weights of all samples were approximately 6 mg. The DSC was calibrated with 10 mg of indium ($T_m^0 = 156.4 \,^\circ\text{C}$, $\Delta H_f^0 = 28.5 \,\text{J/g}$) prior to performing the experiment. The samples were heated to 300 $\,^\circ\text{C}$ at a heating rate of 10 $\,^\circ\text{C/min}$ under a nitrogen atmosphere, and held for 5 min to remove previous thermal history. Nonisothermal crystallization kinetics investigated by cooling these samples from 300 to 30 $\,^\circ\text{C}$ at constant cooling rates of 2.5, 5, 10, 15, 20, 25, and 30 $\,^\circ\text{C/min}$.

2.3. Polarized optical microscopy

Spherulite growth rate was calculated using a polarized optical microscope equipped with a CCD camera (Nikon HFX-11A), and a heated stage (Mettler Toledo FP-82HT). All the samples were melted at 300 °C for 3 min to eliminate previous thermal history, and cooled at a rate of 20 °C/min, which is the maximum cooling rate of the heated stage, until

they reached crystallization temperatures of 225, 230, 235, or 240 °C. By using a CCD camera, the spherulite growths of silica nanoparticle-filled PEN composites were monitored at isothermal crystallization conditions, and spherulite growth images were captured every 5 s. These captured images were analyzed using image analysis (Media Cybernetics Co., Image-Pro[®]), and we calculated the spherulite growth rate of PEN and silica nanoparticle-filled PEN composites.

3. Results and discussion

3.1. Melt viscosity depression

As shown in Fig. 1, the total torque values of silica nanoparticle-filled PEN composites were reduced as the silica content increased during the process. Total torque values measured from Haake rheometer indirectly represents melt viscosity of the molten polymer, and variations of viscosity in conventional processing could estimate using these values. Melt viscosity of the composites were reduced as the silica content increased in Fig. 1, and the same results were obtained from ARES test. As shown in Fig. 2, the apparent viscosity of the composites was decreased as the silica content increased at a frequency range of 0-300 rad/s. Because all the specimens were processed under the same conditions, the melt viscosity depression of silica nanoparticle-filled PEN composites must have been caused mainly by the silica nanoparticles. Im et al. [12] also found decrease in melt viscosity when fumed silica nanoparticles were added to the PET matrix, and Cho et al. [16] reported the reduction of melt viscosity for nylon-6 nanocomposites filled with organo-clays, as measured by capillary rheometry. They suggested two possible reasons for the reduction of the melt viscosity, when nano-size fillers were added to the polymer matrix. The first is the slip between the polymer matrix and the filler, and the second is the degradation of the polymer matrix due to the high shear force and heat during melt compounding. However, when silica nanoparticles



Fig. 1. Apparent viscosity variations with silica content.



Fig. 2. Total torque value variations of silica nanoparticle-filled PEN composites versus silica content.

were used as the filler, they would act as a lubricant during melt compounding rather than in the second way described above, because they have spherical shapes and smooth nonporous surfaces, which would lower the friction coefficient [12].

This property allows the possibility of improving the processability and allows additional applications for nanoparticle-filled polymer composites. In particular, the application of PEN is limited because PEN exhibits a relatively high melt viscosity, which can be attributed to the rigid naphthalene ring in the main chain. Therefore, the processability of PEN would be enhanced by adding small amounts of fumed silica nanoparticles to the PEN matrix.

The SEM microphotographs of the fractured samples prepared under liquid N_2 were shown in Fig. 3. Generally, unmodified fumed silica easily aggregates each other due to the particle–particle interaction [8], and the aggregated fumed silica nanoparticles could also found in our experiments. While the primary particle sizes of the fumed silica was 7 nm, the size distribution of the silica nanoparticles was ranged from tens to 400 nm in the PEN matrix as shown in Fig. 3. However, the silica nanoparticles were dispersed in the PEN matrix quite evenly because the content of silica was very little (up to 0.9 wt%) and sufficient shear force was imposed during the process.

3.2. Crystallization behavior

The crystallization peaks from melting PEN and silica nanoparticle-filled PEN at different cooling rates are shown in Fig. 4. As the cooling rate increased, the crystallization peak temperature (T_p) shifted to lower temperatures both for PEN and silica nanoparticle-filled PEN. When the specimens were cooled quickly, more supercooling was required to initiate crystallization, because the motion of the PEN molecules could not follow the cooling rate [17,18]. At a given cooling rate, T_p of silica nanoparticle-filled PEN composites was higher than that of pristine PEN. As shown in Fig. 5, the overall crystallization time (t_c) was reduced by

$$t_{\rm c} = (T_{\rm s} - T_{\rm e})/a \tag{1}$$

where *a* is the cooling rate, T_s is the initial crystallization temperature, and T_e is the final crystallization temperature. $T_{\rm s}$, $T_{\rm e}$, and $T_{\rm p}$ at various cooling rates are listed in Table 1. The observed increase of T_p and decrease of t_c with increasing silica content are typical characteristics of nucleation-controlled polymer crystallization [19]. Generally, homogeneous nucleation started spontaneously by chain aggregation below the melting temperature and required longer times, whereas heterogeneous nuclei formed as soon as the samples reached the crystallization temperature. Therefore, the crystallization of silica nanoparticle-filled PEN composites proceeds mainly via heterogeneous nucleation by the silica nanoparticles. As listed in Table 2, the degree of crystallinity (X_c) of the composites was increased by the silica content, and these results can be explained by the supercooling temperature. In this research, fumed silica nanoparticles acted as nucleation agents in the PEN matrix under non-isothermal crystallization conditions and the crystallization peak temperatures were shifted to higher temperatures, which indicates that the supercooling of the composites at a given cooling rate was reduced by the silica content. When the polymer crystallized with less supercooling, it crystallized more perfectly than with more supercooling; hence, the degree of crystallinity of silica nanoparticle-filled PEN composites was increased by the silica content at a given cooling rate. The degree of crystallinity of the specimens was calculated from Eq. (2), and the supercooling temperatures and degree of crystallinity of the samples are listed in Table 2.

$$X_{\rm c} = \frac{\Delta H_{\rm exp}}{\Delta H_{\rm f}^0} \times 100 \tag{2}$$

where $\Delta H_{exp} = \Delta H_f - \Delta H_c$ and ΔH_f^0 is the heat of fusion of an infinitely thick crystal [ca. 103.4 J/g [20]], and the absolute crystallinity, X_c , is a decreasing function of the cooling rate.

3.3. Non-isothermal crystallization kinetics

From the DSC curves of melting crystallization, the values of relative crystallinity at different cooling rates, $X_c(T)$, can be calculated according to the following equation:

$$X_{c}(T) = \frac{\int_{T_{0}}^{T} (dH_{c}/dT)dT}{\int_{T_{0}}^{T_{\infty}} (dH_{c}/dT)dT} = \frac{A_{0}}{A_{\infty}}$$
(3)

where T_0 and T_{∞} are the temperatures at which crystallization starts and ends, and A_0 and A_{∞} are areas under the



(c)

(d)

Fig. 3. FE-SEM microphotographs of fractured surface of (a) PEN/silica 0.3 wt%, (b) PEN/silica 0.5 wt%, (c) PEN/silica 0.7 wt%, (d) PEN/silica 0.9 wt%.

normalized DSC curves. Relative crystallinities as a function of temperature for PEN and silica nanoparticle-filled PEN composites are shown in Fig. 6. It can be seen that all these curves have similar sigmoidal shapes, and the curvature of the upper parts of the plot was observed to be due to the spherulite impingement in the later stages of crystallization. The relationship between crystallization temperature T and time t is given by Eq. (4) during the

non-isothermal crystallization process, as follows:

$$t = \frac{|T_0 - T|}{a} \tag{4}$$

where t is the crystallization time, T_0 is the temperature at which crystallization begins (t = 0), T is the crystallization temperature, and a is the cooling rate. According to Eq. (4),

	Sample														
	PEN-Pure			PEN/silica 0.3%			PEN/silica 0.5%			PEN/silica 0.7%			PEN/silica 0.9%		
	$T_{\rm s}$ (°C)	$T_{\rm p}~(^{\circ}{\rm C})$	$T_{\rm e}$ (°C)	$T_{\rm s}$ (°C)	$T_{\rm p}~(^{\circ}{\rm C})$	$T_{\rm e}$ (°C)	$T_{\rm s}$ (°C)	$T_{\rm p}~(^{\circ}{\rm C})$	$T_{\rm e}$ (°C)	$T_{\rm s}$ (°C)	$T_{\rm p}~(^{\circ}{\rm C})$	$T_{\rm e}$ (°C)	$T_{\rm s}$ (°C)	$T_{\rm p}~(^{\circ}{\rm C})$	$T_{\rm e}$ (°C)
2.5 °C/min	241	232	224	241	235	224	242	235	224	245	237	227	246	239	231
5 °C/min	238	223	211	238	224	213	238	227	216	241	227	216	242	230	219
10 °C/min	231	210	186	231	212	191	233	214	194	236	218	196	236	219	198
15 °C/min	224	198	170	225	202	178	230	207	184	232	209	184	233	211	186
20 °C/min	220	194	167	220	199	172	225	201	173	226	203	174	227	206	177
25 °C/min	218	189	163	219	196	159	217	194	170	219	197	172	219	197	173
30 °C/min	213	185	152	213	190	155	213	190	165	219	192	165	216	190	170







Fig. 4. DSC thermograms of (a) PEN and (b) PEN/silica 0.9 wt% during non-isothermal crystallization at different cooling rates.

the value of T on the X-axis in Fig. 6 can be transformed into the crystallization time t as shown in Fig. 7.

Ozawa explained the effect of cooling rate on the nonisothermal crystallization by modifying the Avrami equation, assuming that the crystallization occurs at a constant cooling rate a [21]. According to Ozawa's theory,



Fig. 5. Overall crystallization time versus silica content at various cooling rates.

Table	2
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DSC Data for PEN and silica nanoparticle-filled PEN composites at a cooling rate of 10 $^{\circ}\text{C/min}$

Sample	T_{g}	$T_{\rm c}^{\rm a}$		T _m		$T_{\rm c}^{\rm b}$	ΔT	X_{c}
	(0)	Peak (°C)	$\Delta H_{\rm c}$ (J/g)	Peak (°C)	$\Delta H_{\rm f}$ (J/g)	(0)	(C)	(%)
PEN-Pure	119.2	181.9	17.2	266.0	40.3	212.8	53.2	22.3
PEN/silica 0.3%	119.7	177.4	15.1	266.9	40.2	214.5	52.4	24.2
PEN/silica 0.5%	119.5	177.9	17.2	266.7	44.7	216.4	50.3	26.5
PEN/silica 0.7%	119.3	175.1	13.5	266.5	44.1	219.9	46.6	29.4
PEN/silica 0.9%	119.5	172.0	8.4	266.5	46.5	221.8	44.7	36.8

 $^{\rm a}$ The crystallization temperature measured on the second heating at 10 $^{\circ}{\rm C/min}.$

 $^{\rm b}$ The crystallization temperature measured on the second cooling at 10 $^{\circ}{\rm C}/{\rm min}.$

the relative degree of crystallization at temperature t, X_c (T), can be calculated from the following equations:

$$1 - X_{\rm c}(T) = \exp\left[-\frac{K(T)}{|a|^m}\right]$$
(5)

$$\log[-\ln(1 - X_{c}(T))] = \log K(T) - m \log a$$
(6)



(b)

Fig. 6. Relative crystallinity versus temperature for non-isothermal crystallization of (a) PEN and (b) PEN/silica 0.9 wt% at various cooling rates.



Fig. 7. Relative crystallinity versus time for non-isothermal crystallization of (a) PEN and (b) PEN/silica 0.9 wt% at various cooling rates.

where *a* is the cooling rate, K(T) is a function related to the overall crystallization rate that indicates how fast crystallization proceeds, and m is the Ozawa exponent that depends on the dimension of crystal growth. By plotting log[- $\ln(1 - X_c(T))$] against log a at a given temperature, a straight line should be obtained if the Ozawa analysis is valid, and the kinetic parameters m and K(T) can be derived from the slope and the intercept, respectively. The results of the Ozawa analysis for PEN and silica nanoparticle-filled PEN composites are shown in Fig. 8. Accurate analysis of the non-isothermal crystallization data could not be performed because of the curvature in the plots. The nonisothermal crystallization of PEN and silica nanoparticlefilled PEN composites did not follow the Ozawa equation, probably because of the disregarded assumptions in Ozawa's theory. First, slow secondary crystallization was not considered. This could lower the determined values of the Ozawa exponent. The other factor disregarded in Ozawa's theory is the folded length of the polymer chain, which is a function of the crystallization temperature. If changes in folded chain length depend upon the temperature during dynamic crystallization, the folded chain length should be considered in the derivation of the theory [22].



Fig. 8. Ozawa plots of $\ln[-\ln(1 - X_c(T))]$ versus $\ln a$ for crystallization of (a) PEN and (b) PEN/silica 0.9 wt%.

Lee and Cakmak [23] have also reported that the Ozawa analysis could not describe the non-isothermal crystallization of PEN.

The alternative approach adopted here was the Avrami equation. The Avrami theory has been widely used for the interpretation of the isothermal crystallization process [24, 25]. While the Avrami equation was developed to describe isothermal crystallization kinetics, it has also been used to describe non-isothermal processes [26-28].

$$1 - X_{c}(t) = \exp(-Z_{t}t^{n}) \tag{7}$$

$$\log[-\ln(1 - X_{c}(t))] = n \log t + \log Z_{t}$$
(8)

where $X_c(t)$ is the relative degree of crystallinity at time t; the exponent n is a mechanism constant with a value depending on the type of nucleation and the growth dimension, and the parameter Z_t is a growth rate constant involving both nucleation and growth rate parameters. Although, the physical meanings of Z_t and n cannot be related to the non-isothermal case in a simple way, their use provides further insight into the kinetics of non-isothermal crystallization. Considering the non-isothermal characteristics of the process investigated, the parameter for the value of the crystallization rate, Z_t , should be corrected [26], because the temperature was constantly changing during the process. The parameter characterizing the kinetics of nonisothermal crystallization was given as follows:

$$\log Z_{\rm c} = \frac{\log Z_t}{a} \tag{9}$$

By using Eq. (7), a plot of log $[-\ln(1 - X_c(t))]$ versus log t is shown in Fig. 9. The values of the Avrami exponent n and the rate parameter Z_t could be determined from the slope and intercept, and these values are listed in Table 3. The Avrami exponent n of PEN ranged from 4.0 to 2.3 depending on the cooling rate, which indicated that the spherulite growth occurred with homogeneous nucleation. The Avrami exponents n for silica nanoparticle-filled PEN composites were less than that for PEN at the same cooling rate, indicating that the silica nanoparticles acted as heterogeneous nuclei for the initial nucleation. Therefore, the type of nucleation and the geometry of crystal growth of PEN were significantly changed by the presence of the silica nanoparticles. However, the Avrami equation for the nonisothermal crystallization was valid for the early stages of the crystallization due to the secondary crystallization of the polymers [19,29,30].

Liu et al. [29] proposed a different kinetic equation by

combining the Ozawa and Avrami equations. As the degree of crystallinity was related to the cooling rate a and the crystallization time t (or temperature T), the relation between a and t could be defined for a given degree of crystallinity. Consequently, a new kinetic equation for non-isothermal crystallization was derived by combining Eqs. (6) and (8):

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

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

where the parameter $F(T) = [K(T)/Z_t]^{1/m}$, the Avrami exponent *n* is calculated using Ozawa's method, and *b* is the ratio between the Avrami and Ozawa exponents, i.e. b = n/m. F(T) refers to the value of the cooling rate chosen at unit crystallization time, when the system has a defined degree of crystallinity. It can be seen that F(T) has a definite physical and practical meaning. According to Eq. (11), at a given degree of crystallinity the plot of log *a* against log *t* will give a straight a line with an intercept of log F(T) and a slope of -b. As shown in Fig. 10, plotting log *a* against log *t* gave a linear relationship at a given degree of crystallinity, and the values of F(T) and *b* are listed in Table 4. The F(T)values increased with the relative degree of crystallinity, and *b* ranged from 0.95 to 1.11 for PEN, and from 1.28 to



Fig. 9. Avrami plots of $\log[-\ln(1 - X_c(t))]$ versus $\ln t$ for crystallization of (a) PEN and (b) PEN/silica 0.9 wt%.



Fig. 10. $\log a$ versus $\log t$ from the combined Avrami and Ozawa equation for (a) PEN and (b) PEN/silica 0.9 wt%.

a (°C/min)	PEN-Pu	re	PEN/silica 0.3%		PEN/silica 0.5%		PEN/silica 0.7%		PEN/silica 0.9%	
	n	Z _c	n	Z _c	n	$Z_{\rm c}$	n	Z _c	n	$Z_{\rm c}$
2.5	4.0	0.17	3.2	0.31	3.1	0.37	3.0	0.40	3.0	0.42
5	3.7	0.48	2.9	0.62	2.9	0.67	2.8	0.73	2.8	0.80
10	3.2	0.76	2.7	0.87	2.7	0.87	2.6	0.89	2.6	0.90
15	2.8	0.87	2.5	0.93	2.5	0.94	2.5	0.97	2.4	0.99
20	2.7	0.94	2.5	0.98	2.3	1.05	2.2	1.07	2.1	1.07
25	2.5	0.97	2.3	1.07	2.3	1.13	2.1	1.10	2.1	1.10
30	2.3	0.99	2.0	1.10	2.0	1.20	1.9	1.12	1.7	1.15

Table 3 Values of n and Z_c for PEN and silica nanoparticle-filled PEN composites obtained from Avrami analysis for non-isothermal crystallization processes

1.65 for silica nanoparticle-filled PEN composites. These equations successfully describe the non-isothermal crystallization process of PEN and silica nanoparticle-filled PEN composites as they have done for polypropylene/Montmorillonite nanocomposites [17], Nylon-11 [30], and polyoxymethylene/Montmorillonite nanocomposites [31].

3.4. Nucleation activity

Dobreva et al. [32-34] suggested a simple method for calculating the nucleation activity of foreign substrates in polymer melt. Nucleation activity (ϕ) is a factor by which the work of three-dimensional nucleation decreases with the addition of a foreign substrate. If the foreign substrate is extremely active, ϕ approaches 0, while for inert particles, ϕ approaches 1. For homogeneous nucleation from a melt near the melting temperature, the cooling rates can be written as:

$$\log r = A - \frac{B}{2.3\Delta T_{\rm p}^2} \tag{12}$$

while for the heterogeneous case,

$$\log r = A - \frac{B^*}{2.3\Delta T_{\rm p}^2}$$
(13)

$$\phi = \frac{B^*}{B} \tag{14}$$

where r is the cooling rate, A is a constant, and $\Delta T_{\rm p}$ is the

Table 4 The values of b and F(T) versus degree of crystallinity from Eq. (11) for

PEN and silica nanoparticle-filled PEN composites

1		1				
$X_{\rm c}(t)$ (%) or $X_{\rm c}(T)$ (%)		20	40	60	80	
PEN-Pure	b	0.95	1.03	1.05	1.11	
	$\log F(T)$	1.25	1.37	1.47	1.57	
PEN/silica 0.3%	b	1.28	1.30	1.32	1.35	
	$\log F(T)$	1.30	1.42	1.54	1.62	
PEN/silica 0.5%	b	1.29	1.34	1.36	1.34	
	$\log F(T)$	1.31	1.44	1.54	1.65	
PEN/silica 0.7%	b	1.32	1.34	1.38	1.40	
	$\log F(T)$	1.30	1.42	1.60	1.63	
PEN/silica 0.9%	b	1.35	1.32	1.38	1.41	
	$\log F(T)$	1.31	1.41	1.58	1.61	

degree of supercooling, i.e. $\Delta T_p = T_m - T_p$, and T_p is the temperature corresponding to the peak temperature of the DSC crystallization curves. *B* is a parameter that can be calculated from the following equation:

$$B = \frac{\omega \sigma^3 V_{\rm m}^2}{3nkT_{\rm m}\Delta S_{\rm m}^2 n} \tag{15}$$

where ω is a geometrical factor; σ is the specific energy, $V_{\rm m}$ is the molar volume of the crystallizing substance, *n* is the Avrami exponent, $\Delta S_{\rm m}$ is the entropy of melting, and *k* is the Boltzman constant. Therefore, the nucleation activity, ϕ , was simply calculated by the ratio of the slopes, log *r* versus $1/\Delta T^2$, with and without the nucleation agent, by using Eqs. (12) and (13). Plots of log *r* versus $1/\Delta T^2$ for PEN and silica nanoparticle-filled PEN composites are shown in Fig. 11. In these systems, nucleation activities of silica nanoparticle-filled PEN composites were calculated as 0.95, 0.91, 0.88, and 0.71, respectively. From these results, it can be seen that the nucleation effect increased with increasing silica content, indicating that the fumed silica was acting effectively as a nucleation agent in the PEN matrix [35].

3.5. Spherulite growth rates

Image analysis is a useful method for analyzing the actual spherulite growth shapes and rates during the



Fig. 11. Plots of log r versus $1/\Delta T^2$ for PEN and silica nanoparticle-filled PEN composites.

crystallization process. The spherulite growth rates of PEN and silica nanoparticle-filled PEN composites during isothermal crystallization process are shown in Figs. 12 and 13. In this research, spherulite growth rates of PEN and silica nanoparticle-filled composites were analyzed only for the initial stages of growth, because it was difficult to analyze spherulite images after the particles impinged on each other. As expected, spherulite growths of PEN and silica nanoparticle-filled PEN composites increased with the isothermal crystallization temperatures. The spherulite growth rates calculated from plots of the slope of the radius of spherulite particles against time increased with the silica content. By adding silica nanoparticles, spherulite growth rates of the composites increased with increasing silica content, because the silica particles acted as nucleation agents in the PEN matrix.

3.6. Crystallization activation energy

Considering the influence of the cooling rates on the nonisothermal crystallization process, Kissinger proposed that the activation energy could be determined by calculating the variation of the crystallization peak with cooling rate [36]:

$$\frac{\left[\ln(\phi/T_{\rm p}^2)\right]}{d(1/T_{\rm p})} = \frac{-\Delta E}{R}$$
(16)

where *R* is the gas constant and T_p is the crystallization peak temperature. The crystallization activation energy (ΔE) was calculated from the slope of $\ln[\phi/T_p^2]$ versus $1/T_p$. As shown in Fig. 14, the crystallization activation energies of PEN and silica nanoparticle-filled PEN composites during nonisothermal crystallization were determined to be 105, 91, 86, 79, and 75 kJ/mol, respectively. It can be seen that the crystallization activation energy of the composites was reduced as the silica content increased. From the above results, the silica nanoparticles made the molecular chains of PEN easier to crystallize, and accelerated the crystallization rates during non-isothermal crystallization process.



Fig. 12. Radius of spherulite versus crystallization time for PEN at various crystallization temperatures.



Fig. 13. The spherulite growth rate for PEN and silica nanoparticle-filled PEN composites for various crystallization temperatures.

4. Conclusion

Silica nanoparticle-filled PEN composites were meltblended to improve the mechanical and rheological properties of PEN. Total torque values and melt viscosity of the composites were reduced as the silica content increased because it acted as a lubricant in the PEN matrix. Such additions could be proposed as possibly improving the processability and various applications of PEN.

Crystallization peaks were shifted to higher temperatures, and the overall crystallization time, which indicated that the time to crystallize during non-isothermal crystallization process was reduced by the silica content. The degree of crystallinity of silica nanoparticle-filled PEN composites was increased with the silica content at a given cooling rate during the non-isothermal crystallization process.

The method developed by Liu et al., which combines the theories of Avrami and Ozawa, was successful in describing the non-isothermal crystallization process of PEN and silica nanoparticle-filled PEN composites. The parameter F(T),



Fig. 14. Kissinger plot for evaluating non-isothermal crystallization activation energies of PEN and silica nanoparticle-filled PEN composites.

which has physical and practical significance, increased with the silica content, indicating that the crystallization rate increased with the silica content compared to PEN.

Spherulite growth rates calculated from image analysis increased with increasing silica content, and the crystallization activation energies calculated from Kissinger's method reduced as the silica content increased, as the molecular chain of PEN was more easily crystallized when silica nanoparticles were added to the PEN matrix.

Therefore, silica nanoparticles acted as nucleation agents in the PEN matrix, and the nucleation activities, which indicated the contribution of the filler to the polymer matrix, revealed that fumed silica nanoparticles had a strong nucleation effect on PEN.

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