Non-isothermal crystallization kinetics of syndiotactic polystyrene – polystyrene functionalized SWNTs nanocomposites

H. Xiong, Y. Gao, H. M. Li*

Institute of Polymer Science, Chemistry College, Xiangtan University, Xiangtan 411105, Hunan Province, P. R. China

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Abstract. Non-isothermal crystallization kinetics were characterized by using differential scanning calorimetry (DSC) analysis on neat semicrystalline syndiotactic polystyrene (sPS) and its nanocomposites with polystyrene (PS) functionalized full-length single walled carbon nanotubes (SWNT-PS), which was prepared by copper (I) catalyzed click coupling of alkyne-decorated SWNTs with well-defined, azide-terminated PS. The crystallization behavior of neat sPS polymer was compared to its SWNT based nanocomposites. The results suggested that the non-isothermal crystallization behavior of sPS/SWNT-PS nanocomposites depended significantly on the SWNT-PS contents and cooling rate. The incorporation of SWNT-PS caused a change in the mechanism of nucleation and the crystal growth of sPS crystallites, this effect being more significant at lower SWNT-PS content. Combined Avrami and Ozawa analysis was found to be effective in describing the non-isothermal crystallization of the neat sPS and its nanocomposites. The activation energy of sPS determined from non-isothermal data decreased with the presence of small quantity of SWNT-PS in the nanocomposites and then increased with increasing SWNT-PS contents.

Keywords: *polymer composites, non-isothermal crystallization kinetics, syndiotactic polystyrene, carbon nanotube*

1. Introduction

Carbon nanotubes (CNTs) are unique nanostructured materials with remarkable physical, mechanical and electronic properties [1–4]. These properties make them attractive for applications in many scientific and technological fields such as electronic structures [5], polymer composites [6], and biological systems [7]. Among these potential applications, the prospect of obtaining high-performance CNT based polymeric nanocomposites has attracted the efforts of researchers in both academia and industry [8]. The combination of organic polymer components with CNT fillers in a single material has extraordinary significance for the development of advanced materials with remarkable mechanical, electrical, thermal and multifunctional properties

[9–12]. Moreover, polymer/CNT nanocomposites challenge traditional filled polymers (loadings of 20 wt% or more) in many of these areas by providing similar physical enhancements but with as little as about 1 wt% addition of dispersed nanotubes [13]. Previous CNT based polymeric nanocomposites reports include increased modulus, impact strength, heat distortion temperature, and barrier properties with decreased thermal expansivity [14–16]. In addition, these nanocomposites are finding potential applications such as electrostatically dissipative materials and aerospace materials [17]. Currently, several processing methods, including melt mixing, solution process and *in-situ* polymerization [18–20], are available for producing polymer/CNT composites based on either thermoplastics or thermosets. In addition, new techniques

*Corresponding author, e-mail: lihuaming@xtu.edu.cn
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such as deposition using layer-by-layer assembly have also been applied [21–23]. Although the techniques are inherently different, all of them try to address issues that directly affect the composite properties, such as deagglomeration of bundles and ropes, CNTs dispersion, and interfacial bonding. However, the complete dispersion of nanotubes in a polymer matrix is hindered by the intrinsic van der Waals interactions between nanotubes [24, 25]. An effective method to overcome these barriers involves the chemical functionalization. Several approaches to the functionalization of CNTs, including covalent sidewall coupling reactions [26–28], and noncovalent exohedral interactions [29, 30], have been developed to disperse the CNTs individually and uniformly throughout the matrix. Among these approaches, covalent functionalization of CNTs with polymeric structures has shown strong vitality and great advantages [31–33]. The modifications with polymers could not only improve CNT dispersibility, but also the interfacial polymer-nanotube interaction within composite materials.

Highly stereoregular polystyrene, such as sPS, has been synthesized to produce nearly 100% syndiotactic conformation with a specific metallocene catalyst [34], which has received considerable attention because of its high melting temperature, high crystallinity, rapid crystallization rate, low dielectric constant, good chemical resistance, and enhanced mechanical performance at elevated temperature [35–38]. In spite of these excellent properties, however, sPS has a disadvantage of its inherent brittleness. Thus, an application of sPS might be found predominantly in blends or compositions.

In order to broaden the practical application of sPS, our interest is to study the single walled carbon nanotubes (SWNTs) reinforced sPS nanocomposites. The combination of SWNTs with thermoplastic polymers may provide attractive possibilities to improve the mechanical properties of polymer nanocomposites. As mentioned above, the effective utilization of carbon nanotubes in composite applications depends strongly on the ability to disperse the SWNTs individually and uniformly throughout the matrix. Furthermore, good interfacial bonding is required to achieve load transfer across the SWNT-matrix interface [39–41]. On the other hand, owing to SWNTs intrinsic poor solubility and strong affinity for one another, it is difficult to disperse SWNTs as individual tubes and compatible with sPS. This

problem can be well solved by functionalization the SWNT surface with polymers that are identical or structurally similar to the matrix polymers. Thus SWNT-PS, prepared by copper (I) catalyzed click coupling of alkyne-decorated SWNTs with well-defined, azide-terminated PS [42], were used to reinforce sPS. The SWNT based composites were prepared by directly mixing the solutions of sPS and SWNT-PS. The advantage of this process is that the SWNT-PS exhibits high degrees of solubility in organic solvents, and thus allows dispersing the SWNTs individually and uniformly throughout the sPS matrix. Furthermore, this approach achieves relatively strong interfacial interactions between SWNTs and sPS due to the miscibility between PS and sPS in the amorphous regions.

In this paper, we focused our research on non-isothermal crystallization kinetics of sPS in its SWNT based nanocomposites. Since the mechanical properties of polymer composites are influenced by both their morphology and crystallization behavior [43, 44]. Understanding the non-isothermal crystallization kinetics is critical for providing information for optimal processing that might lead to optimal crystalline morphological structure and macroscopic properties of sPS in composite forms. Therefore, the crystallization behavior and structural development of SWNTs reinforced polymer nanocomposites should be analyzed to realize the full potential of SWNTs for application in thermoplastic matrix-based polymer nanocomposites. By using non-isothermal DSC analysis on the kinetics of crystallization of sPS and its nanocomposites, we hoped to establish relationships for describing the crystallization behavior of sPS in blends with SWNT-PS, in which PS has been known to be miscible with sPS. For these purposes, crystallization kinetics of neat sPS in comparison with the sPS in its nanocomposites with SWNT-PS, respectively, were studied.

2. Experimental

2.1. Materials

The sPS used in these studied was synthesized by bulk polymerization of styrene with a $\text{Cp}^*\text{Ti}(\text{OCH}_2\text{C}_6\text{H}_5)_3/\text{MAO}$ catalytic system at 80°C. The resulting polymer was stirred in a 10 wt% methanol solution of HCl for 5 h to remove the residual metal catalyst, the polymer was then filtered and dried under vacuum at 70°C for 72 h after

which was extracted with methylethyl ketone to remove the atactic component. The purified polymer was characterized to have a very high steric purity (>99% in syndio units as determined by ^{13}C -NMR) and its number average molecular weight and polydispersity determined by gel permeation chromatography were 210 000 and 2.2, respectively. SWNTs were purchased from Carbon Nanotechnologies, Inc. (Houston, TX). SWNT-PS sample having a polystyrene mass content of ca. 50%, as determined by thermogravimetric analysis, was prepared by reacting azide-terminated PS ($M_n = 7000$ g/mol, PDI = 1.10) with alkyne-functionalized SWNTs via copper (I) catalyzed [3+2] Huisgen cycloaddition [42]. 1,1,2-Trichloroethane (TCE) was distilled before use.

2.2. Preparation of sPS/SWNT-PS nanocomposites

Solution-based method was used to produce sPS/SWNT-PS nanocomposites. Specifically, sPS was dissolved at 80°C in TCE at a concentration of 5 mg/ml. SWNT-PS was dissolved in TCE at a concentration of 0.2 mg/ml using an ultrasonic bath sonicator for 5 min. The sonication bath temperature was then increased to 60°C, and the hot sPS solution was added to the nanotube solution. After further sonication for 6 h the mixture was evaporated to dryness on a rotary evaporator *in vacuum*. The solid was dried under vacuum for 72 h to remove any traces of solvent. The nanocomposites were denoted by the weight ratio of sPS to neat SWNTs, such as sPS/SWNT-PS- x , where x was the mass percentage of the neat SWNTs within the materials, determining by TGA analysis.

The sPS/SWNTs composites were prepared using the same method. The composites were denoted as sPS/SWNTs- x , where x is the mass percentage of SWNTs in the composites.

2.3. Characterizations

The thermal behavior of sPS/SWNT-PS, sPS/SWNTs composites were measured with a TA Q10 differential scanning calorimeter equipped with a RCS accessory under nitrogen atmosphere over a temperature range of 50–300°C at a scan rate of 20°C/min. The samples were heated to 300°C at a heating rate of 20°C/min, held at 300°C for 5 min to eliminate any previous thermal history and then

cooled to room temperature at a cooling rate of 20°C/min. Non-isothermal crystallization kinetics were investigated by cooling samples from 300 to 50°C at constant cooling rates of 2.5, 5, 10, 15, and 20°C/min.

3. Results and discussion

3.1. Thermal behavior

The development of SWNT-based polymer composites has been impeded by the inability to disperse SWNTs, which typically appear as ropes, in the polymer matrix due to the lack of chemical compatibility between the two components. A cursory summation of important areas for composites with SWNTs would include homogeneity of dispersion, interfacial compatibility with the matrix, and the exfoliation of SWNTs ropes and bundles. In this study, in order to make SWNTs homogeneously dispersed in and compatible with sPS, we first covalently attached PS onto the surface of SWNTs (SWNT-PS), and then blended with sPS by solution mixing. It is reasonable thought that this process can result in SWNTs homogeneous dispersion, interfacial compatibility with the sPS matrix, due to the high solubility of SWNT-PS in organic solvents as well as the miscibility of sPS and PS [45, 46]. In this research, composites via directly blending of pristine SWNTs suspension with sPS solution were also prepared for comparison.

Figure 1 and Figure 2 shows the DSC cooling and heating curves for the neat sPS, and its composites reinforced with functionalized and unfunctionalized SWNTs as a function of SWNTs content at a scan rate of 20°C/min. Table 1 lists the thermal data for each of the samples shown in Figures 1 and 2. It can be seen that the incorporation of SWNT-PS or SWNTs into the sPS increases the crystallization temperature (T_p) of the matrix in comparison with the neat sPS, confirming that nanotubes (SWNT-PS or SWNTs) can enhance the nucleation of sPS crystallization. Furthermore, the T_p of the sPS/SWNT-PS nanocomposites increases with increasing the load of SWNT-PS, and this increment tended to slow down when the content of nanotubes was above 0.20 wt%. This phenomenon can be explained by the fact that the SWNT-PS can promote the formation of heterogeneous nuclei, with lower energy consumption required to reach critical stability of crystal growth, resulting in them acting as effective nucleating agents in the sPS

Figure 1. DSC cooling and heating curves for the neat sPS (A), and its composites reinforced with unfunctionalized SWNTs as a function of SWNT contents [wt%] at a scan rate of 20°C/min (B) 0.20, (C) 0.30, (D) 0.50, (E) 1.0, (F) 2.0

Figure 2. DSC cooling and heating curves for the neat sPS (A), and its composites reinforced with SWNT-PS as a function of SWNT contents [wt%] at a scan rate of 20°C/min (B) 0.10, (C) 0.20, (D) 0.30, (E) 0.50, (F) 1.0

Table 1. DSC results of the thermal data for sPS/SWNTs and sPS/SWNT-PS nanocomposites with different content of carbon nanotubes

Materials	T _m [°C]	T _p [°C]	ΔH _c [J/g]	ΔH _f [J/g]	X _c [%]
sPS	270.9	235.5	32.27	30.60	57.7
sPS/SWNT-PS-0.10	270.6	239.3	27.42	33.07	62.3
sPS/SWNT-PS-0.20	270.5	241.1	28.38	31.98	60.5
sPS/SWNT-PS-0.30	269.2	242.7	27.63	31.52	59.7
sPS/SWNT-PS-0.50	270.2	242.9	28.08	30.61	58.0
sPS/SWNT-PS-1.0	270.5	244.6	24.38	29.37	56.0
sPS/SWNT-0.20	270.5	236.7	29.55	32.12	60.7
sPS/SWNT-0.30	270.5	239.7	30.15	31.23	59.1
sPS/SWNT-0.50	270.4	240.4	30.00	30.52	57.9
sPS/SWNT-1.0	271.4	241.9	28.41	28.96	55.2
sPS/SWNT-2.0	270.7	243.7	27.85	26.34	50.7

matrix. In addition, it is interesting to note that the increment for the SWNT-PS filled nanocomposites is greater than that of the neat SWNTs filled composites. This result confirms that SWNT-PS can disperse in the sPS matrix better than that has not been modified. Thus, we focused our research on non-isothermal crystallization kinetics of sPS/ SWNT-PS nanocomposites in comparison with the neat sPS.

With respect to the effect of the filler on the melting behavior, double melting peaks were observed for the sPS and SWNTs reinforced sPS (as shown in Figure 1, A–D). However, for the composites containing 1 and 2 wt% SWNTs, one may observe that the small peak at lower temperature starts to disappear. On the other hand, double melting peaks were observed for all SWNT-PS reinforced sPS nanocomposites as shown in Figure 2, B–F. This phenomenon is due to the competition between melting and recrystallization processes during the heating step [47]. Furthermore, a WAXD study near the melting region of about 270°C showed that the double endothermic melting behavior of sPS was caused not by a change in the crystalline form but by a recrystallization to a more perfect crystal [48]. The normalized crystallinity of sPS in the composites, X_c , is given by the Equation (1):

$$X_c = \frac{\Delta H_f}{\Delta H_f^0} \cdot 100 \text{ [%]} \tag{1}$$

where ΔH_f is the melting enthalpy of sPS in the composites, ΔH_f^0 is the melting enthalpy of 100% crystalline sPS ($\Delta H_f^0 = 53 \text{ J/g}$) [49] and w is the weight fraction of sPS in the composites. A variation in the X_c value depending on the nanotube contents was observed for the composites, i. e., for the sPS/SWNT-PS composites, the X_c value increased drastically with the addition of a small amount of SWNT-PS (ca. 0.1 wt%). As the nanotube contents increased further, the X_c value decreased slowly. Similar variation tendency in the X_c value was observed for the sPS/SWNTs composites. This result is due to the effect of the nucleation and the retardation of the crystallization of sPS because nanotubes can act as either a nucleating agent to facilitate sPS crystallization or a diluent to decrease the crystallinity.

Regarding the effect of cooling rate on the crystallization peak temperature (Figure 3), it is found that

Figure 3. Non-isothermal crystallization curves of sPS (red) and sPS/SWNT-PS-0.20 (black) at various cooling rates [°C/min] (A) 20, (B) 15, (C) 10, (D) 5, (E) 2.5

the crystallization peak temperature range becomes broader and shifts to lower temperatures for sPS and its nanocomposites as the cooling rate increased. When the specimens were cooled quickly, more supercooling was required to initiate crystallization, because the motion of the sPS molecules could not follow the cooling rate [50, 51]. 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 sPS/SWNT-PS nanocomposites was higher than that of pure sPS, and the overall crystallization time decreased with the incorporation of SWNT-PS.

3.2. Non-isothermal crystallization behavior

As mentioned above, sPS is one of the most important and widely used thermoplastics. Therefore, it is very important to study the non-isothermal crystallization behavior of the sPS based composites, because the non-isothermal conditions are closer to industrial processing conditions. The relative degree of crystallinity, $X(T)$ as a function of temperature, can be defined as Equation (2):

$$X(T) = \frac{\int_{T_0}^T \frac{dH_c}{dT} dT}{\int_{T_0}^{T_\infty} \frac{dH_c}{dT} dT} \quad (2)$$

where T_0 and T_∞ are the initial and final crystallization temperature, respectively. To use Equation (2)

to analyze non-isothermal crystallization data obtained by DSC, it is necessary to correlate the relationship between crystallization temperature (T) and crystallization time (t), which can be represented as Equation (3):

$$t = \frac{T_0 - T}{a} \quad (3)$$

where T_0 is the initial temperature at which crystallization begins ($t = 0$) and a is the cooling rate. Thus the development of relative crystallinity can be obtained as a function of time by transforming the horizontal temperature scale to a time scale through Equation (2) along with the Equation (3). Figure 4 shows the plots of the relative degree of crystallinity ($X(t)$) versus time for sPS and its composites with SWNT-PS in the non-isothermal crystallization process. Clearly, the time taken to complete crystallization reduced with increasing cooling rate, and the relative degree of crystallinity of the sPS/SWNT-PS nanocomposites was higher than that of pure sPS at the same time for complete crystallization, suggesting that the incorporation of SWNT-PS accelerates the overall crystallization process.

To study the kinetics parameters for the non-isothermal crystallization process, the modified Avrami equation [52] is used to fit experimental results. In the Avrami model, the time dependent crystallinity is modeled as Equations (4) and (5):

$$1 - X(t) = \exp(-Z_t t^n) \quad (4)$$

$$\log Z_c = \frac{\log Z_t}{a} \quad (5)$$

Figure 4. The plots of the relative degree of crystallinity of (a) the neat sPS and (b) the sPS/SWNT-PS-0.20 nanocomposite as a function of time at various cooling rates

where Z_t and Z_c are growth parameters and n is the Avrami exponent. Plots of $\log[-\ln(1 - X(t))]$ and $\log t$ are shown in Figure 5 for the neat sPS and the sPS/SWNT-PS-0.20 nanocomposites. It can be seen that the plots do not exhibit a linear relationship over the entire range of crystallization time, indicating that the modified Avrami equation does not effectively describe non-isothermal crystallization of sPS and its nanocomposites. The kinetics data in the linear region ($20 < X(t) < 60$) were selected to estimate the Avrami parameter for nonisothermal crystallization of sPS and the nanotubes filled

Figure 5. Avrami plots of (a) neat sPS and (b) the sPS/SWNT-PS-0.20 nanocomposite during non-isothermal crystallization

nanocomposites. The values of the Avrami exponent (n), the crystallization half-time ($t_{1/2}$), and the rate parameter (Z_t) determined from the slope and intercept of the selected plots are shown in Table 2. It is found that the Avrami exponent, n , is in the range of 3.34–5.14 for the nanocomposites and the values change with various cooling rates and nanotubes contents. For the pure sPS sample, the n values range from 3.29 to about 3.69 as the cooling rate changes. In addition, it is also found that the values of n for the nanocomposites are higher than that of the pure polymer. This result indicates that the non-isothermal crystallization mechanism of the sPS/SWNT-PS nanocomposites is very complicated, suggesting that the introduction of nanotubes significantly influence the mechanism of nucleation and crystal growth of the sPS. On the other hand, the $t_{1/2}$ value increases with an increase of cooling rate, which is in accordance with the $t_{1/2}$ directly obtained from DSC curves. By comparing with neat sPS, the $t_{1/2}$ values of nanocomposites are somewhat lowered at the same cooling rate, reflecting that the inclusion of nanotubes creates a nucleation effect and an acceleration crystallization of sPS. As shown in Equation (4), Z_t is a rough measure of the kinetics of crystallization, Z_c attempts to quantify the crystallization rate constant after removing the

Table 2. Parameters of the neat sPS and the sPS/SWNT-PS nanocomposites during non-isothermal crystallization

Materials	a [°C/min]	2.5	5	10	15	20
sPS	Z_t	0.00417	0.0955	0.646	2.14	3.80
	Z_c	0.110	0.625	0.957	1.05	1.07
	n	3.69	3.29	3.32	3.65	3.35
	$t_{1/2}$ [min]	3.47	2.07	1.02	0.71	0.56
sPS/SWNT-PS-0.10	Z_t	0.00162	0.0933	1.29	5.13	14.79
	Z_c	0.00162	0.0933	1.29	5.13	14.79
	n	5.14	4.79	4.71	4.24	4.02
	$t_{1/2}$ [min]	3.25	1.85	0.91	0.62	0.51
sPS/SWNT-PS-0.20	Z_t	0.00427	0.00646	1.23	4.37	8.71
	Z_c	0.113	0.578	1.02	1.10	1.11
	n	4.68	4.66	4.02	3.90	3.68
	$t_{1/2}$ [min]	2.93	1.68	0.88	0.63	0.48
sPS/SWNT-PS-0.30	Z_t	0.0162	0.112	1.38	3.16	5.49
	Z_c	0.192	0.646	1.03	1.08	1.09
	n	4.16	4.55	4.00	3.47	3.34
	$t_{1/2}$ [min]	2.47	1.49	0.84	0.59	0.44
sPS/SWNT-PS-0.50	Z_t	0.0130	0.200	1.54	5.54	12.50
	Z_c	0.175	0.724	1.04	1.12	1.13
	n	5.03	4.15	4.01	4.07	3.84
	$t_{1/2}$ [min]	2.21	1.35	0.82	0.57	0.42
sPS/SWNT-PS-1.0	Z_t	0.0589	0.263	1.82	8.20	22.70
	Z_c	0.322	0.766	1.04	1.15	1.17
	n	4.41	4.13	3.97	4.01	4.37
	$t_{1/2}$ [min]	1.75	1.26	0.78	0.54	0.41

kinetic effect of the non-isothermal cooling conditions under which the crystallization experiments are performed. As expected, the values of Z_t and Z_c for the nanocomposites are larger than that for the pure polymer and that the differences become remarkable with increasing cooling rate, again suggesting the presence of nanotubes results in accelerating the kinetics of crystallization.

Ozawa [53] had extended the Avrami equation to the nonisothermal condition, assuming that the amorphous polymer was heated or the polymer melt was cooled at a constant rate and the mathematical derivation of Evans [54] was valid. According to Ozawa's theory, the degree of conversion at temperature T , $X(T)$ can be written as Equations (6) and (7):

$$1 - X(T) = \exp\left[-\frac{K(T)}{a^m}\right] \quad (6)$$

$$\log[-\ln(1 - X(T))] = \log K(T) - m \log a \quad (7)$$

where $X(T)$ is the relative degree of crystallinity, m is the Ozawa exponent depending on the dimension of crystal growth, and $K(T)$ is a measure of the crystallization rate. The Ozawa plots of $\log[-\ln(1 - X(T))]$ versus $\log a$ for sPS and the sPS/SWNT-PS nanocomposites, taking the double logarithmic form of the Equation (6), are shown in Figures 6 and 7. It can be seen that the dependence is not linear, and large curvature is observed in the plots. The experimental facts indicate that the Ozawa equation is not suitable for describing the kinetics in the non-isothermal crystallization process of sPS and its composites. This result may arise due to the secondary crystallization and the dependence of the fold length on temperature for

Figure 6. Ozawa plots of (a) neat sPS and (b) the sPS/SWNT-PS-0.20 nanocomposite during non-isothermal crystallization

Figure 7. Plots of $\log a$ versus $\log t$ from the combined Avrami and Ozawa equations at different relative degree of crystallinity for (a) neat sPS and (b) the sPS/SWNT-PS-0.20 nanocomposite

sPS, as well as instantaneous nucleation, rapid impingement and possibly secondary crystallization for the nanocomposites [55–57].

In order to describe the non-isothermal crystallization process more effectively for comparison, Yin and Mo [58] and Liu and Mo [59] proposed the use of a combined Ozawa and Avrami model to describe the non-isothermal crystallization process, in which the degree of crystallinity is related to the cooling/heating rate a and the crystallization time t (or temperature T), the relation between a and t can be built up at a given degree of crystallinity. This convenient kinetic method has been adopted to deal with the non-isothermal data of many polymer systems [60–62]. The new kinetic equation of non-isothermal crystallization by combining the Equations (4) and (6) is derived as Equations (8) and (9):

$$\log Z_t + n \log t = \log K(T) - m \log a \quad (8)$$

$$\log a = \log F(T) - b \log t \quad (9)$$

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). At a certain degree of crystallinity of sPS and its nanocomposites, the plots of $\log a$ versus $\log t$ according to Equation (8) are shown in Figure 7. It gives a series of straight lines at a given relative degree of crystallinity, suggesting that this analysis may be more effective in describing the non-isothermal crystallization kinetics of sPS and sPS/SWNT-PS nanocomposites. The

kinetic parameter $F(T)$ and the exponent b can be estimated by the intercept and slope of these straight lines, respectively.

The results for b and $F(T)$ are listed in Table 3. It is apparent that the value of $F(T)$ increases with increasing relative degree of crystallinity, indicating that at unit crystallization time, a higher relative degree of crystallinity is obtained with a higher cooling rate. Moreover, the $F(T)$ values for the nanocomposites with low SWNT-PS contents are slightly lower than those for the polymer, suggesting faster kinetics of crystallization, and in agreement with our previous observation that the SWNT-PS act as nucleating agents although the this effect is relatively less profound because the grafted PS shield the tubes from the direct contacts with sPS. The values of b , i. e., the ratio of the Avrami exponent to the Ozawa exponent, are almost constant, varies from 1.18 to 1.10 for the neat sPS, and from 1.18 to 1.12 for the sPS/SWNT-PS nanocomposites.

Table 3. Values of b and $F(T)$ for the sPS and SWNT-PS/sPS-0.20 nanocomposites obtained from the combined Avrami and Ozawa equation

Materials	X(t) [%]	logF(T)	b
sPS	20	0.87	1.18
	30	0.93	1.16
	40	0.97	1.12
	50	1.02	1.11
	60	1.06	1.10
sPS/SWNT-PS-0.10	20	0.82	1.18
	30	0.86	1.17
	40	0.90	1.16
	50	0.93	1.15
	60	0.97	1.14
sPS/SWNT-PS-0.20	20	0.79	1.17
	30	0.85	1.16
	40	0.90	1.15
	50	0.94	1.14
	60	0.98	1.13
sPS/SWNT-PS-0.30	20	0.77	1.18
	30	0.84	1.17
	40	0.89	1.15
	50	0.92	1.15
	60	0.96	1.14
sPS/SWNT-PS-0.50	20	0.75	1.17
	30	0.83	1.16
	40	0.88	1.15
	50	0.93	1.14
	60	0.95	1.13
sPS/SWNT-PS-1.0	20	0.71	1.16
	30	0.79	1.15
	40	0.84	1.14
	50	0.89	1.12
	60	0.92	1.12

3.3. The activation energy for non-isothermal crystallization

For non-isothermal melt crystallization, the activation energy (ΔE_a) of crystallization was derived from the combination of cooling rate and crystallization peak temperature, and Kissinger [63] suggested a method for calculating the ΔE_a for non-isothermal crystallization as Equation (10):

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

where R is the universal gas constant, T_p is the crystallization peak temperature, a is the cooling rate, and ΔE_a is the activation energy required for the transportation of molecules from a molten state to a growing crystal surface. The activation energy of the non-isothermal crystallization for sPS and the sPS/SWNT-PS nanocomposites can be obtained from the slope of the plot of $\ln(a/T_p^2)$ versus $1/T_p$ (Figure 8), according to Equation (10), and the results are shown in Figure 9. It can be seen that the activation energy for the sPS/SWNT-PS nanocomposites is dependent on the nanotubes content. For example, the activation energy of neat sPS is 379 kJ/mol, which is approximately consistent with the value obtained by Wu *et al.* [64] (466 kJ/mol) and Chen *et al.* [65] (315 kJ/mol) for melt crystallization, decreases with the presence of 0.10 wt% nanotube in the nanocomposites (347 kJ/mol) and then increases with increasing nanotube content (407 kJ/mol for 0.30 wt% SWNT-containing nanocomposite and 437 kJ/mol for 1.0 wt% SWNT-con-

Figure 8. Kissinger plots of $\ln(a/T_p^2)$ versus $1/T_p$ for sPS and the sPS/SWNT-PS nanocomposites

Figure 9. The ΔE_a values of sPS and sPS/SWNT-PS from Kissinger theory

taining nanocomposite). The results indicate that the nanotubes seem to perform two functions in the sPS matrix. One is that the tubes act as nucleating agents and may accelerate the non-isothermal crystallization of sPS. On the other hand, SWNT-PS may also adsorb sPS molecular segments and restrict the movement of chain segments, thereby making crystallization difficult [66]. Since the SWNTs surface-bound PS is compatible with sPS. Thus, the addition of appropriate amount of nanotubes into sPS may induce the heterogeneous nucleation and accelerate non-isothermal crystallization of the sPS matrix (a lower ΔE_a), which was confirmed by the kinetic parameters determined for non-isothermal crystallization and crystallization half-time. But the addition of more nanotubes also reduces the transportation ability of polymer chains during crystallization processes (a higher ΔE_a).

4. Conclusions

Polystyrene functionalized SWNTs reinforced sPS nanocomposites were prepared by a solution blending. Non-isothermal crystallization kinetics of pure sPS and the sPS/SWNT-PS nanocomposites has been carried out with DSC techniques. It was found that the non-isothermal crystallization behavior of sPS/SWNT-PS nanocomposites depended significantly on the SWNT-PS content and cooling rate. The crystallization temperature for the sPS/SWNT-PS nanocomposites decreased with increasing cooling rate for a given SWNT-PS content and increased with increasing SWNT-PS content for a given cooling rate. The incorporation of SWNT-PS caused a change in the mechanism of nucleation and the crystal growth of sPS crystallites,

this effect being more significant at lower SWNT-PS content. Combined Avrami and Ozawa analysis was found to be effective in describing the non-isothermal crystallization of the sPS/SWNT-PS nanocomposites. The activation energy of sPS determined from non-isothermal data decreased with the presence of small quantity of sPS/SWNT-PS in the nanocomposites and then increased with increasing sPS/SWNT-PS content. The result indicated that lower nanotubes content probably induced the heterogeneous nucleation (a lower ΔE_a), while higher nanotubes content probably reduced the transportation ability of sPS polymer chains during crystallization processes (a higher ΔE_a), despite the presence of more heterogeneous nucleation.

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