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Polymer 47 (2006) 1379–1389
polymer
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Unique nucleation of multi-walled carbon nanotube and poly(ethylene 2,6-naphthalate) nanocomposites during non-isothermal crystallization

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Received 14 May 2005; received in revised form 7 November 2005; accepted 11 December 2005
Available online 9 January 2006

Abstract

Multi-walled carbon nanotube (MWCNT) and poly(ethylene 2,6-naphthalate) (PEN) nanocomposites are prepared by a melt blending process. There are significant dependence of non-isothermal crystallization behavior and kinetics of PEN/MWCNT nanocomposites on the MWCNT content and cooling rate. The incorporation of MWCNT accelerates the mechanism of nucleation and crystal growth of PEN, and this effect is more pronounced at lower MWCNT content. Combined Avrami and Ozawa analysis is found to be effective in describing the non-isothermal crystallization of the PEN/MWCNT nanocomposites. The MWCNT in the PEN/MWCNT nanocomposites exhibits much higher nucleation activity than any nano-scaled reinforcement. When a vary small quantity of MWCNT was added, the activation energy for crystallization is lower, then gradually increased, and becomes higher than that of pure PEN above 1.0 wt% MWCNT content. The incorporation of MWCNT improves the storage modulus and loss modulus of PEN/MWCNT nanocomposites.

Keywords: Carbon nanotube (CNT); Crystallization; Polymer nanocomposites

1. Introduction

During the rapid advances of science and technology in various industries, extensive research and development has undertaken on high-performance polymer composites for targeted applications in numerous industrial fields. Furthermore, a number of efforts have been made to develop high-performance polymeric materials, with the benefit of nanotechnology, in fields ranging from the scientific to the industrial. These projects include studies of polymer nanocomposites with the introduction of nano-scaled reinforcement into the polymer matrix [1]. Carbon nanotubes (CNT), which were discovered by Iijima [2] in 1991, have attracted a great deal of interest, both as advanced reinforcements and in a wide range of potential scientific and industrial applications. Moreover, this discovery has created a high level of activity in materials research, leading to a practical realization of the extraordinary properties of CNT, with their almost infinite number of possibilities for new materials. CNT that consist of concentric cylinders of graphite layers are a new form of carbon, and can be classified into two types [2,3]: single-walled carbon nanotubes (SWCNT), and multi-walled carbon nanotubes (MWCNT). SWCNT consist of a single layer of carbon atoms through the thickness of the cylindrical wall, with diameters of 1.0–1.4 nm, while MWCNT consist of several layers of coaxial carbon tubes, the diameters of which range from 10 to 50 nm with length of more than 10 μm [2–4]. The graphite nature of the nanotube lattice results in a fiber with high strength, stiffness, and conductivity [5]. Both theoretical and experimental approaches investigating the mechanical properties of CNT suggest that the elastic modulus of CNT may exceed 1.0 TPa with a tensile strength in the range of 10–50 GPa [6–9].

For these reasons, extensive research and development have been directed towards the potential applications of CNT as novel materials for use in many industrial fields. The fundamental research progressed to date on applications of CNT suggests that CNT can be utilized as a promising reinforcement in new kinds of polymer nanocomposites. They are on the scale of nanometers and exhibit remarkable physical characteristics, such as high aspect ratio and high mechanical properties [10]. However, because of their high cost and limited availability, only a few applications in industrial fields have been realized to date.

Currently, three processing techniques are in common use to incorporate CNT into a polymer matrix for fabricating

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doi:10.1016/j.polymer.2005.12.042

CNT/organic polymer nanocomposites: solution mixing or film casting, in situ polymerization, and melt compounding [11–14]. Of these processing techniques, melt compounding has been accepted as the most simple and effective methodm from both an economic and industrial perspective, because this process makes it possible to fabricate high-performance nanocomposites at low cost, and facilitates commercial scale-up.

In general, MWCNT have inferior mechanical performance compared with SWCNT. However, MWCNT have a cost advantage, in that they can be produced in much larger quantities at lower cost compared with SWCNT. In addition, MWCNT are usually individual, longer than SWCNT, and more rigid because of their larger cross section. Because of their high aspect ratio and excellent axial strength, MWCNT are regarded as prospective reinforcements in high-performance nanocomposites. Furthermore, the combination of MWCNT with conventional thermoplastic polymers may provide attractive possibilities to improve the mechanical properties of polymer nanocomposites. The mechanical properties of polymers or polymer composites are influenced by both their morphology and crystallization behavior [15,16]. The crystallization behavior of polymer composites and their crystallization kinetics as a function of processing conditions are of great importance in polymer processing, particularly for the analysis and design of processing operations. Therefore, the crystallization behavior and structural development of CNT-reinforced polymer nanocomposites should be analyzed to realize the full potential of CNT for application in thermoplastic matrix-based polymer nanocomposites. From an industrial perspective, it is very important to understand the non-isothermal crystallization behavior of polymers, particularly if processing techniques for preparing engineering plastics under non-isothermal conditions are being considered. The processing of polymer composites involves complex deformation behaviors, which may affect the nucleation and crystallization behavior of polymer composites. Thus, it is also important to characterize the nucleation and crystallization behavior of polymer composites to optimize the process conditions. However, the crystallization behavior of MWCNT-reinforced polymer nanocomposites has rarely been investigated to date, and most of existing research involves CNT-filled isotactic polypropylene (*i*PP), due to the various crystal modifications and potential industrial applications of *i*PP [17,18]. Few reports can be found in the literature regarding the effect of MWCNT on the non-isothermal crystallization of conventional polyesters.

In this research, MWCNT-reinforced poly(ethylene 2,6-naphthalate) (PEN) nanocomposites were prepared by melt blending to create advanced materials for possible practical applications in various industrial fields. To our knowledge, an attempt to disperse MWCNT in a PEN matrix and to fabricate PEN/MWCNT nanocomposites has not been previously investigated. The crystallization behavior and nucleation effects of the PEN/MWCNT nanocomposites were investigated using non-isothermal crystallization kinetics analysis. The effect of MWCNT on the unique nucleation and crystallization behaviors of PEN during non-isothermal crystallization process are presented. In addition, the dynamic mechanical properties of the PEN/MWCNT nanocomposites were investigated.

2. Experimental

2.1. Materials and preparation

The thermoplastic polymer used was PEN with an intrinsic viscosity of 0.97 dL/g, supplied by Hyosung Corp., Korea. The nanotubes used were MWCNT (degree of purity: >95%) synthesized by a thermal chemical vapor deposition (CVD) process, purchased from Iljin Nanotech Co., Korea. All materials were dried at 120 °C in vacuo for at least 24 h before use, to minimize the effects of moisture. MWCNT-reinforced PEN nanocomposites were prepared by a melt blending process in a Haake rheometer (Haake Technik GmbH, Germany) equipped with a twin-screw. The temperature of the heating zone, from the hopper to the die was set to 280, 290, 295, and 285 °C, and the screw speed was fixed at 20 rpm. For the fabrication of PEN/MWCNT nanocomposites, PEN was melt blended with the addition of various MWCNT content, specified as 0.1, 0.5, 1.0, and 2.0 wt% in the polymer matrix, respectively.

2.2. Characterizations

The thermal behavior of PEN/MWCNT nanocomposites was measured with a TA Instrument 2010 DSC over a temperature range of 30–295 °C at a scan rate of 10 °C/min. The samples were heated to 295 °C at a heating rate of 10 °C/min, held at 295 °C for 8 min to eliminate any previous thermal history and then cooled to room temperature at a cooling rate of 10 °C/min. Non-isothermal crystallization kinetics were investigated by cooling samples from 295 to 30 °C at constant cooling rates of 2.5, 5, 10, 15, and 20 °C/min. Thermogravimetric analysis of the PEN/MWCNT nanocomposites was performed with a TA Instrument SDF-2960 TGA over a temperature range of 30–800 °C at a heating rate of 10 °C/min. Dynamic mechanical analysis of the PEN/MWCNT nanocomposites was performed with a TA Instrument Q-800 dynamic mechanical thermal analyzer (DMTA) using a tensile mode at a fixed frequency of 1 Hz, over a temperature range of 30–250 °C at a heating rate of 5 °C/min. The morphology of pristine MWCNT and the PEN/MWCNT nanocomposites was observed using a JEOL JSM-6340F scanning electron microscope (SEM), and detailed morphological observations were performed using a JEOL 2000FX transmission electron microscope (TEM).

3. Results and discussion

3.1. Morphology

SEM and TEM microphotographs of pristine MWCNT are shown in Fig. 1. MWCNT exhibits highly curved and random coiled features in the PEN/MWCNT nanocomposites, which

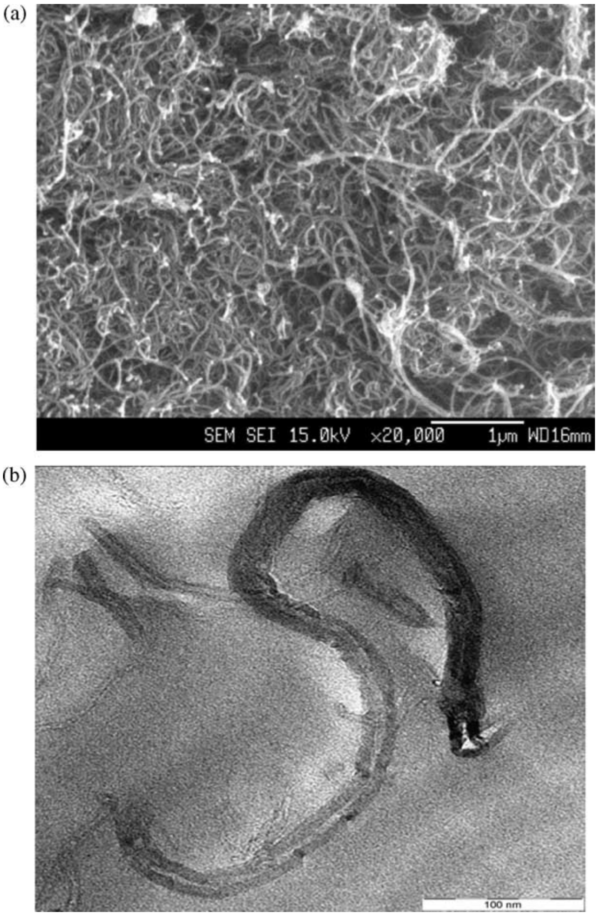

Fig. 1. (a) SEM and (b) TEM microphotographs of MWCNT.

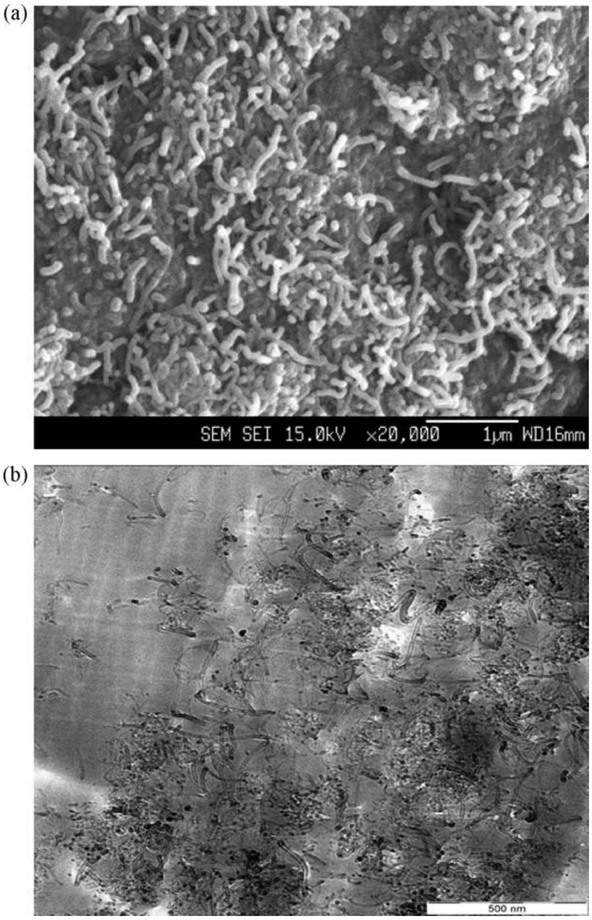

Fig. 2. (a) SEM and (b) TEM microphotographs of PEN/MWCNT 2.0 nanocomposites.

may be attributed to hydrogen bonding and van der Waals attractive interactions between carbon nanotubes [19,20]. The diameters of the MWCNT were approximately 10–30 nm, with a length of several micrometers, implying a high aspect ratio for the MWCNT. The morphologies of the PEN/MWCNT nanocomposites are shown in Fig. 2. From the SEM microphotograph of the fractured PEN/MWCNT nanocomposite, it can be seen that MWCNT form entangled structures in the PEN matrix. In addition, the TEM image shows that MWCNT were randomly dispersed in the PEN matrix, with some entanglements or bundles of MWCNT, indicating highly aggregated MWCNT and weak interactions with the PEN matrix. On a larger scale, however, the MWCNT were uniformly dispersed in the PEN matrix, despite some aggregated MWCNT structures. Research currently in progress is aimed at an improvement in the dispersion of carbon nanotubes at the nano-scale level as well as micro-scale, and functionalization of the carbon nanotubes.

3.2. Thermal behavior

The thermal stability of polymer composites is one of the most important factors for polymer processing and targeted industrial application of polymers. The thermal decomposition temperatures and the residual yields of the PEN/MWCNT nanocomposites increased with increasing MWCNT content, implying that thermal decomposition of the PEN/MWCNT nanocomposites was retarded by incorporating MWCNT into the PEN matrix with higher residual yield. This result may be attributed to a physical barrier effect, resulting from the fact that the fillers would prevent the transport of decomposition products in the PEN/MWCNT nanocomposites [21]. Therefore, the incorporation of a very small quantity of MWCNT significantly improved the thermal stability of the PEN/MWCNT nanocomposites.

DSC heating and cooling traces for the PEN/MWCNT nanocomposites as a function of MWCNT content at a scan rate of 10 °C/min are shown in Fig. 3. The incorporation of MWCNT had little effect on the glass transition and melting temperatures of the PEN/MWCNT nanocomposites. The incorporation of MWCNT into the PEN matrix increased the crystallization temperature of the PEN/MWCNT nanocomposites, with this increment being greatest with lower MWCNT content. This result confirms that the incorporation of a very small quantity of MWCNT enhances the nucleation of PEN crystallization. The MWCNT promote the formation of heterogeneous nuclei, with lower energy consumption required to reach critical stability for crystal growth [22], resulting in them functioning as effective nucleating agents in the PEN matrix. The crystallization peak temperatures of the PEN/MWCNT nanocomposites at various cooling rates are shown

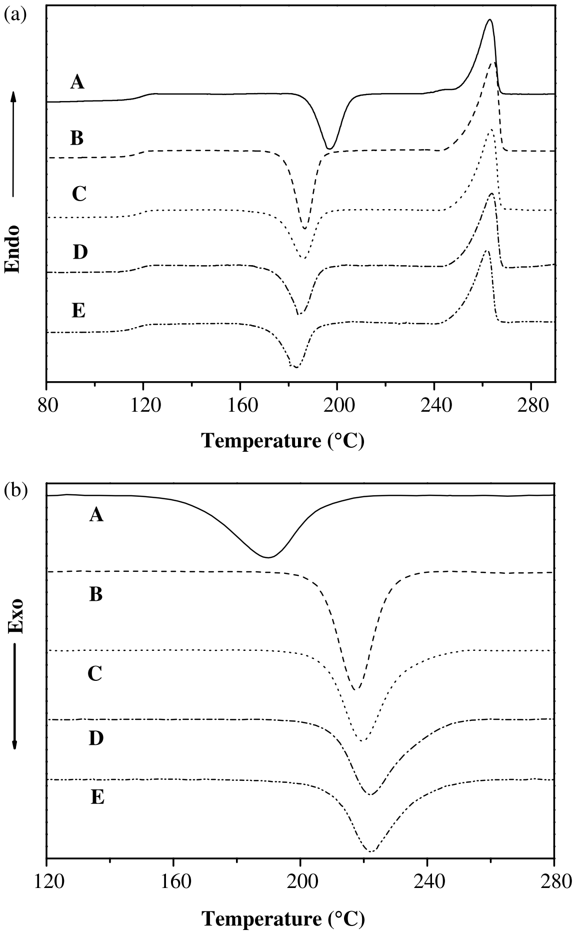

Fig. 3. DSC (a) heating and (b) cooling curves of PEN/MWCNT nanocomposites as a function of MWCNT content (A: PEN; B: PEN/MWCNT 0.1; C: PEN/MWCNT 0.5; D: PEN/MWCNT 1.0, and E: PEN/MWCNT 2.0).

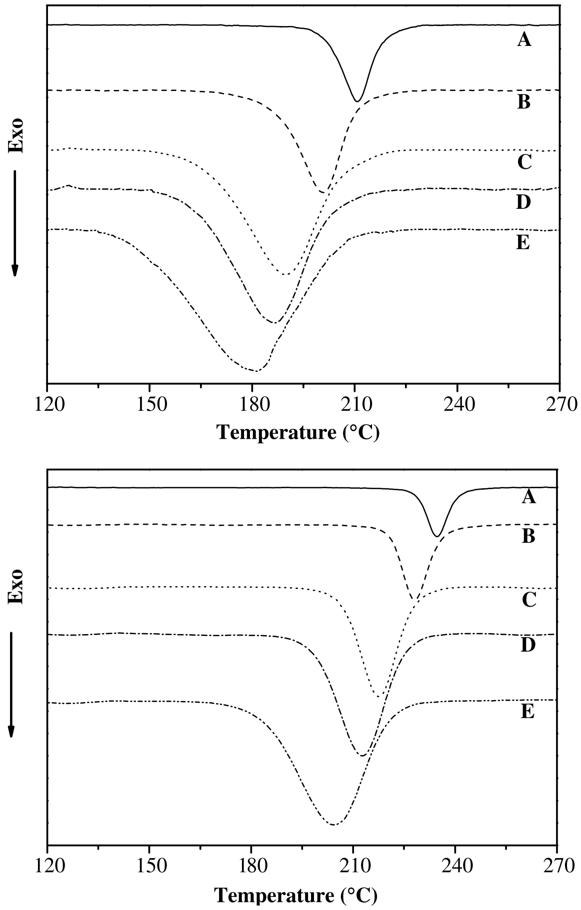

Fig. 4. Non-isothermal crystallization curves of (a) PEN and (b) the PEN/MWCNT 0.1 nanocomposite at various cooling rates (A: 2.5; B: 5; C: 10; D: 15, and E: 20 °C/min).

in Fig. 4. As the cooling rate increased, the crystallization peak temperature range becomes broader and shifts to lower temperatures for PEN and the PEN/MWCNT 0.1 nanocomposites. 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 [23]. With increasing the cooling rate, the crystallization peak temperature corresponding to the maximum crystallization rate shifted to lower temperature, indicating that the lower the cooling rate, the earlier crystallization occurs. In addition, at a given cooling rate, the peak temperature of the PEN/MWCNT nanocomposites were higher than that of pure PEN, and the overall crystallization time decreased with the incorporation of MWCNT. In general, homogeneous nucleation started spontaneously below the melting temperature and required longer times, whereas heterogeneous nuclei formed as soon as the specimens reached the crystallization temperature [24–26]. Therefore, the crystallization of the PEN/MWCNT nanocomposites proceeds through heterogeneous nucleation by MWCNT. DSC results for the PEN/MWCNT nanocomposites as a function of MWCNT content are shown in Table 1. The increase in the crystallization temperature of the PEN/MWCNT nanocomposites with increasing MWCNT content, together with the fact that the PEN/MWCNT nanocomposites have a lower degree of supercooling ($\Delta T = T_m - T_c$) for crystallization with increasing MWCNT content, suggests that MWCNT can effectively act as nucleating agents in the PEN/MWCNT nanocomposites. As shown in Table 1, the degree of crystallinity of the PEN/MWCNT nanocomposites was increased by the MWCNT content, which may be explained by the supercooling temperature. The MWCNT acts as a strong nucleating agent in the PEN matrix under non-isothermal crystallization conditions, and the crystallization temperature shifts to higher temperature, implying that the supercooling of the PEN/MWCNT nanocomposites at a given cooling rate was decreased by the MWCNT. When a polymer crystallized with less supercooling, it crystallized more perfectly than with more supercooling [25,26], and thus, the degree of crystallinity of the PEN/MWCNT nanocomposites increased with the MWCNT content at a given cooling rate.

3.3. Non-isothermal crystallization behavior

From a practical industrial point of view, it is very important to characterize the non-isothermal crystallization behavior of polymeric materials, because the processing of polymers or polymer composites is performed under non-isothermal

Table 1
DSC results for the PEN/MWCNT nanocomposites with MWCNT content

Materials	T_g (°C)	T_c[a]		T_m		T_c[b] (°C)	ΔT[c] (°C)	X_c[d] (%)
		Peak (°C)	ΔH_c (J/g)	Peak (°C)	ΔH_m (J/g)			
PEN	119.9	199.9	17.4	266.6	38.9	203.8	62.8	20.8
PEN/MWCNT 0.1	118.1	188.8	16.5	266.9	39.6	228.0	38.9	22.3
PEN/MWCNT 0.5	118.8	187.7	14.1	266.8	40.9	228.2	38.1	25.9
PEN/MWCNT 1.0	118.4	186.8	11.8	266.3	41.5	229.2	37.6	28.7
PEN/MWCNT 2.0	118.0	186.1	9.9	265.8	42.1	229.7	36.1	31.1

[a] Crystallization temperature measured on the second heating at 5 °C/min.
[b] Crystallization temperature measured on the second cooling at 5 °C/min.
[c] Degree of supercooling, $\Delta T = T_m - T_c$.
[d] Degree of crystallinity, $X_c(\%) = [(\Delta H_f - \Delta H_c)/\Delta H_f^0] \times 100$ ($\Delta H_f^0 = 103.4$ J/g is the heat of fusion of an infinitely thick crystal) (Ref. [25]).

conditions during fabrication of engineering plastics. The relative degree of crystallinity, $X(T)$ as a function of temperature, can be defined as follows

$$X(T) = \frac{\int_{T_0}^{T} (\mathrm{d}H_c/\mathrm{d}T)\mathrm{d}T}{\int_{T_0}^{T_\infty} (\mathrm{d}H_c/\mathrm{d}T)\mathrm{d}T} \tag{1}$$

where T_0 and T_∞ are the initial and final crystallization temperature, respectively. The relative degree of crystallinity as a function of temperature for PEN and the PEN/MWCNT 0.1 nanocomposites at various cooling rates is shown in Fig. 5. It can be seen that all the curves have similar sigmoidal shapes and that crystallization occurred at lower temperature with increasing cooling rate, indicating that at slower cooling rates there is sufficient time to activate nuclei at higher temperatures, and thus, crystallization nucleates at higher temperatures with slower cooling rates [27]. During non-isothermal crystallization, the relationship between crystallization temperature (T) and crystallization time (t) can be represented as follows:

$$t = \frac{T_0 - T}{a} \tag{2}$$

where T_0 is the initial temperature at which crystallization begins ($t = 0$) and a is the cooling rate. Thus, the abscissa of the temperature in Fig. 5 can be transformed into the time scale as shown in Fig. 6, according to the Eq. (2). Crystallization of the PEN/MWCNT nanocomposites occurred at higher temperature and over a longer time with decreasing cooling rate, suggesting that the crystallization may be controlled by a nucleation. Crystallization occurred at higher temperature with decreasing cooling rate, indicating that crystallization nucleated at higher temperature with slower cooling rates. The time taken to complete crystallization reduced with increasing cooling rate, and the relative degree of crystallinity of the PEN/MWCNT nanocomposites was higher than that of pure PEN at the same time for complete crystallization. The values for the peak temperature (T_p) and the crystallization half-time ($t_{1/2}$) obtained from the non-isothermal crystallization thermograms of the PEN/MWCNT nanocomposites at various cooling rates are shown in Table 2. The crystallization half-time can be defined as the time taken to complete half of the non-isothermal crystallization process, i.e. the time required to attain a relative degree of crystallinity of 50%. It can be seen that the T_p and $t_{1/2}$ values for the PEN/MWCNT nanocomposites decreased with increasing cooling rate, indicating that the higher the cooling rate, the shorter the time for complete crystallization. In addition, for a given cooling rate, the T_p values for the PEN/MWCNT nanocomposite are higher than that for pure PEN, while the $t_{1/2}$ values are lower than that for pure PEN. Therefore, the

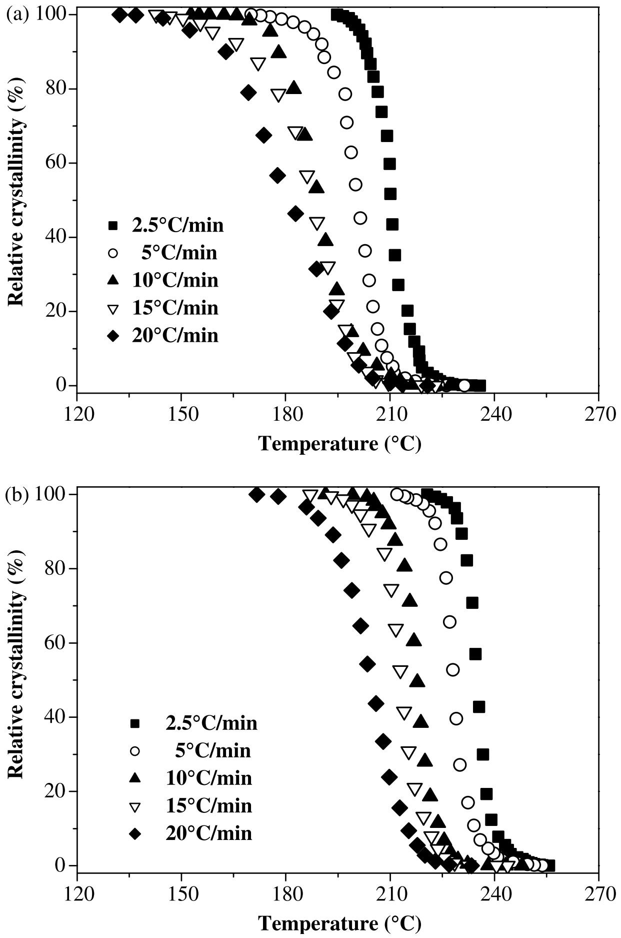

Fig. 5. Relative degree of crystallinity of (a) PEN and (b) the PEN/MWCNT 0.1 nanocomposite as a function of temperature at various cooling rates.

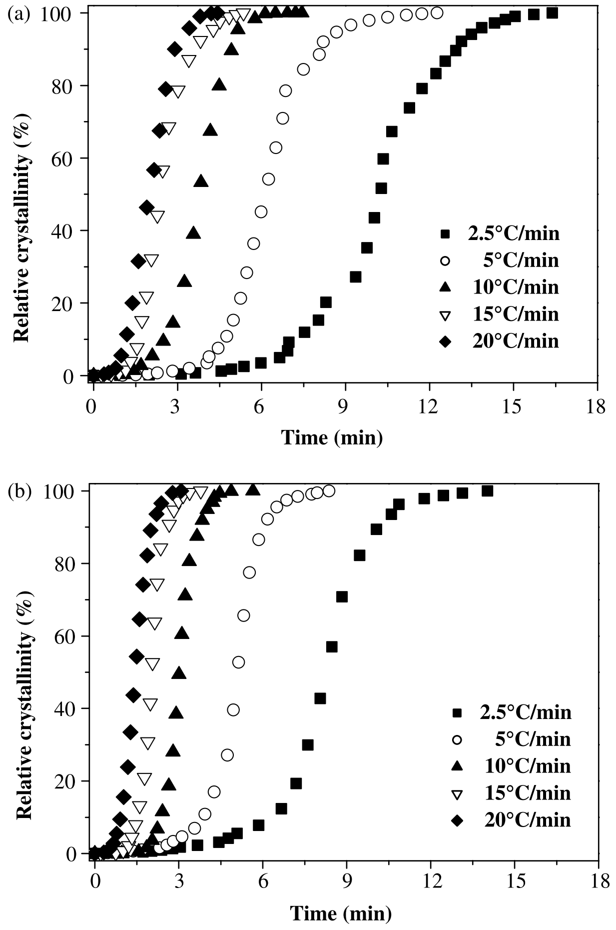

Fig. 6. Relative degree of crystallinity of (a) the PEN and (b) the PEN/MWCNT 0.1 nanocomposites as a function of time at various cooling rates.

incorporation of MWCNT into the PEN matrix increases the crystallization rate of PEN. In order to investigate the effect of MWCNT content on the $t_{1/2}$ values for the PEN/MWCNT nanocomposites, the variation and normalization of the $t_{1/2}$ values, with respect to those for the PEN matrix, are shown in Fig. 7. It can be seen that the lowering of the $t_{1/2}$ values by MWCNT is more pronounced at lower concentration. This result suggests that a lower MWCNT content is more effective for enhancing the crystallization of the PEN matrix.

Non-isothermal crystallization kinetics can be analyzed by using the extension of the Avrami theory [28] proposed by Ozawa [29]. This analysis accounts for the effect of cooling rate on crystallization from the melt by replacing the time variable in the Avrami equation with a variable cooling rate term, that is, by replacing t in Eq. (3) with T/a as shown in Eq. (4)

$$1-X(T) = \exp(-Z_t t^n) \tag{3}$$

$$1-X(T) = \exp\left[-\frac{K(T)}{a^m}\right] \tag{4}$$

where $X(T)$ is the relative degree of crystallinity; the exponent n is a mechanism constant depending on the type of nucleation and growth dimension; Z_t is a growth rate constant involving both

Table 2
Parameters of PEN/MWCNT nanocomposites during non-isothermal crystallization

Materials	Cooling rate (°C/min)	T_p (°C)	Z_c	n	$t_{1/2}$ (min)
PEN	2.5	210.8	9.59×10^{-7}	5.58	10.25
	5	201.0	4.31×10^{-6}	5.81	6.12
	10	190.0	1.11×10^{-3}	4.82	3.98
	15	187.0	1.13×10^{-2}	4.70	2.36
	20	181.3	5.89×10^{-2}	3.89	2.02
PEN/ MWCNT 0.1	2.5	234.6	2.64×10^{-3}	5.81	8.25
	5	228.1	9.65×10^{-2}	5.96	5.09
	10	217.5	4.19×10^{-1}	6.47	3.02
	15	212.5	7.21×10^{-1}	5.36	2.03
	20	204.1	9.10×10^{-1}	6.03	1.43
PEN/ MWCNT 0.5	2.5	235.4	2.92×10^{-3}	6.15	9.59
	5	228.2	1.57×10^{-1}	5.11	5.85
	10	218.3	5.16×10^{-1}	5.07	3.06
	15	213.2	7.11×10^{-1}	5.15	2.36
	20	205.1	8.23×10^{-1}	5.32	1.89
PEN/ MWCNT 1.0	2.5	235.8	4.58×10^{-3}	5.80	9.68
	5	229.2	1.34×10^{-1}	5.48	5.92
	10	220.0	6.31×10^{-1}	4.79	3.12
	15	216.8	7.59×10^{-1}	5.12	2.50
	20	209.0	8.19×10^{-1}	5.52	1.96
PEN/ MWCNT 2.0	2.5	238.0	2.31×10^{-3}	6.42	9.97
	5	229.7	1.26×10^{-1}	5.57	6.09
	10	222.1	5.16×10^{-1}	5.42	3.46
	15	218.6	7.44×10^{-1}	4.89	2.52
	20	211.6	8.21×10^{-1}	4.60	2.07

nucleation and growth rate parameters; a is the cooling rate; m is the Ozawa exponent depending on the dimension of crystal growth, and $K(T)$ is the cooling function related to the overall crystallization rates. Parameters such as Z_t and n have an explicit physical meaning relating to isothermal crystallization, but in non-isothermal crystallization their physical meaning does not have the same significance, due to the constant change in

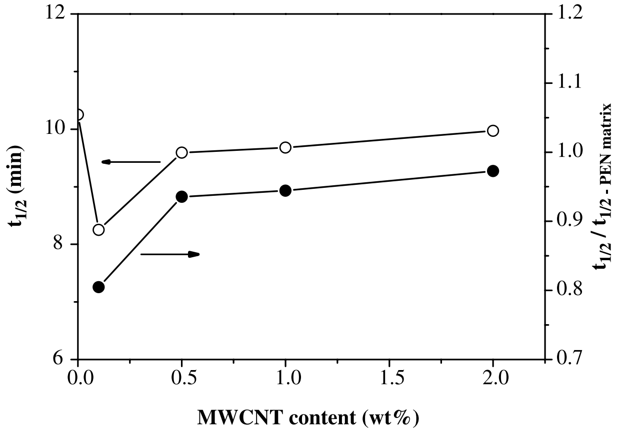

Fig. 7. Effect of MWCNT content on the half-time of crystallization ($t_{1/2}$) for PEN/MWCNT nanocomposites.

temperature, which influences both nucleation and crystal growth.

The Ozawa plot of $\log[-\ln[1-X(T)]]$ versus $\log a$ for PEN and the PEN/MWCNT nanocomposites, taking the double logarithmic form of the Eq. (4) are shown in Fig. 8. The $X(T)$ values calculated at different temperatures decreased with increasing cooling rate at a given temperature. Some curvature in the plot was observed, indicating that the Ozawa exponent is not consistent with temperature during non-isothermal crystallization, and this makes it difficult to estimate the cooling function, $K(T)$ related to the overall crystallization rate. This result may arise due to inaccurate assumption in Ozawa's theory, and he has a disregard for the secondary crystallization and the dependence of the fold length on temperature [30–32]: slow secondary crystallization could lower the determined values of the Ozawa exponent, and if changes in fold length of polymer chains depend on the temperature during dynamic crystallization, the fold length should be considered in the deviation of the theory [30]. Therefore, we deduce that the Ozawa analysis does not effectively describe non-isothermal crystallization of PEN/MWCNT nanocomposites.

Considering the non-isothermal character of the process investigated, Jeziorny [33] suggested that the parameter, Z_t should be corrected as follows:

$$\log Z_c = \frac{\log Z_t}{a} \tag{5}$$

The values of the Avrami exponent (n) and the rate parameter (Z_t) can be determined from the slope and intercept of the plot of $\log[-\ln\{1-X(T)\}]$ versus $\log t$. The plots of $\log[-\ln\{1-X(T)\}]$ versus $\log t$ for PEN and the PEN/MWCNT 0.5 nanocomposites are shown in Fig. 9. It can be seen that the plots exhibit a poor linear relationship, consisting of three linear regions, indicating that the modified Avrami analysis does not effectively describe non-isothermal crystallization of PEN/MWCNT nanocomposites. The kinetic data in the central linear region were selected to estimate the Avrami parameter for non-isothermal crystallization of PEN and the PEN/MWCNT nanocomposites. The values of the Avrami exponent (n) and the rate parameter (Z_t) determined from the slope and intercept of the selected plots are shown in Table 2. The Avrami exponent (n) was in the range of 3.89–5.81 for the PEN, and 4.60–6.47 for the PEN/MWCNT nanocomposites, depending on cooling rate. The dependence of the crystallization kinetics on temperature is a complex function, and many theoretical models based on the Avrami equation have been developed [32–35]. As shown in Table 2, the PEN/MWCNT nanocomposites exhibited values of n

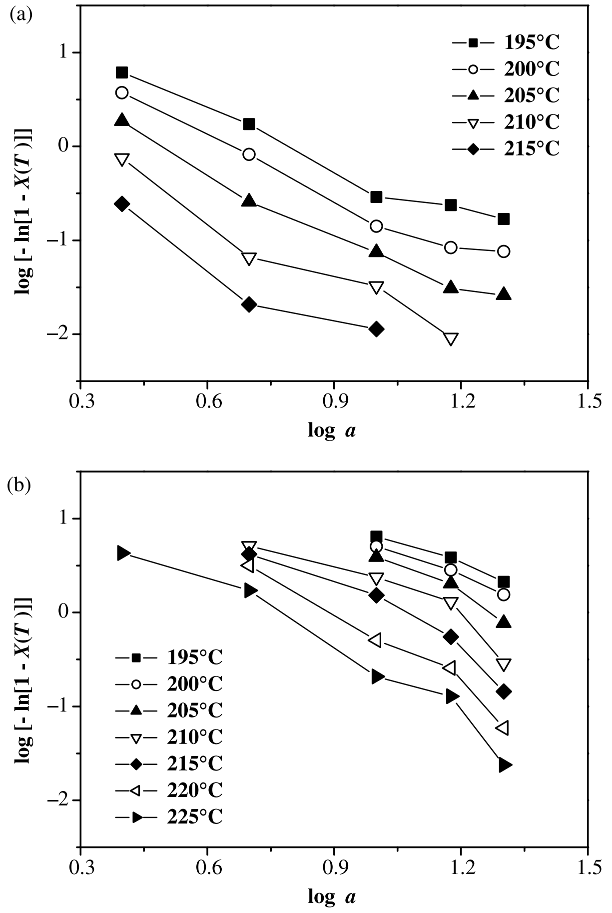

Fig. 8. Ozawa plots of (a) PEN and (b) the PEN/MWCNT 0.5 nanocomposite during non-isothermal crystallization.

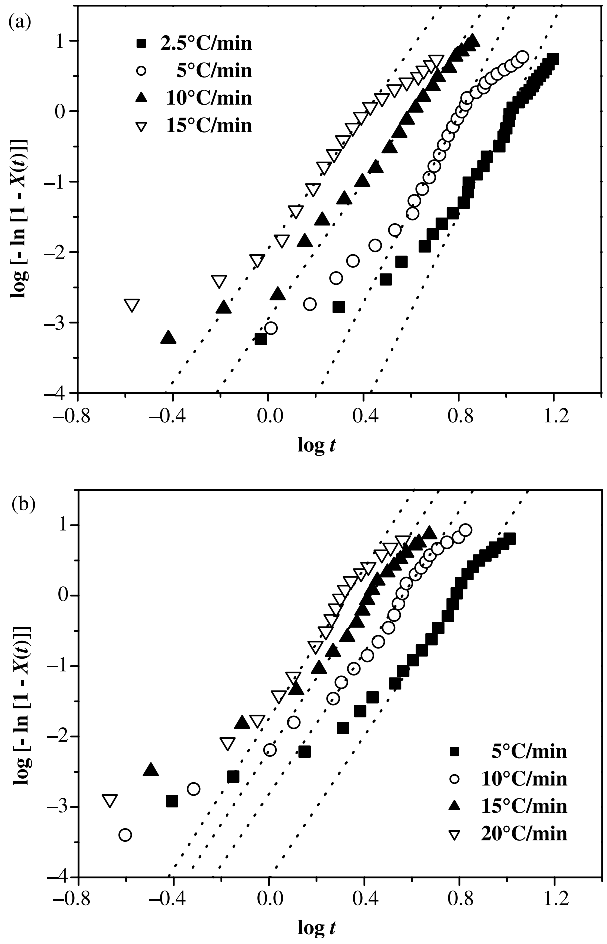

Fig. 9. Avrami plots of (a) PEN and (b) the PEN/MWCNT 0.5 nanocomposite during non-isothermal crystallization.

higher than four. This result indicates that the non-isothermal crystallization mechanism of the PEN/MWCNT nanocomposites is very complicated, suggesting that the MWCNT significantly influences the mechanism of nucleation and crystal growth of the PEN. In addition, the values of Z_c and $t_{1/2}$ decreased with increasing cooling rate.

In order to describe the non-isothermal crystallization process more effectively for comparison, Liu et al. [32] suggested a convenient procedure for characterizing non-isothermal crystallization kinetics by combining the Avrami and Ozawa equations based on the assumption that the degree of crystallinity is correlated to the cooling rate and crystallization time. Therefore, their relationship for non-isothermal crystallization can be derived by combining the Eqs. (3) and (4) as follows:

$$\log Z_t + n \log t = \log K(T) - m \log a \tag{6}$$

$$\log a = \log F(T) - b \log t \tag{7}$$

where the kinetic parameter, $F(T) = [K(T)/Z_t]^{1/m}$ represents the value of the cooling rate chosen at unit crystallization time when the systems have a defined degree of crystallinity; a is the cooling rate, and b is the ratio of the Avrami exponent (n) to the Ozawa exponent (m). From Eq. (6), the plots of log a versus log t at a certain degree of crystallinity are shown in Fig. 10, and these exhibit a good linear relationship, suggesting that this analysis may be more effective in describing the non-isothermal crystallization kinetics of PEN/MWCNT nanocomposites. The values of log $F(T)$ and b were determined from the slope and intercept of the plots are shown in Table 3. It can be seen that the value of $F(T)$ increased with increasing relative degree of crystallinity, indicating that at unit crystallization time, a higher relative degree of crystallinity was obtained with a higher cooling rate. The value of b, i.e. the ratio of the Avrami exponent to the Ozawa exponent, varied from 1.126 to 1.358, and from 1.125 to 1.362, for the PEN and the PEN/MWCNT nanocomposites, respectively. This result suggests that the presence of MWCNT as a nucleating agent influences the non-isothermal crystallization process involving the type of nucleation and crystal growth for the PEN/MWCNT nanocomposites.

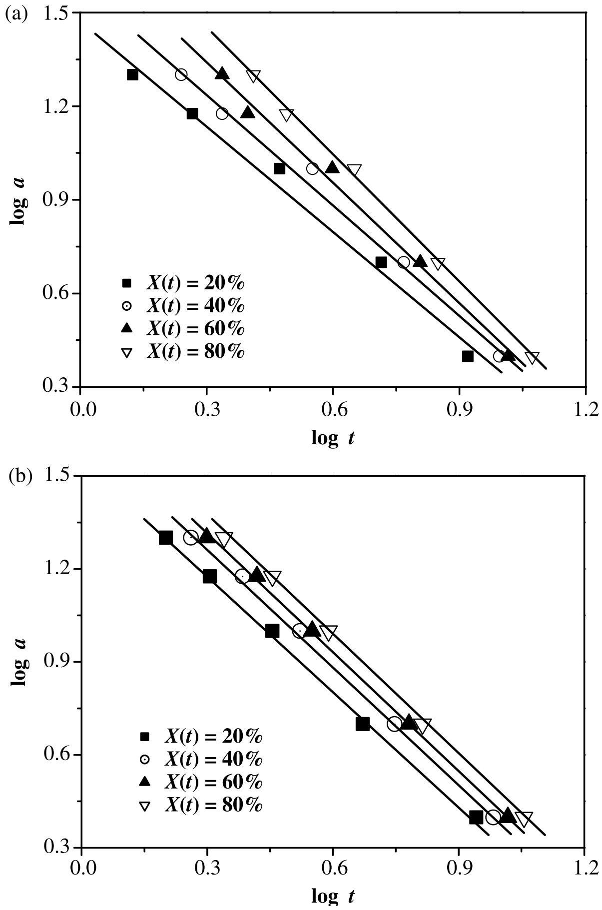

Fig. 10. Plots of log a versus log t from the combined Avrami and Ozawa equations at different relative degrees of crystallinity for the PEN/MWCNT 0.5 nanocomposite.

Table 3
Values of b and $F(T)$ for the PEN and PEN/MWCNT nanocomposites obtained from the combined Avrami and Ozawa equation

Materials	$X(T)$ (%)	log $F(T)$	B	E_a (kJ/mol)
PEN	20	1.478	1.126	138.2
	40	1.598	1.181	
	60	1.729	1.291	
	80	1.858	1.358	
PEN/MWCNT 0.1	20	1.410	1.125	128.2
	40	1.498	1.176	
	60	1.563	1.224	
	80	1.631	1.253	
PEN/MWCNT 0.5	20	1.552	1.235	136.2
	40	1.651	1.270	
	60	1.695	1.272	
	80	1.747	1.279	
PEN/MWCNT 1.0	20	1.551	1.323	155.9
	40	1.661	1.305	
	60	1.725	1.327	
	80	1.812	1.362	
PEN/MWCNT 2.0	20	1.538	1.233	159.7
	40	1.671	1.289	
	60	1.717	1.292	
	80	1.783	1.318	

3.4. Nucleation activity and activation energy for non-isothermal crystallization

For the dynamic crystallization kinetics of polymer melts in the presence of nucleating agents, Dobreva et al. [36] suggested a simple method for calculating the nucleation activity of different substrates. It is known that the nucleation activity (ϕ) is a factor by which the work of thee-dimensional nucleation decreases with the addition of a foreign substrate [36–38]. If the foreign substrate is extremely active, the nucleation activity approaches zero, while for inert particles, it is unity. For nucleation from melts near their melting temperature, the cooling rate can be represented as follows:

$$\log a = A - \frac{B}{2.3\Delta T_p^2} \tag{8}$$

where a is the cooling rate; A is a constant; ΔT_p is the degree of supercooling, i.e. $\Delta T_p = T_m - T_p$, T_p is the temperature corresponding to the peak temperature of DSC crystallization, and $B=\varpi\sigma^3V_m^2/3kT_m\Delta S_m^2n$ is a parameter related to three-dimensional nucleation (V_m is the molar volume of the crystallizing substance; ΔS_m is the entropy of melting; ϖ is a geometrical factor; σ is the specific surface energy; n is the Kolmogorov–Avrami exponent, and k is the Boltzmann constant). The nucleation activity can be calculated from the following equation [36–38]

$$\phi = \frac{B^*}{B^0} \tag{9}$$

where B^0 and B^* are the values of B for homogeneous and heterogeneous nucleations, respectively. The values of B^0 and B^* can be obtained from the slope of the plot of log a versus $1/\Delta T_p^2$, and thus, the nucleation activity can be calculated from Eq. (9) by using these values. The plots of log a versus $1/\Delta T_p^2$ for PEN and the PEN/MWCNT nanocomposites are shown in Fig. 11. The values for the nucleation activity (ϕ) of the PEN/MWCNT nanocomposites were calculated as 0.29, 0.26, 0.27, and 0.23, respectively. This result demonstrates that MWCNT acts as an excellent nucleating agent for the PEN/MWCNT nanocomposites. In our previous research on the PEN/silica nanocomposite [26], the ϕ value for silica nanoparticles was estimated to be 0.71 in the PEN matrix. For the montmorillonite/nylon 1212 nanocomposite, the ϕ value for the clay was calculated as 0.71 in the nylon 1212 matrix [23]. In addition, Alonso et al. reported that for the talc/isotactic polypropylene nanocomposite system, the ϕ value for the untreated talc was approximately 0.56, while that for the talc modified with silane coupling agent was estimated to be approximately 0.45 in the isotactic polypropylene matrix [39]. From the above results, it can be deduced that MWCNT in the PEN/MWCNT nanocomposites exhibit much higher nucleation activity than any other nano-scaled reinforcement reported to date.

The activation energy for non-isothermal crystallization can be derived from the combination of cooling rate and crystallization peak temperature, and Kissinger [40] suggested a method for calculating the activation energy for non-isothermal crystallization as follows

$$\frac{\mathrm{d}\left[\ln(\Phi/T_p^2)\right]}{\mathrm{d}(1/T_p)} = -\frac{\Delta E_a}{R} \tag{10}$$

where R is the universal gas constant; T_p is the crystallization peak temperature; Φ is the cooling rate, and ΔE_a is the crystallization activation energy. The activation energies of the non-isothermal crystallization for PEN and the PEN/MWCNT nanocomposites were obtained from the slope of the plot of $\ln(\Phi/T_p^2)$ versus $1/T_p$, according to Eq. (7), and the results are shown in Table 3. The activation energy of crystallization for PEN/MWCNT nanocomposites containing lower MWCNT content ($\leq$0.5 wt%) was lower than that of PEN, while the activation energy increased with further increasing MWCNT content compared with that of PEN. The variation in the activation energy for non-isothermal crystallization of PEN/MWCNT nanocomposites may be explained by changes in the crystallization mechanism and the free energy of nucleation with the degree of supercooling [41]. In this PEN/MWCNT nanocomposite system, the MWCNT seem to perform two functions in the PEN matrix. One is that MWCNT act as nucleating agents and may accelerate the non-isothermal crystallization of PEN/MWCNT nanocomposites, which was confirmed by the kinetic parameters determined for non-isothermal crystallization and crystallization half-time. MWCNT may also adsorb PEN molecular segments and restrict the movement of chain segments [20], thereby making crystallization difficult. The PEN molecular segments require more energy to rearrange, resulting in an increment in the activation energy of non-isothermal melt crystallization. The incorporation of MWCNT may accelerate non-isothermal crystallization of the PEN matrix. Furthermore, this effect of the MWCNT is more pronounced at lower MWCNT content ($\leq$0.5 wt%), as described in the result showing a lower activation energy and crystallization half-time for non-isothermal crystallization compared with the PEN matrix.

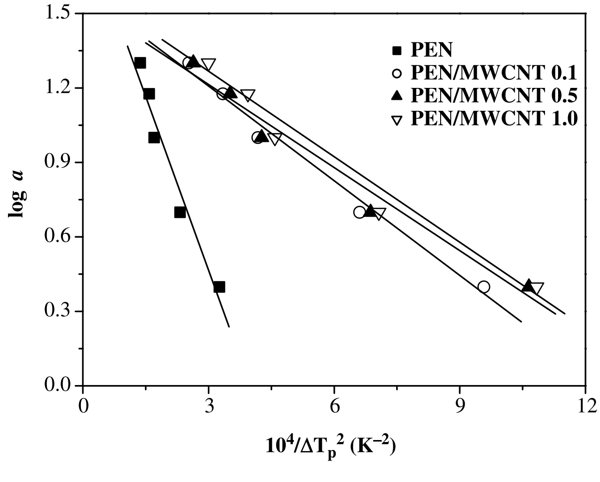

Fig. 11. Plots of log a versus $1/\Delta T_p^2$ for PEN/MWCNT nanocomposites as a function of MWCNT content.

3.5. Dynamic mechanical analysis

The storage modulus (E') and loss modulus (E'') of the PEN/MWCNT nanocomposites are shown in Fig. 12. As the molecular motion within a polymer changes, the modulus of a polymer varied with temperature. The storage modulus of a polymer decreases rapidly, whereas the loss modulus and tan δ undergoes a maximum when a polymer is heated though the glass transition region. The apparent glass transition region was revealed by a rapid decrease in the storage modulus of the PEN/MWCNT nanocomposites, and this temperature corresponding to the T_g of the PEN matrix was not affected by the addition of MWCNT. The incorporation of a very small quantity of MWCNT significantly improved the storage modulus and loss modulus of the PEN/MWCNT nanocomposites. This behavior of the PEN/MWCNT nanocomposites may be explained both by some physical interactions between the MWCNT and the

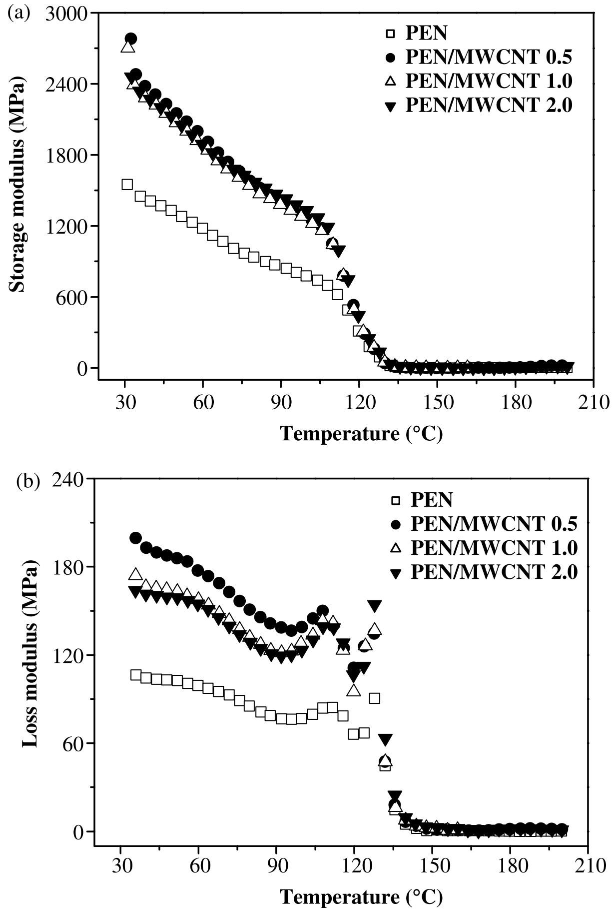

Fig. 12. Storage modulus and loss modulus of the PEN/MWCNT nanocomposites of various MWCNT content as a function of temperature.

PEN matrix due to the high surface area of the MWCNT, and the stiffening effect of the MWCNT in the PEN matrix; this effect being more pronounced at lower MWCNT content. The PEN/MWCNT nanocomposites exhibited a plateau region above 130 °C, implying that after a critical temperature, the storage modulus of the PEN/MWCNT nanocomposites was not significantly affected by the incorporation of MWCNT and they exhibited a strong dependence of the storage modulus on the polymer matrix [42,43]. Wu and Liu [43] reported that at the temperature above 140 °C, it has almost reached the softening point of the PEN matrix, which strongly reduce the elastic response of the PEN/layered silicate nanocomposites. The loss modulus of the PEN/MWCNT nanocomposites increased with the incorporation of the MWCNT, but with further increase in the MWCNT content above 1 wt%, the loss modulus decreased. This behavior may be explained by the fact that the increasing degree of agglomeration of MWCNT at higher MWCNT content results in less energy dissipating in the PEN/MWCNT nanocomposites under viscoelastic deformation [44]. The tan δ peak of the PEN/MWCNT nanocomposites as a function of temperature is shown in Fig. 13. The position of the tan δ peak of the PEN/MWCNT nanocomposites was not significantly affected by the incorporation of MWCNT, while the peak height decreased.

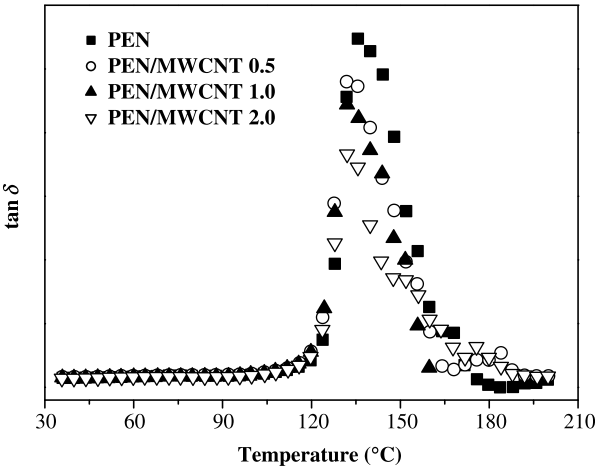

Fig. 13. Variation of tan δ peak of PEN/MWCNT nanocomposites of various MWCNT content as a function of temperature.

4. Conclusion

MWCNT-reinforced PEN nanocomposites were prepared by a melt blending in a twin-screw extruder. Non-isothermal crystallization of PEN/MWCNT nanocomposites depended significantly on the MWCNT content and cooling rate. The crystallization temperature for the PEN/MWCNT nanocomposites decreased with increasing cooling rate for a given MWCNT content and increased with MWCNT content for a given cooling rate. The incorporation of MWCNT accelerates the mechanism of nucleation and crystal growth of PEN, this effect being more significant at lower MWCNT content. Combined Avrami and Ozawa analysis was found to be effective in describing the non-isothermal crystallization of the PEN/MWCNT nanocomposites. The MWCNT in the PEN/MWCNT nanocomposites exhibits much higher nucleation activity than any nano-scaled reinforcement. When a vary small quantity of MWCNT was added, the activation energy for crystallization is lower, then gradually increased, and becomes higher than that of pure PEN at high MWCNT content. The incorporation of MWCNT improved the storage modulus and loss modulus of the PEN/MWCNT nanocomposites, with this effect also being more pronounced at lower MWCNT content.

Acknowledgements

This research was supported by Korea Science and Engineering Foundation directed Engineering Research Center, Center for the Advanced Functional Polymers (Project No. R11-1997-044-07022-0).

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