



Thermal Analysis of Multi-walled Carbon Nanotubes by Kissinger's Corrected Kinetic Equation

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ABSTRACT

Carbon nanotubes (CNTs) have been a popular material in recent years, but their thermal characteristics have not been understood completely. We investigated the unique thermal stability of multi-walled carbon nanotubes (MWCNTs) and used nitric acid (HNO₃) to purify MWCNTs to promote its activation energy (E_a). The study used differential scanning calorimetry (DSC), thermogravimetric analyzer (TGA), and Fourier transform infrared (FTIR) spectrometer to analyze as-grown MWCNTs and modified MWCNTs. For DSC, the heating rate was chosen to be 0.25 to 2.0 °C/min. From DSC results, E_a and exothermic onset temperature (T₀) of the modified MWCNTs increased with increasing HNO₃ concentration. The TGA results showed that both as-grown and modified MWCNTs' decomposition temperatures were higher than 500°C in air. The infrared spectra of as-grown MWCNTs and modified MWCNTs have shown that the gas phase composition is CO₂ after TGA linked with FTIR. By Kissinger's corrected kinetic equation, E_a increased with increasing HNO₃ concentration. Through this study, we realized that as-grown MWCNTs and modified MWCNTs are thermally hazardous materials with high potential heat of decomposition, especially under fire exposure. Thus, it is important to know the thermal hazard characteristics of material with a measure to prevent its thermal damage during perturbed situations.

Keywords: Multi-walled carbon nanotubes (MWCNTs); Nitric acid (HNO₃); Activation energy (E_a); Differential scanning calorimetry (DSC); Kissinger's corrected kinetic equation.

INTRODUCTION

In 1991, Dr. Sumio Iijima discovered multi-walled carbon nanotubes (MWCNTs) via arc-discharge (Iijima, 1991). Since then, carbon nanotubes (CNTs) have attracted tremendous interest globally. They have unique physicochemical as well as electrical properties and have various emerging applications in field emission, hydrogen storage, and chemical sensors (Lu *et al.*, 2005). They not only can adsorb volatile organic compounds (VOC) (Cheng, 2008; Sone *et al.*, 2008) and heavy metal (Li *et al.*, 2003) but also act as a filter (Tsai *et al.*, 2008).

CNTs have van der Waals' attraction so that commonly causes significant agglomeration. This characteristic of CNTs could obstruct its application with other materials. Attaching functional groups can markedly increase the

dispersion of nanotube materials (Park, *et al.*, 2003). To modify CNTs can improve the mechanical properties of nanocomposites. There are various modification methods for CNTs that have been reported, such as microwave-assisted heating, thermal oxidation, and chemical oxidation (Chin *et al.*, 2007). Among them, chemical oxidation is frequently used, including nitric acid (HNO₃), hydrogen peroxide (H₂O₂), mixture of H₂O₂ and hydrochloric acid (HCl) or a mixture of sulfuric acid (H₂SO₄) and HNO₃ (Hou *et al.*, 2008).

However, reports of thermal analysis for as-grown MWCNTs and modified MWCNTs are still scanty in the open literature (Pritchard, 2004; Jin *et al.*, 2007). In this study, the thermal decomposition of MWCNTs was characterized for the thermal hazards, investigated, as well as the thermal stability and the gas phase composition identified during TGA test. Finally, we used Kissinger's corrected kinetic equation to analyze and elucidate the thermokinetic parameters derived from the experimental data.

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EXPERIMENTAL AND METHODS

Modification of MWCNTs

The first step used the as-grown MWCNTs with 3 N, 5 N, 10 N and 15 N HNO₃ in a round bottomed flask equipped with a condenser. The dispersion was refluxed under magnetic stirring at 60°C for 12 hr (Ovejero *et al.*, 2006). Moreover, the resulting dispersion was diluted in water and filtered. The resulting solid was washed up to neutral pH. Finally, the sample was dried in an oven.

Attenuated Total Reflection–Fourier Transform Infrared (ATR–FTIR) Spectrometer

The second step used attenuated total reflection–Fourier transform infrared (ATR–FTIR) spectrometer to identify the surface functional groups of the modified MWCNTs. First, the surface of ATR was cleaned by methanol before the sample was applied. The reason was to ensure that the infrared reflecting medium, germanium (Ge), was not polluted. After waiting for the methanol to be evaporated completely, the powder of as-grown MWCNTs and modified MWCNTs were covered with the infrared reflecting medium and fixed on ATR–FTIR. The frequency range of FTIR was set to be from 4,000 to 400 1/cm. Finally, the FTIR spectrum was taken to compare with the standard spectra. We could observe whether the functional group followed our expectations of bond formation on modified MWCNTs or not.

Differential Scanning Calorimetry (DSC)

The third step used the DSC 821° Mettler TA 8000 system and STAR° analysis software to conduct the experiment (Mettler Toledo, 2005). The thermal curve from DSC can be preliminarily used to evaluate the thermal properties for the material of interest. The first purpose was to understand experimental data on a material's thermal parameters, such as exothermic onset temperature (T₀) and ΔH, with respect to time. Then, the experimental data were taken to analyze the thermokinetics, for instance, activation energy (E_a), reaction order, extent of reaction and so on.

As-grown MWCNTs and modified MWCNTs both were packed in an aluminum pan and heating rates were set from 0.1 to 10 °C/min (Chang *et al.*, 2009). In this way, the precision and reproducibility of the experimental results were examined and evaluated with a sound response. For the sake of better precision, the heating rate was chosen to be from 0.25 to 2.0 °C/min.

Thermogravimetric Analyzer (TGA) Linked with Fourier Transform Infrared (FTIR) Spectrometer

The fourth step adopted the PerkinElmer Paris 1 system to perform a weight loss percentage and decomposition experiment (PerkinElmer, 2006). Initially, the temperature was set from 30 to 950°C for TGA. Then, sample was taken in 21 vol.% oxygen environment and the heating rate was 4 °C/min. By this experiment, we can gain the weight loss percentage and decomposition temperature of as-grown MWCNTs and modified MWCNTs.

By means of TGA linked with FTIR, the gas phase sample compositions could be identified simultaneously. The frequency range of FTIR was from 4,000 to 400 1/cm (PerkinElmer, 2006; Yang *et al.*, 2007).

Kissinger's Corrected Kinetic Equation

Kissinger's corrected kinetic equation is the most typical and extensive model that is prevalently applied to evaluate the kinetics. For the results a line can be drawn through the experimental data from thermal analysis and Kissinger's corrected kinetic equation. Eq. (1) expresses the Kissinger's corrected kinetic equation:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\frac{AR}{E_a} - \frac{E_a}{RT_p} \quad (1)$$

where β is heating rate (°C/min); A is pre-exponential factor (1/sec); E_a is activation energy (kJ/mol); T_p is peak temperature (K); R is gas constant (= 8.314 J/mol K).

Therefore, using the slope of the line and Eq. (1), the E_a of the sample can be determined (Kissinger, 1957; Soliman, 2007; Chou *et al.*, 2008; You *et al.*, 2009).

RESULTS AND DISCUSSION

Results of ATR–FTIR Tests

As indicated from the references, the surface of as-grown MWCNTs which were modified with HNO₃ can bond on the carboxyl group (–COOH) (Kuznetsova *et al.*, 2000). By ATR–FTIR analysis, FTIR spectrum showed the peak of carbonyl group (C=O) (1,740–1,720 1/cm) and hydroxyl group (O–H) (3,300–2,500 1/cm).

Fig. 1 shows the FTIR spectrum of as-grown MWCNTs, MWCNTs modified with 5 N HNO₃, and MWCNTs modified with 15 N HNO₃. It can be seen that the three curves have similar peaks at 3,273 1/cm (O–H) and 1,735 1/cm (C=O). Otherwise, the hydroxyl group and carbonyl group peaks of 15 N HNO₃ curve are more intense than the other two curves. Consequently, we proved our study can succeed to bond on carboxyl group on the surface of MWCNTs (Ovejero *et al.*, 2006).

DSC Tests

The study applied DSC 821° to conduct a heating experiment in order to understand the sample's stability and exothermic phenomenon of thermal decomposition reaction. By DSC scanning, the results of as-grown MWCNTs are presented in Table 1 and Fig. 2. As temperature was increased, the sample was triggered for exothermic reaction. The conclusion could be generalized from DSC scanning results: when heating rate is increased, the corresponding peak temperature (T_p) and T₀ also increase. This phenomenon is called the "thermal delay effect".

Therefore, the results showed that MWCNTs decomposition occurred under oxidation when the temperature reached 300°C in air. The peak from the thermal curve was distributed from 512 to 601°C and heat of decomposition was from 30,810 to 40,360 J/g.

After that, the same method was used to analyze modified MWCNTs with different HNO₃ solution concentrations, as can be seen in Table 2 and Fig. 3. When increasing HNO₃ concentration, E_a and T₀ of the modified MWCNTs were augmented. For 3 N, T₀ was 358°C. However, when concentration was raised to 5, 10 and 15 N,

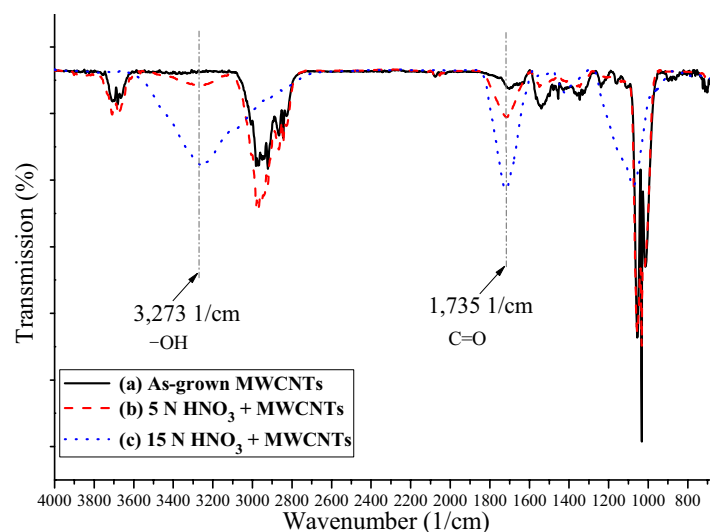


Fig. 1. ATR-FTIR spectra, (a) As-grown MWCNTs, (b) 5 N HNO₃ + MWCNTs, (c) 15 N HNO₃ + MWCNTs.

Table 1. Results of experimental data for as-grown MWCNTs by DSC tests at heating rates of 0.25–2.0 °C/min.

Heating rate (°C/min)	T ₀ (°C)	T _p (°C)	ΔH _d (J/g)	E _a (kJ/mol)
0.25	298	512	40,360	91.07+/-0.71
0.5	305	542	30,810	137.38+/-0.97
1	316	567	32,660	152.12+/-0.72
2	337	601	33,050	152.06+/-0.25

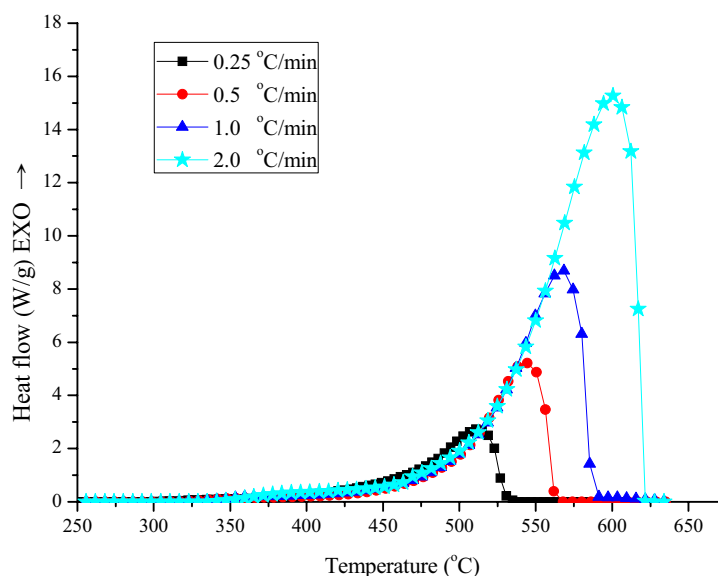


Fig. 2. DSC experimental data of as-grown MWCNTs with heating rates from 0.25 to 2.0 °C/min.

Table 2. Results of experimental data for as-grown MWCNTs and modified MWCNTs by DSC tests at heating rate of 1.0 °C/min.

Sample	T ₀ (°C)	T _p (°C)	E _a (kJ/mol)
As-grown	316	567	152.12+/-0.72
3 N	358	568	152.42+/-0.39
5 N	376	573	154.01+/-0.59
10 N	398	578	155.03+/-0.38
15 N	420	575	158.28+/-0.34

T₀ increased to 376, 398 and 420°C, respectively; E_a was gradually increased to 154.01, 155.03 and 158.28 kJ/mol, respectively.

Through the experimental results, we inferred HNO₃ concentration is a key factor to affect E_a. The literature indicates that when MWCNTs are dipped in HNO₃ solution, a bond of MWCNTs is formed on carboxyl groups at the surface of MWCNTs (Kuznetsova *et al.*, 2000). The carboxyl groups at the surface of the MWCNTs became a hydrogen bond, as depicted in Fig. 4. All of the

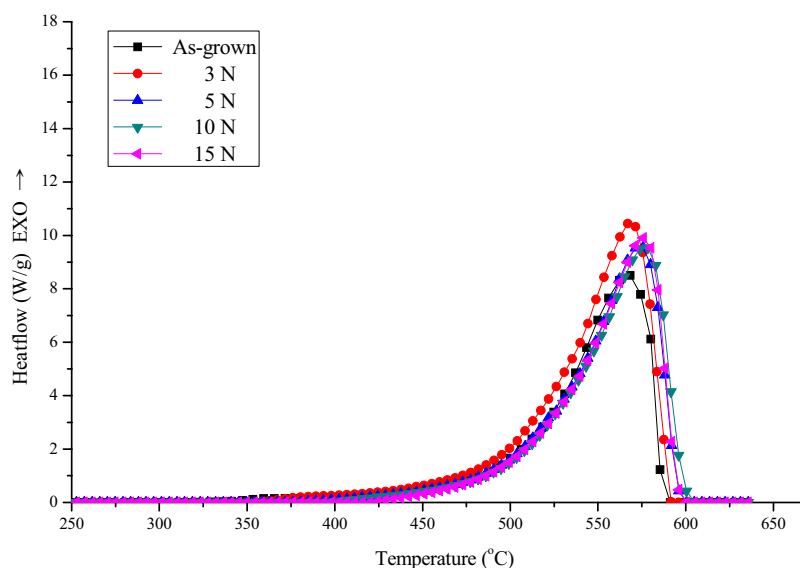


Fig. 3. DSC experimental data of HNO₃/MWCNTs at heating rate of 1.0 °C/min.

carboxyl groups at the surface of MWCNTs came to form a hydrogen bond net, so that T_0 and E_a were increased, leading to the thermal delay effect.

TGA Tests

Fig. 5 shows the as-grown MWCNTs result received from TGA tests. Heating rate of heating furnace was 0.25, 0.5, 1.0 and 2.0 °C/min. As as-grown MWCNTs presented to lose weight, the onset temperature of as-grown MWCNTs was 486°C, 522°C, 537°C, and 551°C. This result reveals that when heating rate is increased, the decomposition temperature is also enhanced.

After that, the modified MWCNTs were loaded in a

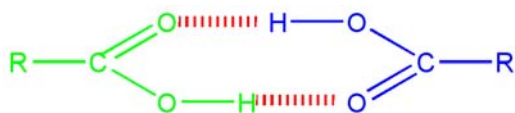


Fig. 4. Carboxyl group at surface of MWCNTs become hydrogen bond. The dotted line stands for hydrogen bond.

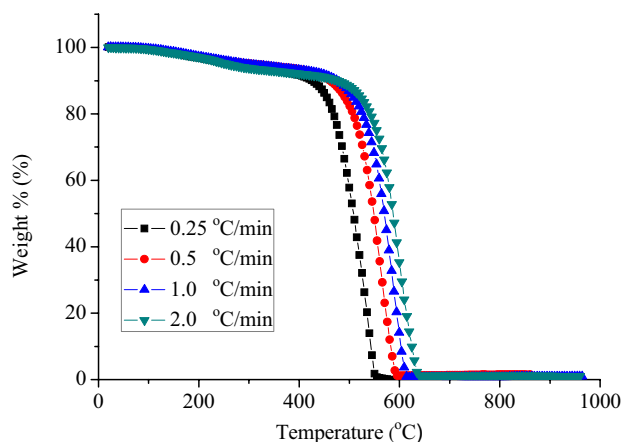


Fig. 5. Weight loss vs decomposition temperature by TGA with heat rates of 0.25–2.0 °C/min for as-grown MWCNTs.

platinum pan for TGA at 2.0 °C/min. In Fig. 6, the decomposition temperatures are 575°C, 589°C, 594°C, and 597°C corresponding to 3 N, 5 N, 10 N, and 15 N of HNO₃. Hence, T_0 of the modified MWCNTs was increased with increasing HNO₃ concentration at the same heating rate. We can infer that such results are also related to the hydrogen bond, as disclosed in Fig. 4. The carboxyl group at the surface of MWCNTs grew to form a hexagon hydrogen bond net. This could enhance E_a of MWCNTs and increase the thermal stability of the material, so that decomposition temperature rose. The greater the HNO₃ concentration, the more carboxyl group can be bonded on MWCNTs. Furthermore, decomposition temperature also increased obviously.

Results of FTIR

Fig. 7 demonstrates the infrared spectrum of product which was detected by FTIR during TGA test. The FTIR spectrum showed two intense peaks at 2,360 and 668 1/cm in Fig. 8. By comparing with standard infrared spectra, the stretch peak of carbon dioxide (CO₂) is at 2,360 1/cm. Therefore, the gas phase product of MWCNTs was validated as CO₂.

The FTIR spectra of modified MWCNTs which were modified by different HNO₃ concentrations were investigated by the same way. All FTIR spectra were similar to as-grown MWCNTs, as denoted in Fig. 7. In every spectrum a peak of CO₂ was present. Therefore, we can conjecture CO₂ is the product of as-grown and modified MWCNTs after oxidation. Here, the TGA test was a complete combustion process.

Kissinger's Corrected Kinetic Equation

$\frac{1}{T_p}$ and $\ln\left(\frac{\beta}{T_p^2}\right)$ item could be obtained by DSC results of heating rate and exothermic T_p . Therefore, $\frac{1}{T_p}$ was represented for x axis and $\ln\left(\frac{\beta}{T_p^2}\right)$ denoted for

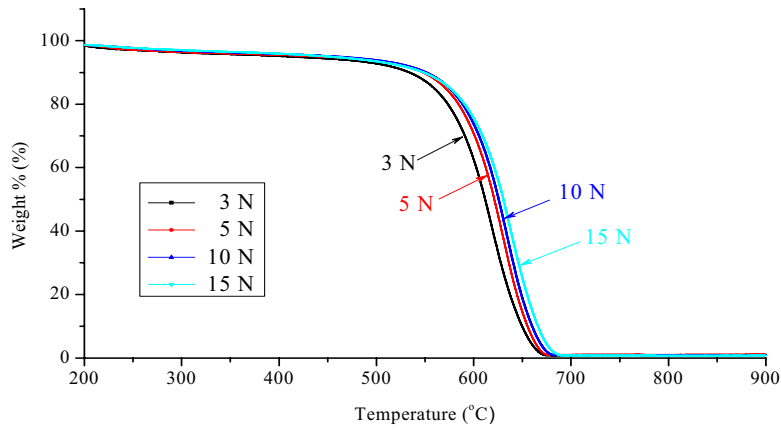


Fig. 6. Weight loss vs decomposition temperature by TGA with heating rate of 2.0 °C/min for modified MWCNTs.

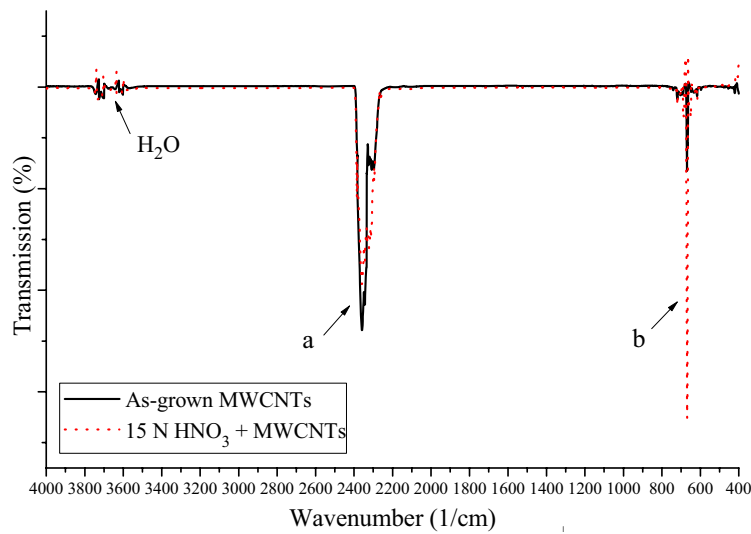


Fig. 7. Infrared spectra of MWCNTs catalyzed after TGA test, the characteristic functional groups of CO₂ at (a) 2,360 and (b) 668 1/cm.

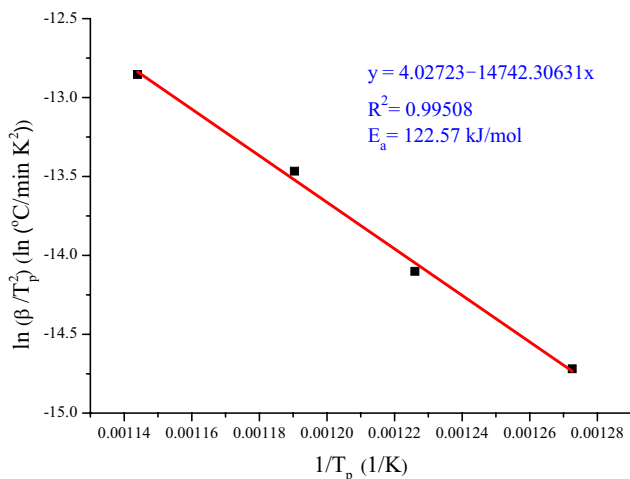


Fig. 8. Typical Kissinger plot from the experimental data at four heating rates for as-grown MWCNTs.

y axis to draw a figure. After four heating rates and four T_p were substituted into Eq. (1), a graph and a linear regression equation could be acquired:

$$y = a + bx \tag{2}$$

By taking x axis and y axis as $\frac{1}{T_p}$ and $\ln\left(\frac{\beta}{T_p^2}\right)$, so

$$b = slope = -\frac{E_a}{R} \tag{3}$$

Through transposing Eq. (3), a value of E_a could be obtained:

$$E_a = b \times 8.314 \times 10^{-3} \text{ kJ/mol} \tag{4}$$

As mentioned above, E_a was determined step by step to correspond to concentration, as can be seen in Fig. 8.

By Kissinger’s corrected kinetic equation, the E_a of as-grown MWCNTs and modified MWCNTs through four different HNO₃ concentrations can be acquired. Furthermore, HNO₃ concentration and E_a formed a graph that became a curve and had a significant tendency, as can be seen in Fig. 9. Consequently, E_a was augmented by increasing HNO₃ concentration. On the other hand, when modifying

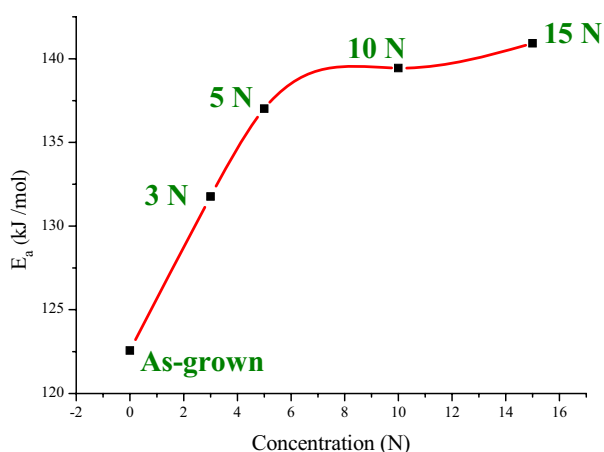


Fig. 9. Activation energy vs HNO₃ concentrations from Kissinger's corrected kinetic equation.

MWCNTs by HNO₃ in the future, this curve can be applied to determine which concentration corresponds to a specific E_a.

CONCLUSIONS

According to the DSC and TGA data, the thermal delay effect on an increasing heating rate increased with the T₀. From DSC results, E_a and T₀ of the modified MWCNTs increased with increasing HNO₃ concentration. The TGA results showed the same phenomenon. Both MWCNTs' and modified MWCNTs' decomposition temperatures were higher than 500°C in air. By linking TGA with FTIR, the gas phase product of MWCNTs was identified as CO₂.

As a result of Kissinger's corrected kinetic equation from DSC data, E_a was augmented by increasing HNO₃ concentration. In principle, the carboxyl group at the surface of MWCNTs is made up of a carbonyl group and hydroxyl group. The carboxyl group at the surface of MWCNTs becomes a hydrogen bond. With the increase of hydrogen bond, it becomes a hydrogen bond net around the outer layer MWCNTs. In this situation, E_a of modified MWCNTs will be enhanced. Consequently, E_a of modified MWCNTs is higher than as-grown. This situation could also prove that modified MWCNTs' decomposition temperatures change because of the E_a by TGA decomposition experiment. Through the above-mentioned, we can investigate "concentration vs E_a" to correspond to the degree of thermal hazard.

Through this study, we determined that both as-grown MWCNTs and modified MWCNTs are thermally hazardous materials with high potential heat, especially under fire exposure. Thus, it is important to know the thermal hazard characteristics of a material with a measure to prevent thermal damage during perturbed situations.

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NOMENCLATURE

A	pre-exponential factor, m ³ /mol sec
E _a	activation energy, kJ/mol
R	gas constant, 8.314 J/K mol
T ₀	exothermic onset temperature, °C
T _p	peak temperature, °C
β	heating rate, °C/min

REFERENCES

- Chang, C.W., Chou, Y.C., Tseng, J.M., Liu, M.Y. and Shu, C.M. (2009). Thermal Hazard Evaluation of Carbon Nanotubes with Sulfuric Acid by DSC. *J. Therm. Anal. Calorim.* 95: 639–643.
- Cheng, W.H. (2008). Adsorption Characteristics of Granular Activated Carbon and SPME Indication of VOCs Breakthrough. *Aerosol Air Qual. Res.* 8: 178–187.
- Chin, Monica C.J., Shih, L.C., Tsai, H.J. and Liu, T.K. (2007). Adsorption of o-Xylene and p-Xylene from Water by SWCNTs. *Carbon* 45: 1254–1260.
- Chou, W.J., Wang, C.C. and Chen, C.Y. (2008). Thermal Behaviors of Polyimide with Plasma-modified Carbon Nanotubes. *Polym. Degrad. Stab.* 93: 745–752.
- Hou, P.X., Liu, C. and Cheng, H.M. (2008). Purification of Carbon Nanotubes. *Carbon* 46: 2003–2025.
- Iijima, S. (1991). Helical Microtubules of Graphitic Carbon. *Nature* 354: 56–58.
- Jin, J., Song, M. and Pan, F. (2007). A DSC Study of Effect of Carbon Nanotubes on Crystallisation Behavior of Poly (ethyl oxide). *Thermochim. Acta.* 456: 25–31.
- Kissinger, H.E. (1957). Reaction Kinetics in Differential Thermal Analysis. *Anal. Chem.* 29: 1702–1706.
- Kuznetsova, A., Mawhinney, B.D., Naumenko, V., Yate Jr. J.T. and Smalley, R.E. (2000). Enhancement of Adsorption Inside of Single-walled Nanotubes: Opening the Entry Ports. *Chem. Phys. Lett.* 321: 292–296.
- Li, Y.H., Wang, S., Luan, Z., Ding, J., Xu, C. and Wu, D. (2003). Adsorption of Cadmium (II) from Aqueous Solution by Surface Oxidized Carbon Nanotubes. *Carbon.* 41: 1057–1062.
- Lu, C., Chung, Y.L. and Chang, K.F. (2005). Adsorption of Trihalomethanes from Water with Carbon Nanotubes. *Water Res.* 39: 1183–1189.
- Mettler Toledo (2005). STAR[®] Thermal Analysis, Sweden.
- Ovejero, G., Sotelo, J.L., Romero, M.D., Rodríguez, A., Ocaña, M.A., Rodríguez, G. and García, J. (2006). Multiwalled Carbon Nanotubes for Liquid-Phase Oxidation. Functionalization, Characterization, and Catalytic Activity. *Ind. Eng. Chem. Res.* 45: 2206–2212.
- Park, S.J., Cho, M.S., Lim, S.T., Choi, H.J. and Jhon, M.S. (2003). Synthesis and Dispersion Characteristics of Multi-Walled Carbon Nanotube Composites with Poly (methyl methacrylate) Prepared by In-Situ Bulk Polymerization, *Macromol. Rapid Commun.* 24: 1070–1073.
- PerkinElmer (2006). Pyris 1 Getting Started Guide, United Kingdom.
- PerkinElmer (2006). SPECTRUM 100 Series Getting

- Started Guide, United Kingdom.
- Pritchard, D.K. (2004). Literature Review–Explosion Hazards Associated with Nanopowders, Crown Copyright.
- Soliman, A.A. (2007). Derivation of the Kissinger Equation for Non-isothermal Glass Transition Peaks. *J. Therm. Anal. Calorim.* 89: 389–392.
- Sone, H., Fugetsu, B., Tsukada, T. and Endo, M. (2008). Affinity-based Elimination of Aromatic VOCs by Highly Crystalline Multi-walled Carbon Nanotubes. *Talanta* 74: 1265–1270.
- Tsai, S.J. (Candace), Ashter, A., Ada, E., Mead, J.L., Barry, C.F. and Ellenbecker, M.J. (2008). Airborne Nanoparticle Release Associated with the Compounding of Nanocomposites Using Nanoalumina as Fillers. *Aerosol Air Qual. Res.* 8: 160–177.
- Yang, T.T., Kuo, Y.M., Hung, H.F., Shie, R.H. and Chang, P. (2007). Gas Pollutant Emissions from Smoldering Incense Using FTIR. *Aerosol Air Qual. Res.* 7: 417–431.
- You, M.L., Liu, M.Y., Wu, S.H., Chi, J.H. and Shu, C.M. (2009). Thermal Explosion and Runaway Reaction Simulation of Lauroyl Peroxide by DSC Tests. *J. Therm. Anal. Calorim.* 96: 777–782.

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