

Thermal Decomposition Behavior of Carbon Nanotube Reinforced Thermotropic Liquid Crystalline Polymers

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ABSTRACT: Thermotropic liquid crystalline polymers (TLCP), 4-hydroxybenzoic acid (HBA)/6-hydroxyl-2-naphthoic acid (HNA) copolyester, and HNA/hydroxylbenzoic acid (HAA)/terephthalic acid (TA) copolyester reinforced by carbon nanotube (CNT) were prepared by melt compounding using Hakke internal mixer. The thermal behavior and degradation of CNT reinforced HBA/HNA copolyester and HNA/HAA/TA copolyester have been investigated by dynamic thermogravimetric analysis under nitrogen atmosphere in the temperature range 30 to 800°C to study the effect of CNT on the thermal decomposition behavior of the TLCP/CNT nanocomposites. The thermal decomposition temperature at the maximum rate, residual yield, integral procedural decomposition temperature, and activation energy for thermal decomposition was studied to investigate thermal stability of TLCP/CNT nanocomposites. The thermal stability of CNT reinforced HBA/HNA copolyester was increased by addition of a very small

quantity of CNT and the residual weight was 42.4% and increased until 50.8% as increasing CNT contents. However, the thermal stability of CNT reinforced HNA/HAA/TA copolyester was decreased initially when a very small quantity of CNT added. The residual weight was decreased from 50.4% to 45.1%. After addition of CNTs in the TLCP matrix, the thermal stability of CNT reinforced HNA/HAA/TA copolyester increased as increasing content of CNT and the residual weight was increased until 53% as increasing CNT contents. The activation energy was calculated by multiple heating rate equations such as Friedman, Flynn-Wall-Ozawa, Kissinger, and Kim-Park methods to confirm the effect of CNT in two different TLCP matrices. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2060–2070, 2011

Key words: activation energy; degradation; liquid crystalline polymer; nanoparticles; thermogravimetric analysis (TGA)

INTRODUCTION

Polymer nanocomposites reinforced by nanofillers have received a great deal of attention from both scientific field and industry because of their outstanding improvements in the physical properties despite of low filler contents. There were various attempts to develop advanced polymer nanocomposites by incorporating various nanofillers into polymer matrix. Among many fillers, carbon nanotubes (CNTs) have been considered as promising agents in polymer matrix reinforcement because of its excellent properties such as high mechanical strength, electrical, and thermal conductivity with a high aspect ratio and a small size.^{1–4} However, because of its high cost, there were only a few applications in the industrial fields. Therefore, the fabrication of the polymer nanocomposites reinforced by CNT should be

required at cheap manufacturing costs.⁵ There were a few processing techniques in common use to fabricate CNT/polymer nanocomposites: solution mixing or film casting, *in situ* polymerization, and melt compounding.^{6–9} Among these processing techniques, melt compounding process has been considered as the most simple and effective technique because it was economic and industrial perspective to fabricate advanced nanocomposites at low cost.¹⁰

Thermotropic liquid crystalline polymers (TLCPs) have outstanding mechanical properties, stiffness, good chemical resistance, and dimensional stability.^{11–13} Because of these properties, TLCPs have been utilized as high-performance engineering plastics in various industrial fields where high thermal stability is required.^{14,15} The thermal stability of polymers was very important for determining their processing and applications because it influences the final properties, such as dimensional stability and the upper limit use temperature. Therefore incorporation of a small quantity of expensive CNTs into TLCP matrix with low processing cost provides a good possibility to improve the thermal stability and other physical properties of CNT reinforced polymer composites.^{16,17}

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Thermal decomposition kinetics were investigated in detail to study the thermal stability of CNT reinforced TLCP nanocomposites. The thermal decomposition kinetics of polymer composites can be evaluated by single heating rate and multiple heating rate methods. The assumption about the reaction order to calculate value of the activation energy was not needed in the multiple heating rate method and the kinetic analysis of thermal decomposition of polymer composites has fewer errors and more accurate results than single heating rate methods.^{18,19} Because process of commercial plastics was actually performed in nonisothermal condition, the thermal decomposition kinetics of CNT reinforced TLCP nanocomposites in nonisothermal condition were expected to offer the useful information in industrial fields.²⁰

In this study, polymer nanocomposites reinforced by a small quantity of CNTs were prepared by melt compounding using Hakke internal mixer with a low cost method for possible application in industrial fields. The effects of CNTs on thermal decomposition behavior of CNT reinforced TLCP nanocomposites were considered and thermal decomposition kinetics of four multiple heating rate methods such as, Friedman,²¹ Flynn-Wall-Ozawa,^{22,23} Kissinger,²⁴ and Kim-Park²⁵ methods were studied to calculate the activation energies (E_a) of thermal degradation.

Theoretical background

To study thermal decomposition kinetics analysis, thermogravimetric analysis (TGA) was used. TGA kinetics analysis was investigated by measurement of fractional weight loss and rate of degradation according to temperature change. The fraction of conversion (α) could be calculated as follows:

$$\alpha = \frac{w_0 - w}{w_0 - w_f} \quad (1)$$

where W was instantaneous weight which was measured, W_0 was the initial weight before thermal decomposition, and W_f was final weight of samples after thermal decomposition, respectively. A typical model for decomposition kinetic process could be expressed as follows:

$$\frac{d\alpha}{dt} = q \frac{d\alpha}{dT} = K(T)F(\alpha) \quad (2)$$

where $q = dT/dt$, t , and T were the heating rate, reaction time, and temperature, respectively. If the degradation reaction follows the n -th order reaction, $F(\alpha)$ was expressed as:

$$F(\alpha) = (1 - \alpha)^n \quad (3)$$

$F(\alpha)$ depended on the mechanism of the thermal decomposition reaction and the function $K(T)$ could be expressed by the Arrhenius equation as follow:

$$K(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

where A , R , and E_a were the pre-exponential factor, gas constant, and activation energy, respectively. The basic equation of thermal degradation kinetics could be obtained by combination of eqs. (2)–(4) as follows:

$$\frac{d\alpha}{dt} = q \frac{d\alpha}{dT} = (1 - \alpha)^n A \exp\left(-\frac{E_a}{RT}\right) \quad (5)$$

Eq. (5) was differentiated or integrated to obtain various equations for the estimation of the thermal decomposition kinetic parameters.²⁶

Friedman method

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln(Z) + n \ln(1 - \alpha) - \frac{E_a}{RT} \quad (6)$$

where n was the reaction order and Z was the frequency factor. The Friedman method²¹ was based on the basic Arrhenius equation for thermal degradation kinetics and assumes that the decomposition process was independent on temperature and dependent on the only instantaneous weight of samples. The plot of $\ln(d\alpha/dt)$ versus $1/T$ should be linear with slope ($= -E_a/R$). From this slope of the linear plot, E_a could be obtained. Because a set of linear plots could be obtained at different conversion, the average E_a can be calculated from the results.

Flynn-Wall-Ozawa method

The Flynn-Wall-Ozawa method^{22,23} was the simple method for obtaining activation energies directly from weight loss against temperature at several heating rates. This method was used to determine E_a by plotting of the logarithm of the heating rate as a function of the inverse of the temperature at different conversions.²⁶ The eq. (5) could be arranged by being integrated at the initial condition ($\alpha = 0$ at $T = T_0$) as follow:

$$F(\alpha) = A \int_0^T \exp\left(-\frac{E_a}{RT}\right) dT \quad (7)$$

Then, eq. (7) could be simplified by Doyle's approximation²⁷ as follows:

$$\log q = \log\left(\frac{AE_a}{F(\alpha)R}\right) - 2.315 - 0.4567\left(\frac{E_a}{RT}\right) \quad (8)$$

This method assumed that A and E_a are independent of T and α . The E_a could be calculated from the slope of $\ln q$ versus $1/T$ for a constant α . The advantage of this method was that the calculation of E_a had no relationship with real degradation process, and also the reaction order was not necessary. However, only the activation energy was obtained by this method.

Kissinger method

$$\ln\left(\frac{q}{T_{dm}^2}\right) = \ln\left[\frac{n(1-\alpha_m)^{n-1}ZR}{E_a}\right] - \frac{E_a}{RT_{dm}} \quad (9)$$

where T_{dm} and α_m were the absolute temperature and conversion at the maximum rate of thermal decomposition. The Kissinger method²⁴ assumed that $n(1-\alpha_m)^{n-1}$ was independent on heating rate and reaction order was constant and nearly equal to unity. The equation gave only one value of E_a and E_a could be obtained from the slope of plot of $\ln(q/T_{dm}^2)$ versus $1/T_{dm}$ at maximum weight loss, which was equal to $-E_a/R$.

Kim-Park method

$$\ln q = \ln Z + \ln\left(\frac{E_a}{R}\right) + \ln\left[1 - n + \left(\frac{n}{0.9440}\right)\right] - 5.3305 - 1.0516\left(\frac{E_a}{RT_{dm}}\right) \quad (10)$$

The Kim-Park method²⁵ assumed that the weight loss at the maximum decomposition rate was independent on the heating rate (q), E_a , and a pre-exponential factor. This method was used to obtain E_a from thermogravimetry (TG) and derivative thermogravimetry (DTG) curves at various heating rates. E_a could be determined from the slope of $\ln q$ versus $1/T_{dm}$. Because the approximate value of 0.9440 was used as a conversion factor in this method, more accurate E_a was calculated than other methods that conversion factor was unity.

EXPERIMENTAL

Materials and preparation of the composites

The following two TLCPs, 4-hydroxybenzoic acid (HBA)/6-hydroxyl-2-naphthoic acid (HNA) copolyester (Polyplastics Co., Japan) and HNA/*p*-hydroxyaniline (HAA)/terephthalic acid (TA) copolyester (Polyplastics Co., Japan) were used in this research. The chemical structures of these materials were shown in Figure 1. HBA/HNA copolyester was a random copolymer and had a 73/27 mol % molar ratio of HBA/HNA. HNA/HAA/TA copolyester

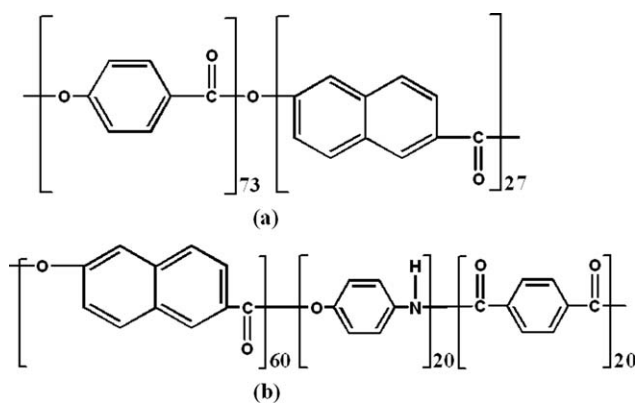


Figure 1 Chemical structures of (a) HBA/HNA copolyester and (b) HNA/HAA/TA copolyester.

was a random copolyesteramide composed of 60 mol % HNA, 20 mol % HAA, and 20 mol % TA. The CNTs used in the reinforcement (degree of purity >95%) were synthesized by the thermal chemical vapor deposition process, purchased from Iljin Nanotech, Korea. All materials were dried at 120°C *in vacuo* at least 24 h before use to minimize the effect of moistures. CNT reinforced HBA/HNA and HNA/HAA/TA copolyester were prepared by melt compounding process using a Haake Rheomix 600 internal mixer (Gebr. HAAKE GmbH, Germany) at 290°C for 10 min, with a fixed roter speed of 60 rpm. CNT reinforced TLCP nanocomposites were prepared by melt blending process using Hakke internal mixer. For fabrication of composites, TLCPs were melt-blended with the incorporation of various CNT content, specified as 0.1, 0.5, 1.0, 2.0, 5.0, and 10.0 wt % in the TLCP matrix.

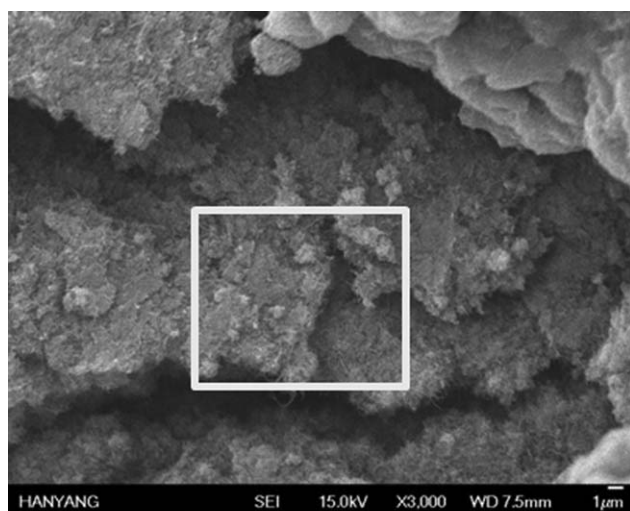
Characterization

Thermogravimetric analysis (TGA) of CNT reinforced TLCPs was performed using PerkinElmer Pyris 1 thermo gravimetric analyzer over the temperature range of 30 to 800°C under nitrogen atmosphere with a flow rate of 30 mL/min. Dynamic TGA measurements of CNT reinforced TLCPs were performed at various heating rates of 5, 10, and 20°C/min and the sample weight was about 10 mg. The morphology of CNT reinforced TLCPs was observed by using a JEOL JSM-6340F field emission scanning electron microscope (FE-SEM). The activation energy of thermal degradation was calculated by Friedman, Flynn-Wall-Ozawa, Kissinger, and Kim-Park methods.

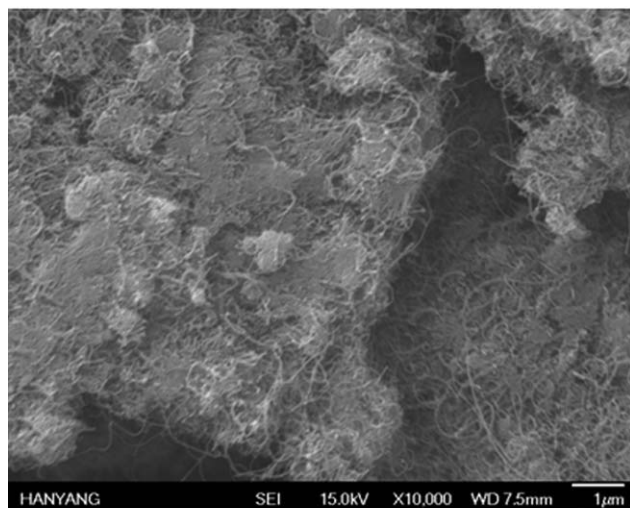
RESULTS AND DISCUSSION

Morphology

Morphology of CNT reinforced HBA/HNA copolyester and enlarged image are shown in Figure 2.



(a)



(b)

Figure 2 SEM images of (a) CNT reinforced HBA/HNA copolyester and (b) enlarged SEM image of selected region in (a).

CNTs were well dispersed in HBA/HNA copolyester matrix and interconnected structure appeared by forming nanotube-nanotube or nanotube-polymer matrix interactions. Because CNTs were very small in size, CNTs had a large surface area and high aspect ratio, thus agglomeration or bundle formation was appeared. Therefore, interconnected structure between CNTs and the molten polymer matrix was formed easily. This interconnected structures induced by CNT played a role as protective layers on the polymer matrix resulting in a good physical barrier effect and retarding the thermal decomposition of the polymer nanocomposites.²⁶ Schartel et al.²⁸ reported similar research that fiber-network character of the incorporated CNTs of polyamide (PA)/CNT nanocomposites influenced the fire retardation suggesting that the interconnected structures

stabilized the melt in pyrolysis zone and residue. This effect of CNTs on the thermal decomposition behavior could also be explained by high thermal stability of CNT and restriction of polymer chains at the presence of CNTs.²⁹ Another factor was high thermal conductivity of CNT which caused effective heat dissipation resulting in increase of thermal stability of polymer composites.³⁰

Thermal stability

Thermal stability of polymers is very important for process and application of polymers because it determines the upper limit of service temperature and the environmental conditions. TGA thermograms of CNT reinforced HBA/HNA and HNA/HAA/TA copolyesters with CNT contents at 20°C/min are shown in Figure 3. All curves of composites showed only one primary weight loss step decomposition, which was due to the random scission of TLCP polymer chains.³¹ The curve patterns of composites were similar to that of neat TLCP. That

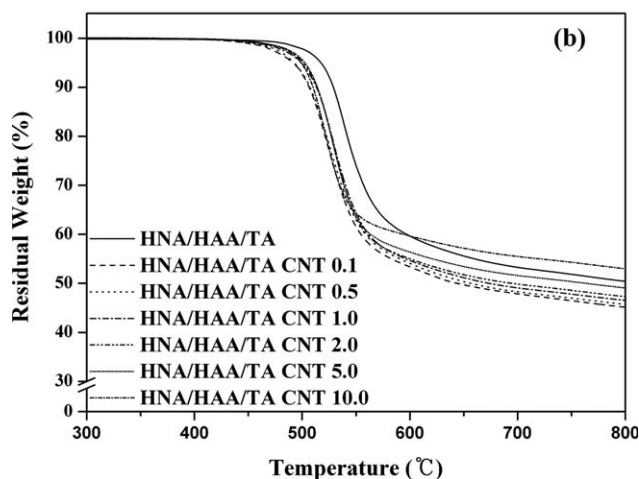
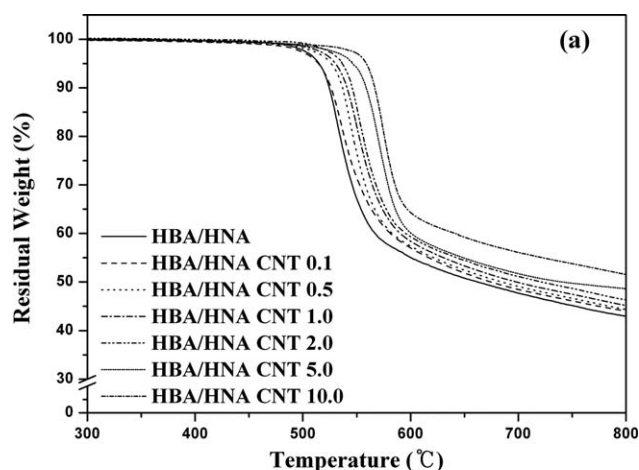


Figure 3 TGA thermograms of CNT reinforced (a) HBA/HNA and (b) HNA/HAA/TA copolyesters at various CNT contents under nitrogen atmospheres.

TABLE I
Thermal Decomposition Parameters of CNT Reinforced HBA/HNA and HNA/HAA/TA Copolyesters with Different CNT Contents

	T_{id} (°C)	T_{dm} (°C)	A^*	K^*	IPDT (°C)	W_R (%)
HBA/HNA	467.9	536.0	0.717	2.032	951.8	42.4
HBA/HNA CNT 0.1	488.7	536.9	0.761	2.043	972.7	42.5
HBA/HNA CNT 0.5	490.1	537.1	0.776	2.061	985.7	42.5
HBA/HNA CNT 1.0	493.0	538.1	0.786	2.073	993.2	43.0
HBA/HNA CNT 2.0	504.8	538.7	0.795	2.116	1,001.4	45.6
HBA/HNA CNT 5.0	518.8	552.6	0.812	2.138	1,007.0	48.2
HBA/HNA CNT 10.0	538.1	559.1	0.857	2.148	1,020.2	50.8
HNA/HAA/TA	475.7	534.6	0.829	2.452	1,134.9	50.4
HNA/HAA/TA CNT 0.1	420.2	525.5	0.799	2.217	1,092.9	45.1
HNA/HAA/TA CNT 0.5	422.9	526.7	0.805	2.241	1,103.2	45.7
HNA/HAA/TA CNT 1.0	435.4	531.6	0.808	2.274	1,104.2	46.5
HNA/HAA/TA CNT 2.0	452.1	532.2	0.809	2.317	1,105.3	47.3
HNA/HAA/TA CNT 5.0	461.6	532.4	0.813	2.417	1,126.6	49.0
HNA/HAA/TA CNT 10.0	470.7	533.5	0.826	2.669	1,196.7	53.0

means the thermal decomposition of CNT reinforced TLCP composites was caused by decomposition of TLCP. As shown in Figure 3(a), addition of CNT could lead to enhance the decomposition temperature and residual yields of CNT reinforced HBA/HNA copolyester, and this effect was more dominant as increasing CNT contents. However, different thermal decomposition behavior of CNT reinforced HNA/HAA/TA copolyester was shown in Figure 3(b). The decomposition temperature and residual yields of CNT reinforced HNA/HAA/TA copolyester were decreased even when very small quantity of CNT added. After addition of CNTs in the TLCP matrix, decomposition temperature and residual yields of CNT reinforced HNA/HAA/TA copolyester increased as increasing content of CNT. The thermal decomposition parameters to determine thermal stability were shown in Table I. The initial decomposition temperature (T_{id}), thermal decomposition temperature at the maximum rate (T_{dm}) which is associated with increase of the thermal stability,³² residual yield in a TGA thermogram at 800°C (W_R) and integral procedure decomposition temperature (IPDT) were measured to evaluate thermal stability of CNT reinforced HBA/HNA and HNA/HAA/TA copolyesters. The schematic TGA thermogram to determine Integral procedural decomposition temperature (IPDT) of polymer was shown in Figure 4 based on the Doyle's proposition. IPDT³³ value was calculated as follows:

$$\text{IPDT} = A^* \times K^*(T_f - T_i) + T_i \quad (11)$$

$$A^* = \frac{A_1 + A_2}{A_1 + A_2 + A_3} \quad \text{and} \quad K^* = \frac{A_1 + A_2}{A_1}$$

The area ratio of the total experimental curve divided by total TGA thermogram (A^*), the coefficient of A^* (K^*), initial experimental temperature (T_i), and

final experimental temperature (T_f) were determined to obtain IPDT.

As shown in Table I, the values of T_{dm} and IPDT were increased from 536.0°C and 951.8 (neat HBA/HNA copolyester) to 559.1°C and 1,020.2 (CNT 10 wt % reinforced HBA/HNA copolyester). The residual weight of HBA/HNA copolyester was 42.4% and increased until 50.8% (CNT 10 wt % reinforced HBA/HNA copolyester) as increasing CNT contents. This effect was resulted from excellent thermal stability and physical barrier effect of CNT which retarded thermal decomposition of CNT reinforced HBA/HNA copolyester. Additionally, high-thermal conductivity of CNT in composites influenced thermal stability of CNT reinforced HBA/HNA copolyester.³⁰ However, T_{dm} and IPDT values were decreased from 534.6°C and 1,134.9 to 525.5°C and 1,092.9 when 0.1 wt % CNT was incorporated to HNA/HAA/TA copolyester matrix. The residual

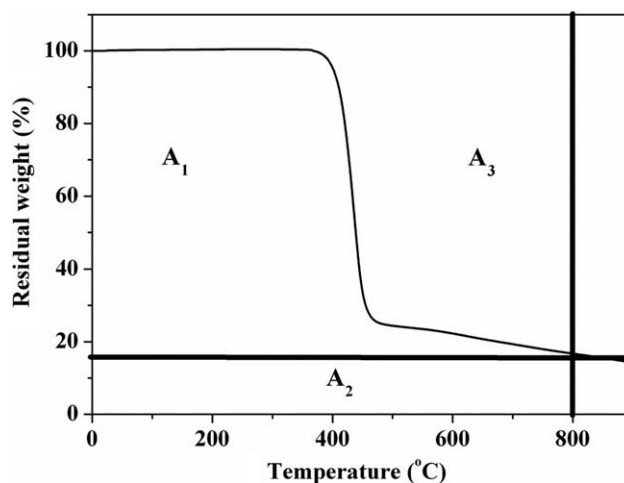


Figure 4 Schematic TGA thermogram for determining the IPDT.

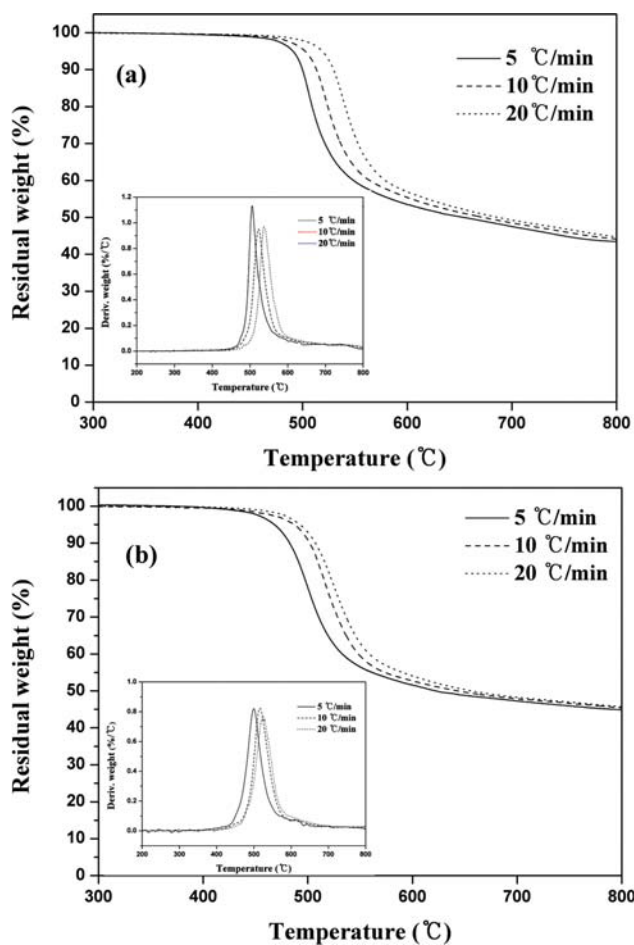


Figure 5 TGA and DTG thermograms of CNT 1.0 wt % reinforced (a) HBA/HNA and (b) HNA/HAA/TA copolyesters under nitrogen. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

weight was also decreased from 50.4% to 45.1% when CNT 0.1 wt % was incorporated. After incorporation of CNT to HNA/HAA/TA copolyester matrix, T_{dm} and IPDT values were increased until 533.5°C and 1,196.7 (CNT 10 wt % reinforced HNA/HAA/TA copolyester). The residual weight of CNT reinforced HNA/HAA/TA copolyester was also increased until 53.0% as increasing CNT contents. This result came from incorporation of CNT into HNA/HAA/TA copolyester matrix with amide group in the main chain. Paik et al.³⁴ reported that compactness of chains restricted the thermal degradation of polymer chains. Because of the higher compactness of chains, the more time to reach the thermal equilibrium was required and therefore, slower decomposition process occurred. HNA/HAA/TA copolyester had an amide group in the main chain and conform the higher compactness formation caused by hydrogen bonding between amide groups. However, this higher compactness formation was unfolded at melt compounding and the com-

compactness of HNA/HAA/TA copolyester might be disturbed by addition of CNT with abundant π -electrons while melt compounding process because of interaction between CNT and amide group. Therefore, thermal stability of HNA/HAA/TA copolyester was decreased when CNT was incorporated into HNA/HAA/TA copolyester matrix and then, thermal decomposition behavior of CNT reinforced HNA/HAA/TA copolyester was similar with CNT reinforced HBA/HNA copolyester as increasing CNT contents after addition of CNT.

TGA and derivative thermogravimetric (DTG) thermograms of CNT 1.0 wt % reinforced HBA/HNA (a) and HNA/HAA/TA (b) copolyesters at various heating rates in nitrogen are shown in Figure 5. The thermal decomposition was due to the random scissions of polymer chains. TGA thermograms and DTG peak positions were shifted toward the higher temperature region as increasing heating rates, and the single peak was appeared in DTG curves implying only one weight loss step of

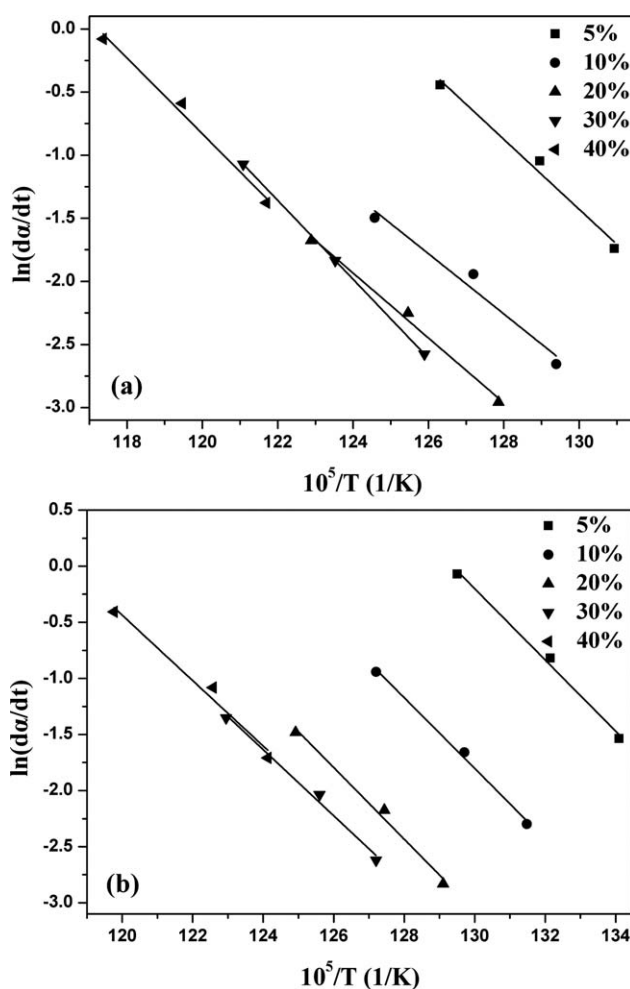


Figure 6 Friedman plots of CNT 1.0 wt % reinforced (a) HBA/HNA and (b) HNA/HAA/TA copolyesters for calculating E_a of thermal decomposition.

TABLE II
 E_a (kJ/mol) and r^2 Values of CNT Reinforced HBA/HNA and HNA/HAA/TA Copolymers by the Friedman Method

	Degree of decomposition (%)					Average
	5	10	20	30	40	
HBA/HNA						
E_a	214.3	204.1	224.2	257.1	214.7	222.9
r^2	0.99	0.91	0.93	0.94	0.95	
HBA/HNA CNT 0.1						
E_a	217.9	187.3	195.9	229.3	293.4	224.8
r^2	0.91	0.85	0.91	0.95	0.99	
HBA/HNA CNT 0.5						
E_a	333.9	319.7	259.2	163.9	74.9	230.3
r^2	0.89	0.83	0.82	0.94	0.99	
HBA/HNA CNT 1.0						
E_a	230.6	198.3	213.7	259.9	249.6	230.4
r^2	0.97	0.94	0.99	1	0.98	
HBA/HNA CNT 2.0						
E_a	246.4	239.9	265.7	282.0	204.6	247.7
r^2	0.85	0.95	0.99	0.99	0.93	
HBA/HNA CNT 5.0						
E_a	90.3	224.6	309.5	360.1	432.2	283.4
r^2	0.89	0.91	0.99	0.97	0.91	
HBA/HNA CNT 10.0						
E_a	396.3	414.5	368.6	312.7	160.7	330.6
r^2	0.99	0.91	0.99	0.99	0.99	
HNA/HAA/TA						
E_a	217.9	264.2	266.5	298.0	364.8	282.3
r^2	0.92	0.94	0.99	0.95	0.94	
HNA/HAA/TA CNT 0.1						
E_a	176.5	208.4	190.2	233.7	192.2	200.2
r^2	0.94	0.99	0.98	0.99	0.92	
HNA/HAA/TA CNT 0.5						
E_a	303.1	195.4	160.5	188.1	195.4	208.5
r^2	0.87	0.99	0.94	0.87	0.85	
HNA/HAA/TA CNT 1.0						
E_a	202.3	211.5	299.8	259.3	222.6	239.1
r^2	0.95	0.96	0.97	0.97	0.91	
HNA/HAA/TA CNT 2.0						
E_a	235.6	239.8	258.7	290.9	251.5	255.3
r^2	0.87	0.89	0.93	0.90	0.95	
HNA/HAA/TA CNT 5.0						
E_a	262.2	265.3	244.7	242.5	264.1	255.8
r^2	0.99	0.98	0.98	0.96	0.99	
HNA/HAA/TA CNT 10.0						
E_a	216.7	209.2	550.6	204.7	186.6	273.6
r^2	0.99	0.99	0.72	0.99	0.93	

thermal decomposition because of random scissions of polymer chains. The results revealed that thermal decomposition process was strongly influenced by the heating rates. When the heating rate was rapid, the polymer chains did not have enough time to reach thermal equilibrium because of slow diffusion of heat and therefore, higher thermal decomposition temperature was appeared.³⁵

Kinetic analysis of thermal decomposition

Kinetics of thermal degradation analysis equations such as Friedman, Flynn-Wall-Ozawa, Kissinger and

Kim-Park methods were comparatively investigated to obtain activation energy (E_a) of thermal decomposition of CNT reinforced HBA/HNA and HNA/HAA/TA copolyesters at the multiple heating rates.

The Friedman method was widely used to calculate E_a . Generally, the polymer with higher E_a value was more difficult to decompose because more energy was needed during thermal decomposition. The Friedman plots of $\ln(d\alpha/dt)$ against $1/T$ for CNT reinforced HBA/HNA and HNA/HAA/TA copolyesters were shown in Figure 6. The high linear relationship of the Friedman plots was exhibited at different conversion and then E_a can be calculated

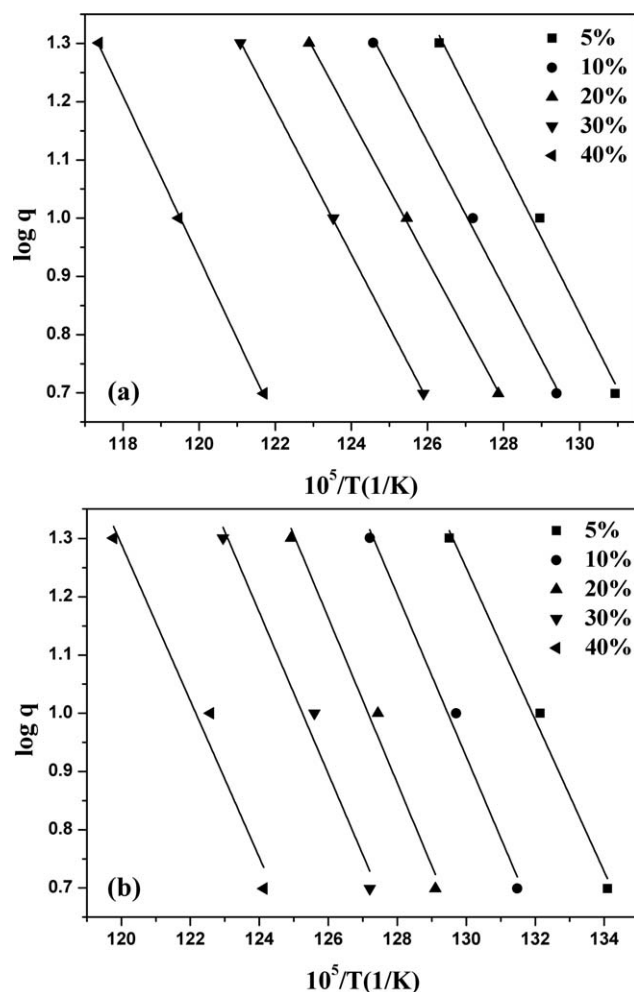


Figure 7 Flynn-Wall-Ozawa plots of CNT 1.0 wt % reinforced (a) HBA/HNA and (b) HNA/HAA/TA copolyesters for calculating E_a of thermal decomposition.

by the slope which means $-E/R$. The average E_a and correlation coefficient (r^2) of CNT reinforced HBA/HNA and HNA/HAA/TA copolyesters with increasing CNT contents were listed in Table II. As shown in Table II, the E_a value of HBA/HNA copolyester was 222.89 kJ/mol and tended to increase with the contents of incorporated CNT. However, E_a value of HNA/HAA/TA copolyester initially decreased from 282.31 to 200.20 kJ/mol when 0.1 wt % CNT added and then increased with increase of CNT contents.

The Flynn-Wall-Ozawa method was one of the integral based calculation methods and derived by separating the variables. The Flynn-Wall-Ozawa plots of $\log(q)$ against $1/T$ for each conversion using three heating rates (5, 10, and 20°C/min) were shown in Figure 7. The average E_a values were calculated by slopes of plots which means $-0.4567E/RT$ and the lower E_a values were obtained in Flynn-Wall-Ozawa method than Friedman method. The average E_a and r^2 calculated from slopes of plots

were summarized in Table III. Similarly CNT reinforced HBA/HNA copolyester was more difficult to decompose as increasing CNT and the thermal decomposition of HNA/HAA/TA copolyester was occurred more easily when 0.1 wt % CNT added. CNT reinforced HNA/HAA/TA copolyester was more difficult to decompose with increase of CNT contents after addition of CNT. This result was confirmed by obtaining values of r^2 close to unity.

Kissinger method involves the absolute temperature at the maximum weight loss rate (T_{dm}) obtained from DTG curves at different heating rates. T_{dm} was corresponded to the inflection point of TGA curves corresponding to temperature at the maximum decomposition rate. E_a can be determined without having lots of details about reaction mechanism by Kissinger's approximation that if value of $n(1 - \alpha_m)^{n-1}$ was constant, E_a can be calculated from a plot of $\ln(q/T_{dm}^2)$ against $1/T_{dm}$ and the plots of CNT reinforced HBA/HNA and HNA/HAA/TA copolyesters were shown in Figure 8.

Kim-Park method was also used to determine thermal decomposition parameters and the various TGA data with different heating rates (5, 10, and 20°C/min) were considered. The plots by Kim-Park method for CNT reinforced HBA/HNA and HNA/HAA/TA copolyesters were shown in Figure 9. The points of Kissinger and Kim-Park plots were the output of the calculation, and the straight lines were fitted for the corresponding points. These lines exhibited high linear relationship that means the Kissinger and Kim-Park methods were effective to investigate thermal decomposition behaviors of CNT reinforced TLCP composites. The slopes of Kissinger and Kim-Park plots became steep remarkably in CNT reinforced HBA/HNA copolyesters, however, the variation of slopes was less remarkable in HNA/HAA/TA copolyesters. The E_a and r^2 calculated from the slope of Kissinger and Kim-Park plots with increase of CNT contents were summarized in Table IV. Average E_a values obtained from Tables II and III by Friedman and Flynn-Wall-Ozawa methods were also tabulated alongside in Table IV for clarity of comparison. The E_a values of neat HBA/HNA and HNA/HAA/TA copolyesters in Kissinger method (144.80 and 256.50 kJ/mol) were slightly smaller than Kim-Park method (150.13 and 256.53 kJ/mol) when the two methods were compared. There was remarkable improvement of E_a when a small quantity of CNT was incorporated into HBA/HNA copolyester matrix. However decrease of E_a was investigated when a small quantity of CNT was incorporated into HNA/HAA/TA copolyester matrix. Two methods revealed that effect of significant improvement of thermal stability by incorporating CNT was investigated in CNT reinforced HBA/HNA copolyester as increasing CNT contents.

TABLE III
 E_a (kJ/mol) and r^2 Values of CNT Reinforced HBA/HNA and HNA/HAA/TA Copolyesters by the Flynn-Wall-Ozawa Method

	Degree of decomposition (%)					Average
	5	10	20	30	40	
HBA/HNA						
E_a	100.1	169.3	174.7	200.7	271.6	183.3
r^2	0.99	0.99	0.99	0.99	0.99	
HBA/HNA CNT 0.1						
E_a	195.3	198.3	206.8	220.0	231.7	210.4
r^2	0.96	0.96	0.99	0.99	0.98	
HBA/HNA CNT 0.5						
E_a	220.4	218.9	211.7	215.2	244.3	222.1
r^2	0.97	0.91	0.96	0.97	0.99	
HBA/HNA CNT 1.0						
E_a	235.5	226.9	220.4	227.9	252.8	232.7
r^2	0.99	0.99	0.99	0.99	0.99	
HBA/HNA CNT 2.0						
E_a	274.9	266.3	257.4	257.9	242.1	259.7
r^2	0.96	0.98	0.97	0.91	0.89	
HBA/HNA CNT 5.0						
E_a	303.7	271.8	265.7	300.7	271.3	282.5
r^2	0.89	0.94	0.95	0.96	0.94	
HBA/HNA CNT 10.0						
E_a	423.9	443.5	416.9	380.5	166.5	366.3
r^2	0.96	0.99	0.99	0.99	0.98	
HNA/HAA/TA						
E_a	219.7	217.7	243.3	285.7	363.9	266.1
r^2	0.87	0.93	0.90	0.97	0.89	
HNA/HAA/TA CNT 0.1						
E_a	182.9	188.9	200.8	212.5	118.9	196.3
r^2	0.99	0.98	0.96	0.84	0.99	
HNA/HAA/TA CNT 0.5						
E_a	204.1	200.7	202.5	190.3	232.0	205.9
r^2	0.99	0.99	0.99	0.97	0.95	
HNA/HAA/TA CNT 1.0						
E_a	226.9	132.7	258.2	212.2	304.3	226.9
r^2	0.96	0.88	0.89	0.75	0.75	
HNA/HAA/TA CNT 2.0						
E_a	220.9	245.1	275.9	272.4	157.7	234.5
r^2	0.99	0.99	0.99	0.99	0.72	
HNA/HAA/TA CNT 5.0						
E_a	253.6	258.5	252.6	244.7	239.6	249.8
r^2	0.98	0.97	0.96	0.95	0.78	
HNA/HAA/TA CNT 10.0						
E_a	235.0	248.4	253.3	280.6	259.8	255.4
r^2	0.81	0.88	0.90	0.97	0.96	

However, slight improvement of thermal stability by incorporating CNT was investigated as increasing CNT contents and even value of E_a was decreased when quantity of CNT was increased from 1.0 wt % to 2.0 wt % in CNT reinforced HNA/HAA/TA copolyester. The two methods exhibited good reliability by obtaining high r^2 .

In this study, thermal decomposition behavior of CNT reinforced TLCP composites was dependent on heating rate and CNT contents. The three different heating rates were needed to investigate the above four thermal decomposition kinetic analysis. The similar tendency was observed in four kinetic methods of thermal decomposition. The incorporation of

CNT increased or decreased thermal stability of composites acting physical barrier in HBA/HNA copolyester matrix or disturbing compactness of HNA/HAA/TA copolyester matrix. Dynamic kinetic analysis of CNT reinforced TLCP composites supported that thermal stability of composites was strongly influenced by addition of CNT changing E_a of thermal decomposition.

CONCLUSIONS

The CNT reinforced HBA/HNA and HNA/HAA/TA copolyesters were prepared by melt compounding process using a Haake internal mixer, and

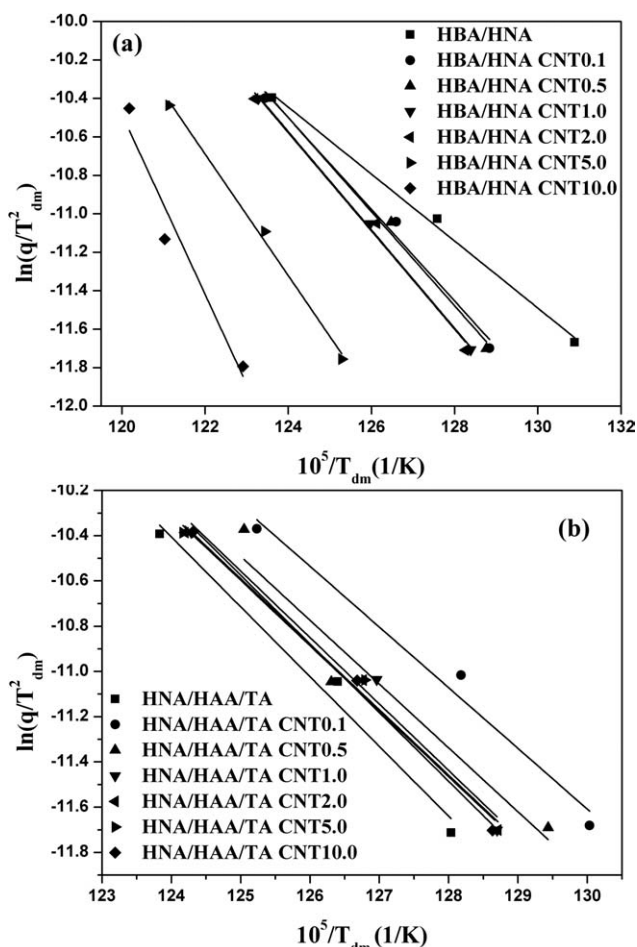


Figure 8 Kissinger plots of CNT reinforced (a) HBA/HNA and (b) HNA/HAA/TA copolyesters for calculating E_a of thermal decomposition.

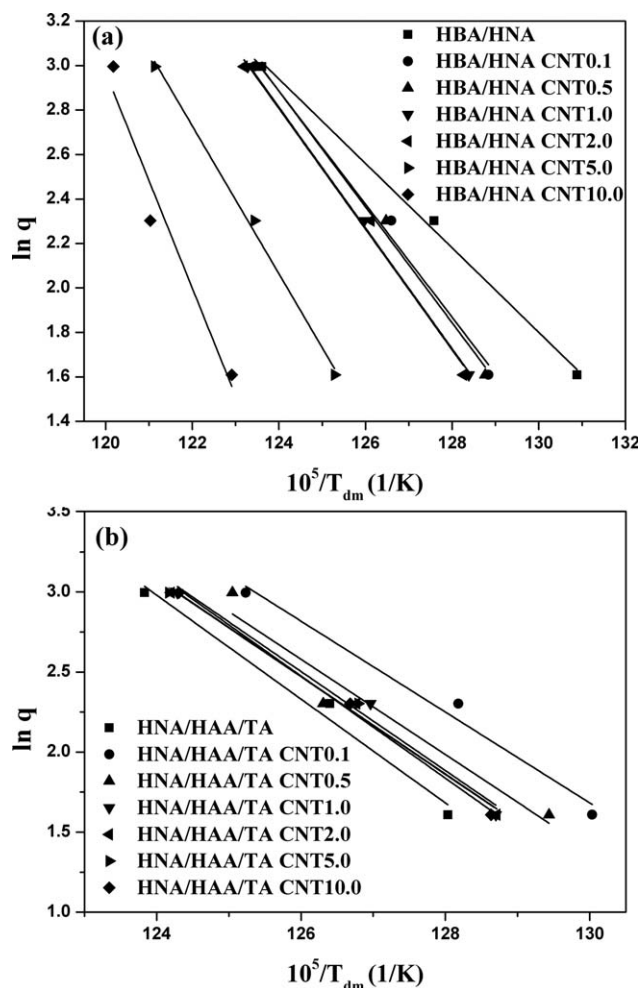


Figure 9 Kim-Park plots of CNT reinforced (a) HBA/HNA and (b) HNA/HAA/TA copolyesters for calculating E_a of thermal decomposition.

TABLE IV
 E_a and r^2 Values of CNT Reinforced HBA/HNA and HNA/HAA/TA Copolyesters by the Kissinger and Kim-Park Methods

	Kissinger		Kim-Park		Friedman	Flynn-Wall-Ozawa
	E_a (kJ/mol)	r^2	E_a (kJ/mol)	r^2	Average E_a (kJ/mol)	Average E_a (kJ/mol)
HBA/HNA	144.8	0.99	150.1	0.99	222.9	183.3
HBA/HNA CNT 0.1	198.3	0.98	201.1	0.98	224.8	210.4
HBA/HNA CNT 0.5	203.4	0.99	205.9	0.99	230.3	222.1
HBA/HNA CNT 1.0	212.6	0.99	214.7	0.99	230.4	232.7
HBA/HNA CNT 2.0	212.4	0.98	214.6	0.98	247.7	259.7
HBA/HNA CNT 5.0	262.9	0.99	262.8	0.99	283.4	282.5
HBA/HNA CNT 10.0	388.9	0.90	382.9	0.91	330.6	366.3
HNA/HAA/TA	256.5	0.96	256.5	0.97	282.3	266.1
HNA/HAA/TA CNT 0.1	223.0	0.96	224.5	0.97	200.2	196.3
HNA/HAA/TA CNT 0.5	234.6	0.87	235.5	0.89	208.5	205.9
HNA/HAA/TA CNT 1.0	244.2	0.97	244.8	0.97	239.1	226.9
HNA/HAA/TA CNT 2.0	240.7	0.99	241.4	0.99	255.3	234.5
HNA/HAA/TA CNT 5.0	240.7	0.98	241.4	0.98	255.8	249.8
HNA/HAA/TA CNT 10.0	252.3	0.99	252.5	0.99	273.6	255.4

thermal decomposition behavior of them was investigated using TGA. The single decomposition steps of CNT reinforced HBA/HNA and HNA/HAA/TA copolyesters were observed in nitrogen atmosphere. The results demonstrated that thermal decomposition behavior was influenced by CNT content and heating rate. The thermal decomposition kinetic parameters were investigated by the Friedman, Flynn-Wall-Ozawa, Kissinger, and Kim-Park methods. The kinetic parameters were significantly controlled by the heating rate, conversion level, and calculation methods. It was found that CNT was well dispersed in TLCP matrix on the morphology analysis. This well-dispersed CNT influenced the CNT/TLCP composites by acting as physical barriers in the TLCP matrix or disturbing compactness of TLCP against thermal decomposition. The enhancement of thermal stability of CNT reinforced HBA/HNA copolyester was observed as increasing CNT contents. However, thermal stability of CNT reinforced HNA/HAA/TA copolyester was decreased when a small quantity of CNT was added and then had a tendency to increase with increase of CNT contents. It was confirmed by determining activation energies of thermal decomposition calculated by four different kinetic methods. As a result, although incorporation of CNT into TLCP matrix did not affect bond dissociation energy of polymer chains, it had a considerable influence to thermal decomposition behavior by affecting activation energy of thermal decomposition.

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