

Thermal Decomposition Behavior and Durability Evaluation of Thermotropic Liquid Crystalline Polymers

Sang Mi Shin and Seong Hun Kim*

Department of Fiber and Polymer Engineering, Hanyang University, Seoul 133-791, Korea

Jun Kwang Song

Department of Material Analysis, Center for Reliability Technical, Korea Testing Laboratory, Seoul 152-718, Korea

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Abstract: The thermal decomposition behavior and degradation characteristics of four different thermotropic liquid crystalline polymers (TLCPs) were studied. The thermal decomposition behavior was determined by means of thermogravimetric analysis (TGA) at different heating rates in nitrogen and air. The order of the thermal stability was as follows: multi-aromatic polyester > hydroxybenzoic acid (HBA)/hydroxynaphthoic acid (HNA) copolyester > HNA/hydroxyl acetaniline (HAA)/terephthalic acid (TA) copolyester > HBA/Poly(ethylene terephthalate) (PET) copolyester. The activation energies of the thermal degradation were calculated by four multiple heating rate methods: Flynn-Wall, Friedman, Kissinger, and Kim-Park. The Flynn-Wall and Kim-Park methods were the most suitable methods to calculate the activation energy. Samples were exposed to an accelerated degradation test (ADT), under fixed conditions of heat (63 ± 3 °C), humidity ($30\pm 4\%$) and Xenon arc radiation (1.10 W/m²), and the changes in surface morphology and color difference with time were determined. The TLCPs decomposed, discolored and cracked upon exposure to ultraviolet radiation.

Keywords: thermotropic liquid crystal polymer (TLCP), thermal decomposition, thermogravimetric analysis (TGA), durability, degradation.

Introduction

Thermotropic liquid crystal polymers (TLCPs) have outstanding strength and stiffness, a high heat distortion temperature and dimensional stability, good ultraviolet radiation resistance, a highly oriented structure and low moisture uptake.¹⁻⁴ These characteristics make TLCPs useful for a wide range of applications. TLCPs have been utilized as fibers, rods, and sheets in the materials industry, as well as microelectronic devices such as chip carriers, connectors, and switches.⁵ Recently, aromatic polyester TLCPs have been used as high performance engineering plastics.^{6,7} They have high heat-resistance and excellent mechanical properties due to their rigid, rod-like aromatic chain structure, resulting in their utilization in various industrial fields where the higher thermal stability is required.

As polymeric materials are often used outdoors for long periods of time, they degrade owing to heat, sunlight, oxygen in the atmosphere, humidity, and stress. This results in the deterioration of their chemical and physical properties and the life of the material becomes limited.⁸ Therefore, any

polymeric material that is to be used in outdoor applications must have excellent resistance to all environmental conditions.⁹ Thermal decomposition behavior of polymers is very important because it affects the final properties, such as the upper temperature limit of use and dimensional stability. The reliability of polymeric materials can be improved and the competitiveness of a product enhanced through evaluation of durability and life estimation.¹⁰ There are few techniques available that can be used to evaluate the durability of TLCP materials.

Thermogravimetric analysis (TGA) is commonly used to determine characteristics of thermal decomposition kinetics and thermal stability of polymers. The thermal decomposition kinetics of polymers and composites can be investigated based on single heating rate and multiple heating rate methods.^{11,12} The methods for calculating the kinetics parameters to characterize the thermal decomposition of the polymers can be divided into two groups: One is the single heating rate method, such as the Friedman, Freeman-Carroll, Chang, and Coats-Redfern methods, and another is the multiple heating rate method, like the Flynn-Wall, Reich, Friedman, Kim-Park, Kissinger, and Hernandez-Sanchez methods.¹² The multiple heating rate method makes no

*Corresponding Author. E-mail: kimsh@hanyang.ac.kr

assumption about the reaction order in the calculation of the activation energy. Therefore, the kinetic analysis of thermal decomposition of polymer composites, for the estimation of the kinetic parameters, by the multiple heating rate method results in fewer errors than the single heating rate method.¹³ Although much research has been carried out into the physical properties and thermal behavior of polymers, not much research and development has been carried out on the kinetic analysis of thermal decomposition of TLCPs.

In this study, the kinetic analysis of thermal decomposition of TLCPs was investigated using TGA data obtained at different heating rates. The thermal stability and mechanism of thermal decomposition were considered. Four multiple heating rate methods were used to calculate the activation energies of thermal decomposition and the advantages and disadvantages of each method were determined. In addition, weathering of the TLCPs was carried out in an accelerated degradation test using a Xenon arc, and changes in mechanical properties and surface morphology were determined.

Experimental

Materials. The following four TLCPs were used: hydroxybenzoic acid (HBA)/hydroxyl-naphthoic acid (HNA) copolyester (Polyplastics Co., Japan), HNA/hydroxy acetaniline (HAA)/terephthalic acid (TA) copolyester (Polyplastics Co., Japan), HBA/poly(ethylene terephthalate) (PET) copolyester (Unitika Co., Ltd., Japan), and a multi-aromatic polyester

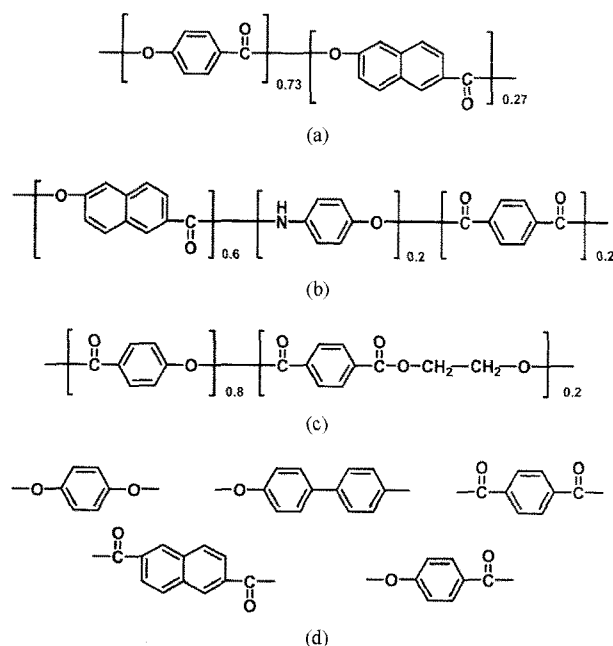


Figure 1. Chemical structures of TLCPs: (a) HBA/HNA copolyester, (b) HNA/HAA/TA copolyester, (c) HBA/PET copolyester, and (d) multi-aromatic polyester.

(Du Pont, USA). The chemical structures of these materials are shown in Figure 1. HBA/HNA copolyester has a 73/27 molar ratio of HBA/HNA. HNA/HAA/TA copolyester is composed of 60 mol% HNA, 20 mol% HAA, and 20 mol% TA. HBA/PET copolyester is the semi-rigid copolyester composed of 80 mol% HBA and 20 mol% PET. The multi-aromatic polyester is synthesized from TA, HBA, hydroquinone, dihydroxy biphenyl, and NDA (naphthalene dicarboxylic acid). The component rate of monomers in multi-aromatic polyester is not disclosed by the maker. All the pellets were dried in a vacuum oven at 120 °C for at least 24 h prior to use to remove moisture.

Characterizations. TGA analyses were performed using a TA instrument, SDT Q 600. The temperature was increased from 30–1,000 °C, at heating rates of 5, 10, and 20 °C/min. Measurements were made in both nitrogen and in air (because plastic goods are typically used in an air atmosphere, it was considered important to study the thermal degradation behavior under similar conditions). The TLCPs were used in the pellet state and the sample weight was about 13 mg. The TLCPs' activation energies of thermal decomposition were determined by the Flynn-Wall, Friedman, Kissinger, and Kim-Park methods.

TLCP films with a thickness of 1.0 mm were prepared using a CARVER 4125 compression molding machine (Fred S. CARVER Inc.). Accelerated degradation tests (ADTs) were performed to investigate changes in the materials over time under selected environmental conditions. A Weather-Ometer CI4000 (Atlas Co.), assembled according to ISO 4838-2, was used. The films were exposed to 63±3 °C, 30±4% humidity, and radiation of wavelength 420 nm. Changes in the surface morphology of degraded samples were studied using a Hitachi S-4700 scanning electron microscope. Measurements of the color difference were carried out using a Minolta 3600D color difference meter.

TGA Kinetics Method of Thermal Degradation. TGA kinetics analysis is determined by measurement of fractional mass loss and degradation rate according to temperature change. The fraction of conversion, α , is defined as:

$$\alpha = \frac{W_0 - W}{W_0 - W_f} \quad (1)$$

where, W is the actual weight at any degradation time, W_0 is the initial weight, and W_f is the final weight at the end of thermal degradation process. The rate of degradation, $d\alpha/dt$, can be expressed as the product of the function of temperature and the function of conversion:

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = k(T) \cdot f(\alpha) \quad (2)$$

where $\beta = dT/dt$ is the heating rate. If thermal degradation behavior follows the Arrhenius equation, then $k(T)$ is constant and the rate of degradation is expressed as:

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

where E_a is the activation energy, A is a pre-exponential factor and R is the gas constant. It is assumed that the degradation reaction follows the n -th order reaction:

$$f(\alpha) = (1 - \alpha)^n \quad (4)$$

The combination of eqs. (2), (3), and (4) gives eq. (5)¹⁴:

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = (1 - \alpha)^n A e^{-E_a/RT} \quad (5)$$

Eq. (5) is integrated or differentiated to derive various equations for obtaining the kinetic parameters.⁸

The multiple heating methods used in this study to determine the thermal decomposition kinetics of the TLCPs are as follows:

Flynn-Wall Method.

$$\ln\beta = \ln\left(\frac{ZE_a}{R}\right) - \ln F(\alpha) - \frac{E_a}{RT} \quad (6)$$

The Flynn-Wall method¹⁵ is a simple method for determining activation energies directly from weight loss against temperature data obtained at several heating rates. The technique assumes that A , $(1 - \alpha)^n$, and E_a are independent of T , and that A and E_a are independent of α . The value of the activation energy (E_a) can be calculated from the slope of the plot of $\ln\beta$ versus $1/T$ for a fixed weight loss. This method cannot yield the other kinetic parameters except for the activation energy.

Friedman Method.

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln Z + n \ln(1 - \alpha) - \left(\frac{E_a}{RT}\right) \quad (7)$$

The Friedman method¹⁶ assumes that the chemistry of the degradation process is independent of temperature and is dependent only on the instantaneous weight of the material. E_a can be obtained from the slope ($= -E_a/R$) of plot $\ln(d\alpha/dt)$ versus $1/T$ for a constant α .

Kissinger Method.

$$\ln\left(\frac{\beta}{T_{dm}^2}\right) = \ln\left[\frac{n(1 - \alpha_m)^{n-1} ZR}{E_a}\right] - \frac{E_a}{RT_{dm}} \quad (8)$$

Here T_{dm} is the absolute temperature at the maximum rate of the thermal decomposition and α_m is the weight loss at the maximum decomposition rate. The Kissinger method¹⁷ assumes that $\ln(1 - \alpha_m)^{n-1}$ is not dependent on the heating rate. It also assumes that the reaction order remains constant, and is very nearly equal to unity. The value of the activation energy can be calculated from the slope of the plot of $\ln(\beta/T_{dm}^2)$ versus $1/T_{dm}$ at the maximum weight loss.

Kim-Park Method.

$$\ln\beta = \ln Z + \left(\frac{E_a}{R}\right) + \ln\left[1 - n + \left(\frac{n}{0.944}\right)\right] - 5.3305 - 1.0516\left(\frac{E_a}{RT_{dm}}\right) \quad (9)$$

The Kim-Park method¹⁸ assumes that α_m is independent of the heating rate, activation energy, and a pre-exponential factor. The activation energy can be obtained by plotting $\ln\beta$ against $1/T_{dm}$. Because the approximate value of a conversion factor is used (0.9440), this technique can be used to more accurately calculate the activation energy than the other methods, in which the value of the conversion factor is unity.

Results and Discussion

Thermal stability of polymer materials is the most important factor for polymer processing and polymer applications. The thermogravimetry (TG) and derivative thermogravimetry (DTG) curves of the HNA/HAA/TA copolyester at various heating rates in nitrogen and air are shown in Figure 2.

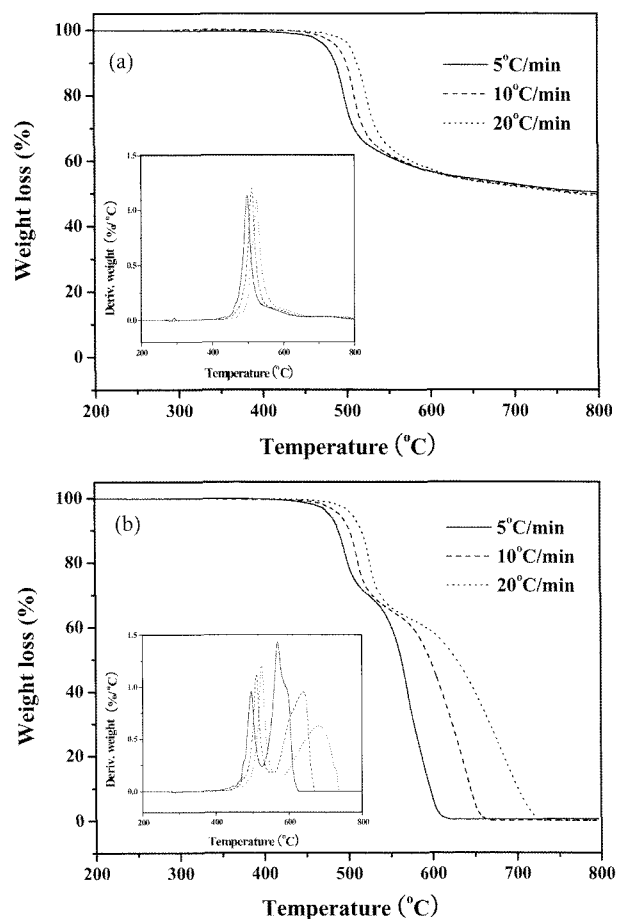


Figure 2. TG and DTG curves of HNA/HAA/TA copolyester at various heating rates in (a) nitrogen and (b) air.

The thermograms of the TLCPs show that the heating rate and the atmosphere significantly influence the thermal decomposition. The TG curves shifted to higher temperatures as the heating rate increased. Polymer molecules do not have enough time to absorb the heat and reach thermal

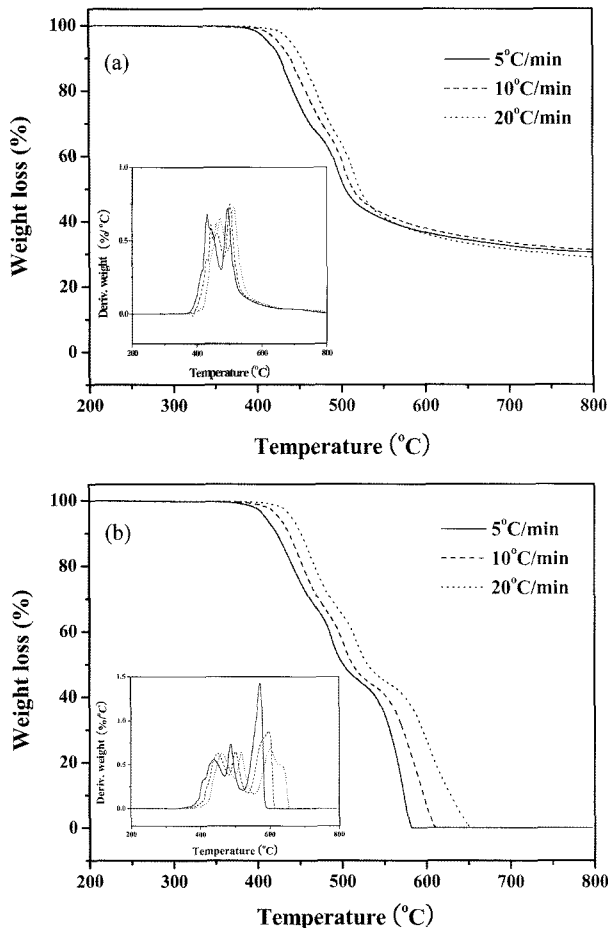


Figure 3. TG and DTG curves of HBA/PET copolyester at various heating rates in (a) nitrogen and (b) air.

equilibrium as the heating rate increases, which makes the degradation rate slower. In the presence of nitrogen the DTG curves showed a single peak, implying that the thermal decomposition process occurred in a single step. In an air atmosphere the thermal decomposition occurred in two steps and there was little or no residue, implying the acceleration of thermo-oxidation. The TGA curves of HBA/HNA copolyester and the multi-aromatic polyester resemble those of the HNA/HAA/TA copolyester. In contrast to the three other materials, the thermal decomposition of HBA/PET copolyester proceeded with two steps in nitrogen and with three steps in air, as shown in Figure 3. The TGA results of the TLCPs at different heating rates are shown in Table I. As the heating rate was increased, the temperature at initial thermal decomposition and the maximum decomposition rate shifted toward a higher temperature. TGA experiments were carried out in a nitrogen atmosphere and at a heating rate of 10 °C/min to determine the maximum rate of weight loss. The following results were obtained: 514 °C for the HBA/HNA copolyester, 510 °C for the HNA/HAA/TA copolyester, 442 °C for the HBA/PET copolyester, and 530 °C for the multi-aromatic polyester. The order of T_{dm} for the TLCPs was: HBA/PET copolyester < HNA/HAA/TA copolyester < HBA/HNA copolyester < multi-aromatic polyester. Generally, an increase in T_{dm} is associated with an improvement of the thermal stability.¹⁹ Therefore, these results show that the multi-aromatic polyester had the best thermal stability. Furthermore, the HBA/HNA copolyester had better thermal stability than the HNA/HAA/TA copolyester. This result corresponds with the findings of Jin *et al.*²⁰ The average bond dissociation energy of C-N is lower than that of C-O, and the naphthoyl structure makes the HNA/HAA/TA copolyester less thermally stable than the HBA/HNA copolyester. Furthermore, because the HBA/PET copolyester is a semi-rigid, rod-like aromatic polyester, it is less thermally stable than the wholly aromatic polyester.²¹ The residual weight remaining after thermal decomposition has

Table I. TGA Results of the TLCPs at Difference Heating Rates in Nitrogen and Air

Materials	Heating Rate (°C/min)	Nitrogen			Air		
		T_i^a (°C)	T_{max}^b (°C)	W_R^c (%)	T_i^a (°C)	T_{max}^b (°C)	W_R^c (%)
HBA/HNA Copolyester	5	435.0	500.4	43.2	409.9	502.3	0.6
	10	437.3	513.8	42.8	441.5	515.1	0.0
	20	457.0	527.5	43.0	456.9	531.5	0.4
HNA/HAA/TA Copolyester	5	432.1	497.8	50.4	440.0	496.9	0.5
	10	453.2	509.3	49.7	455.2	511.4	0.1
	20	474.1	524.7	49.2	471.5	524.2	0.2
HBA/PET Copolyester	5	390.2	439.5	30.5	380.1	441.1	0.0
	10	401.2	449.8	31.2	394.8	449.9	0.3
	20	410.9	463.5	28.8	412.7	464.6	0.9
Multi-aromatic Polyester	5	450.0	516.9	39.5	438.3	513.8	0.3
	10	467.7	530.0	40.6	455.4	531.9	0.7
	20	480.9	544.1	39.6	475.5	546.0	0.0

^aInitial decomposition temperature. ^bTemperature of maximum rate of weight loss for the first stage. ^cResidual yield in TGA at 800 °C.

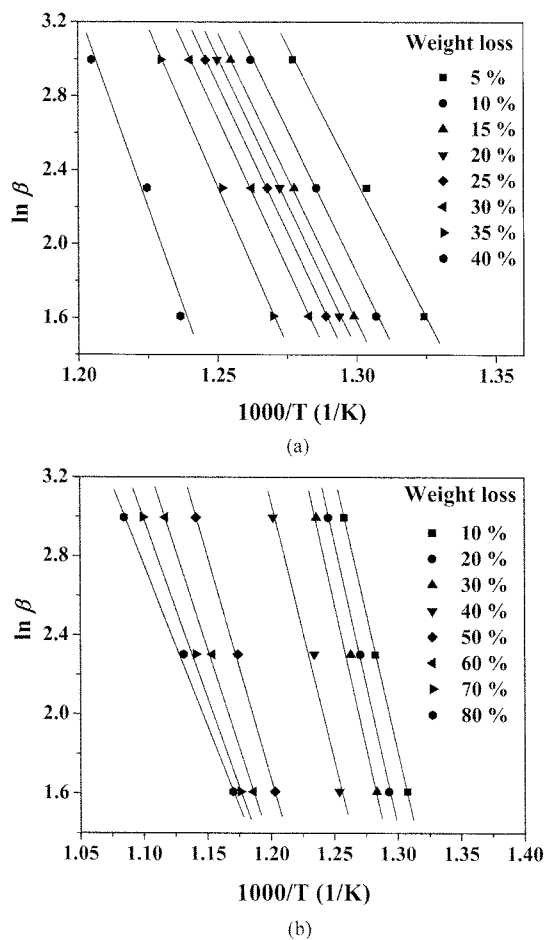


Figure 4. Flynn-Wall plots of $\ln \beta$ against $1/T$ for HNA/HAA/TA copolyester in (a) nitrogen and (b) air.

no relationship to thermal stability.

The kinetic analysis of thermal decomposition makes it possible to predict the thermal stability and thermal decomposition behavior of polymers. As mentioned earlier, the multiple heating methods used in this research were the Flynn-Wall, Friedman, Kissinger, and Kim-Park methods. The Flynn-Wall plots of $\ln \beta$ versus $1/T$ for the HNA/HAA/TA copolyester in nitrogen and air are shown in Figure 4. The activation energies of thermal degradation for TLCPs under nitrogen and air, as obtained by the Flynn-Wall method, are shown in Figure 5. Figure 5(b) shows that the activation energy values of thermal degradation of the TLCPs in air have a maximum point between 30% and 40% weight loss percentage, and then decrease gradually. At this point, the first stage was completed and the second stage had begun. Hence, there was a greater error here. When Figures 5(a) and (b) are compared it is seen that the first stage of the degradation mechanisms in air is similar to the degradation mechanisms under nitrogen. The activation energies as calculated by the Friedman method are closer to those obtained by the Flynn-Wall method. However, the activation energy

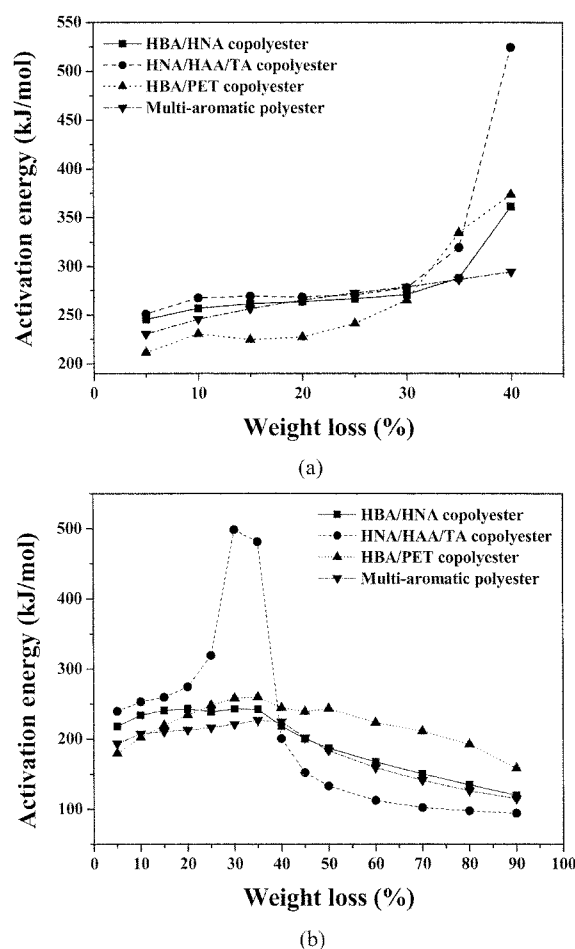


Figure 5. Activation energies of thermal degradation for TLCPs under (a) nitrogen and (b) air as obtained by the Flynn-Wall method.

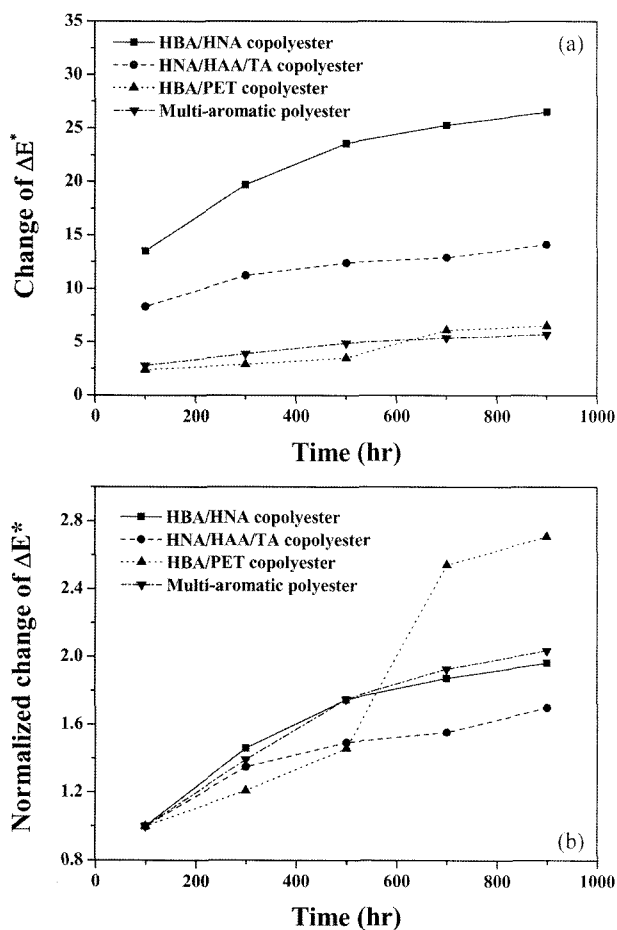
cannot be obtained at a particular weight loss because of an upward slope of the plots of $\ln d\alpha/dt$ against $1/T$. The correlation coefficient of the Friedman method is lower than that of the Flynn-Wall method. Consequently, the Flynn-Wall method was a more suitable method. The kinetic parameters for the thermal decomposition of the TLCPs in nitrogen and air as calculated from the Kissinger and Kim-Park methods are given in Tables II and III. The activation energies of the TLCPs were lower in air than in nitrogen because of thermo-oxidative degradation. Furthermore, the activation energy

Table II. Activation Energies of Thermal Degradation for TLCPs under Nitrogen and Air Obtained by the Kissinger Method

Materials	Nitrogen		Air	
	R	E_a	R	E_a
HBA/HNA Copolyester	0.9999	234.7	0.9978	225.2
HNA/HAA/TA Copolyester	0.9989	230.2	0.9991	219.7
HBA/PET Copolyester	0.9972	231.8	0.9978	206.4
Multi-aromatic Polyester	0.9995	225.2	0.9978	198.7

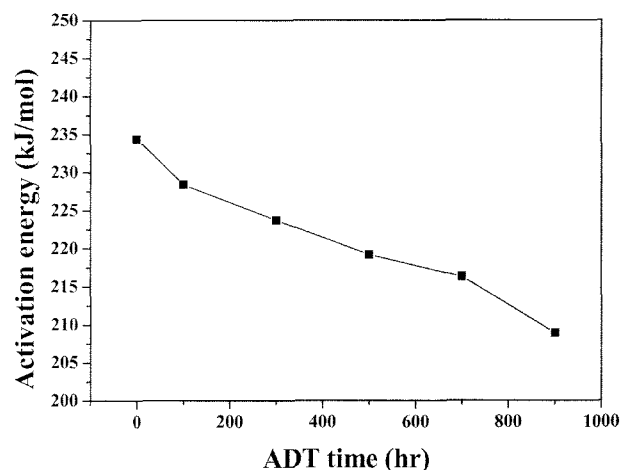
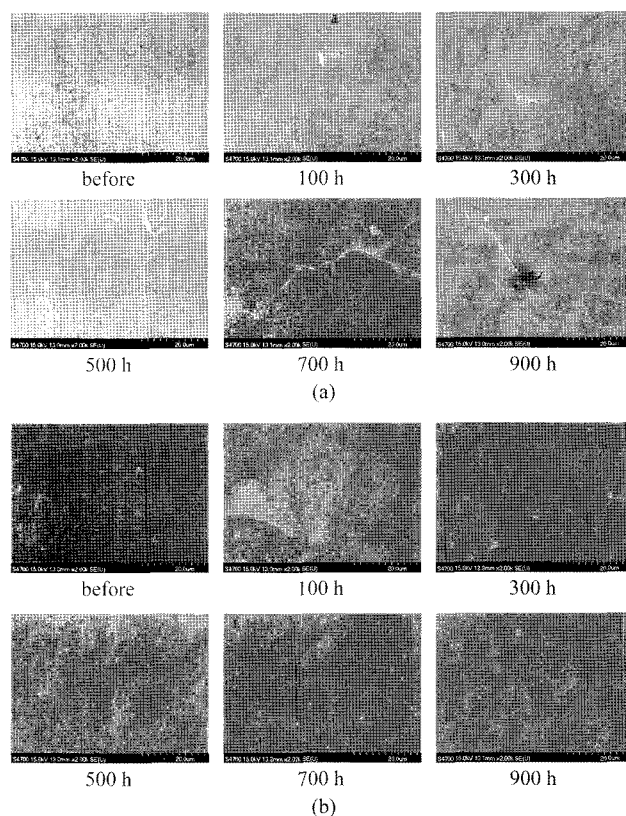
Table III. Activation Energies of Thermal Degradation for TLCPs under Nitrogen and Air Obtained by the Kim-Park Method

Materials	Nitrogen		Air	
	R	E_a	R	E_a
HBA/HNA Copolyester	1.0000	253.9	0.9982	233.2
HNA/HAA/TA Copolyester	0.9991	237.9	0.9993	228.0
HBA/PET Copolyester	0.9976	238.3	0.9982	215.2
Multi-aromatic Polyester	0.9996	233.4	0.9987	208.2

**Figure 6.** (a) Change of color difference and (b) normalized change of color difference for TLCPs with time of accelerated degradation test.

and correlation coefficient values obtained from the Kim-Park method were higher than those from the Kissinger method.

Figure 6(a) shows the change of color difference for the TLCPs after 100, 300, 500, 700, and 900 h irradiation. All the TLCPs were discolored after 100 h exposure to a Xenon arc lamp. Figure 6(a) shows that the color difference of the TLCPs increased with increasing time of the accelerated degradation test. The HBA/PET copolyester and the multi-aromatic polyester had low color difference values of 2.8

**Figure 7.** Activation energy of thermal degradation of HBA/HNA copolyester as calculated by the Flynn-Wall method after accelerated degradation test.**Figure 8.** SEM microphotographs of surfaces of (a) HBA/HNA copolyester and (b) HNA/HAA/TA copolyester with time of accelerated degradation test.

and 2.4 respectively after 100 h accelerated degradation test. The HBA/HNA copolyester was the most sensitive of color difference by exposure to UV. A graph of the normalized change of color difference is shown in Figure 6(b). The HBA/HNA copolyester, HNA/HAA/TA copolyester and multi-aromatic

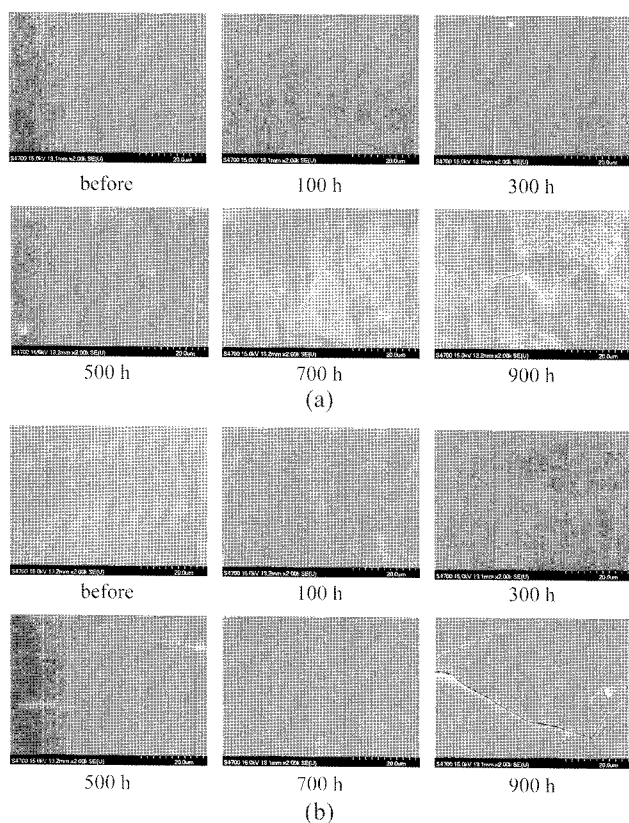


Figure 9. SEM microphotographs of surfaces of (a) HBA/PET copolyester and (b) multi-aromatic polyester with time of accelerated degradation test.

polyester were badly discolored from 100 to 300 h, while the HBA/PET copolyester was badly discolored from 500 to 700 h. The Flynn-Wall method was used for determining the activation energy of the thermal decomposition of the HBA/HNA copolyester specimen exposed to UV radiation at 5% weight loss. As shown in Figure 7, the activation energy values for thermal degradation exhibited a decreasing tendency as the test time of the accelerated degradation test increased. Therefore, UV light and heat must be considered as the major variable affecting the polymer degradation. Scanning electron microphotographs of the surfaces of the TLCPs both before and after the accelerated degradation tests are shown in Figures 8 and 9. The HBA/HNA copolyester and the multi-aromatic polyester cracked after 100 h in the accelerated degradation test, and the number of cracks increased with time. Cracks in the HBA/PET copolyester appeared after 700 h UV exposure and, as there were many cracks, the mechanical strength deteriorated. Hence, the mechanical properties of these TLCPs were reduced upon exposure to UV. The HNA/HAA/TA copolyester was unchanged. These results suggest that the HNA/HAA/TA copolyester had stronger UV resistance than other three materials.

Conclusions

The thermal decomposition behavior of four TLCPs was investigated using TGA. The multi-aromatic polyester had the best thermal stability of the four TLCPs in both air and nitrogen. The activation energies of the thermal degradation were calculated by the Flynn-Wall, Friedman, Kissinger, and Kim-Park methods. The activation energy of thermal decomposition was lower in air than in nitrogen owing to thermo-oxidative degradation. It was found that the Flynn-Wall and Kim-Park methods were the most suitable methods to determine activation energy. After an accelerated degradation test was performed for 100, 300, 500, 700, and 900 h, changes in surface morphology and color differences were observed. As the time of the accelerated degradation test increased, so the color difference of the TLCPs increased. Since the HNA/HAA/TA copolyester was not cracked, it was considered to have the best strength among the materials tested in this study.

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