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THERMAL HAZARD EVALUATION OF CARBON NANOTUBES WITH SULFURIC ACID BY DSC

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Many concerns over unsafe or unknown properties of multi-walled carbon nanotubes (MWNTs) have been raised. The thermal characteristics regarding stability would represent potential hazards during the production or utilization stage and could be determined by calorimetric tests for various thermokinetic parameters. Differential scanning calorimetry (DSC) was employed to evaluate the thermokinetic parameters for MWNTs at various compositions.

Thermoanalytical curves showed that the average heat of decomposition (ΔH_d) of the MWNTs samples in a manufacturing process was about 31,723 J g^{-1}, by identifying them as an inherently hazardous material. In this study, significant thermal analysis appeared in the presence of sulfuric acid (H_2SO_4). From the DSC experiments, the purification process of MWNTs could induce an unexpected reaction in the condition of batch addition with reactants of H_2SO_4. The results can be applied for designing emergency relief system and emergency rescue strategies during a perturbed situation or accident.

Keywords: *DSC, heat of decomposition, multi-walled carbon nanotubes (MWNTs), sulfuric acid (H_2SO_4), thermokinetic parameters*

Introduction

Since the discovery of multi-walled carbon nanotubes (MWNTs) by Iijima in 1991 [1], MWNTs have received considerable interest and attention because of their exotic and prominent mechanical, chemical and physical properties. They have been employed popularly in various fields, such as the adsorption of the metal ions for environmental protection. Hence, MWNTs have been the subject of more research interest in recent years. However, there is still scant research of thermal analysis for MWNTs seen in the open literature [2–7]. Through concerted efforts, we attempted to elucidate the inherently thermal hazardous characteristic of MWNTs [8, 9].

In this study, the thermal decomposition of MWNTs with H_2SO_4 was first characterized by differential scanning calorimetry (DSC). Via the thermal curves by DSC, we could determine the effects upon H_2SO_4, which may result in unexpected reactions with MWNTs. Afterwards, we adopted the method of isothermal model on DSC to investigate the thermal hazards while manufacturing MWNTs and evaluate thermokinetic parameters under isothermal conditions [10–12]. As the results, thermokinetic parameters could be acquired by thermal curves and the Arrhenius equation, such as reaction rate constant (k), reaction order (n), frequency factor (A) and activation energy (E_a). To prevent the system from any runaway reactions or even thermal explosion under perturbed conditions, these critical thermokinetic parameters must be received, analyzed and applied for safety studies.

Experimental

Samples

MWNTs were directly purchased from ConYuan Biochemical Technology Co. Ltd., Taiwan. The H_2SO_4 was deliberately chosen. As planned, it was selected to be 0.1, 0.5 and 1 N and provided the MWNTs a long soak about a week before being measured for the study [13].

Tests conducted by DSC

Scanning experiments were carried out on a Mettler TA8000 system coupled with a DSC821^e measuring cell that can withstand pressure up to about 100 bar. STAR^e software was applied for acquiring curve traces [14, 15]. An aluminum standard pan was employed to avoid evaporation of the MWNTs during scanning experiment. For more accuracy in testing, the scanning

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rates chosen for the temperature range were from 300–640°C with 1°C min^{-1} under atmospheric air.

Reactions can be investigated within 400–600°C, for the working temperature range of this thermostat. Under high temperature, DSC is a highly sensitive calorimeter for stability testing of various types of materials. Measurements were performed isothermally in the temperature range from 470–590°C [10, 16].

Results and discussion

Analysis for surface structure

The two kinds of materials and those after non-isothermal experiment were observed by HRTEM (high-resolution transmission electron microscope), as illustrated in Fig. 1. We knew the catalyst of MWNTs soaked in H_2SO_4 was purged obviously by HRTEM and the structure has evidently changed after DSC tests. The externals do not have to be tubular shape by high temperature tests any more.

Non-isothermal analyses of MWNTs

We investigated the analysis of thermal decomposition for MWNTs by using a dynamic screening experiment

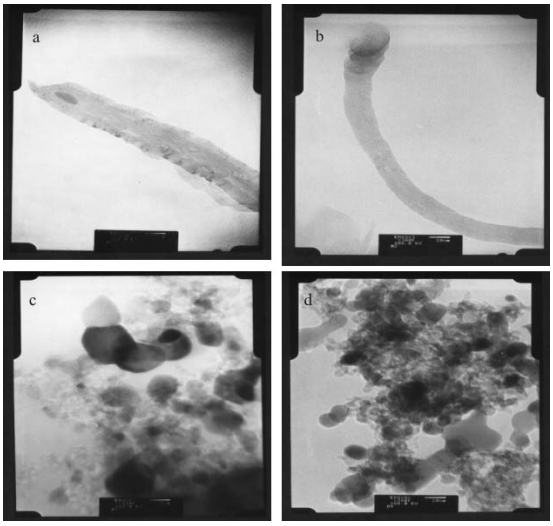

Fig. 1 Morphology by HRTEM for a – MWNTs, b – MWNTs soaked in H_2SO_4 solution, c – MWNTs after DSC test and d – MWNTs soaked in H_2SO_4 solution after DSC test

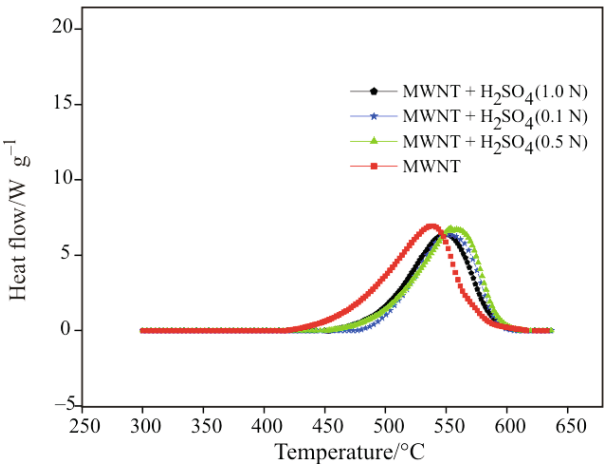

Fig. 2 Thermal curves of MWNTs and MWNTs comparing with various concentrations H_2SO_4 by DSC with heating rate of 1°C min^{-1}

and compared with MWNTs added with H_2SO_4. The results were shown in Fig. 2 and Table 1. We could find the effect of mixing H_2SO_4 with MWNTs from Fig. 2. Here, H_2SO_4 conspicuously increased the onset temperature (T_0). For example, the T_0 of MWNTs was 360°C; whereas, with the additive H_2SO_4, it rose to 474°C. As a result, the purification reactions were strongly influenced for MWNTs.

Isothermal analysis

MWNTs were employed in purification under constant temperature conditions. Isothermal analysis of calorimetric tests had the advantage of determining both thermodynamic and kinetic parameters, which could be utilized to study the stability of MWNTs. The thermal curves of MWNTs were obtained by DSC at five constant temperatures, as presented in Fig. 3 and Table 2, listing the experimental data of MWNTs. Figure 3 discloses that each reaction curve rose to the maximum and then diminished down based upon individual isothermal temperatures. The shape of this reaction was recognized as n^{th} order at 470–590°C. At initial reaction, MWNTs resulting from n^{th} order decomposition were then catalyzed during isothermal stage.

Table 1 Safety parameters of MWNTs comparing with various concentrations H_2SO_4 and MWNTs by DSC tests

Substance	Composition	Mass/mg	T_0/°C	T_p/°C	ΔH_d/J g^{-1}
MWNTs	multi-walled	0.57	360	539	31723
MWNTs+H_2SO_4	H_2SO_4 (0.1 N)	0.43	397	550	27650
MWNTs+H_2SO_4	H_2SO_4 (0.5 N)	0.54	441	555	25591
MWNTs+H_2SO_4	H_2SO_4 (1 N)	0.47	474	552	21688

Table 2 Experimental data of MWNTs conducted by DSC under isothermal condition

No.	Isothermal temperature/°C	Mass/mg	Reaction time/min	Time to peak value/min	ΔH_d/J g^{-1}
1	470	1.32	1707	96	18518
2	500	0.90	773	31	26375
3	530	0.85	298	13	31983
4	560	0.93	123	9	33775
5	590	0.93	66	3	35164

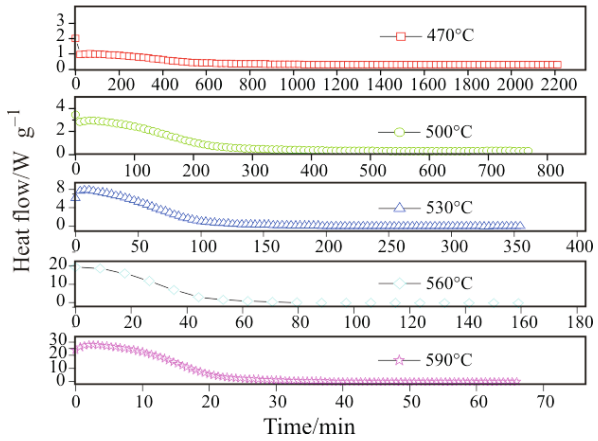

Fig. 3 Heat flow *vs*. time for thermal decomposition of MWNTs under various isothermal conditions

Kinetic analysis

Using DSC to analyze the heat flow *vs*. time curves at five temperatures indicated that, at initial reaction, the reaction rate (r) began to accelerate and went through a maximum value. To determine rate constant (k) by Eq. (1), n is the reaction order.

$$r=\frac{\mathrm{d[MWNTs]}}{\mathrm{d}t}=k[\mathrm{MWNTs}]^n \qquad (1)$$

In the case of MWNTs, we simply discussed one n. If we attempted to evaluate the n, we could use the complicated simulation model. The k belongs to Arrhenius type; the peak power would follow the Arrhenius law as expressed in Eq. (2) which is related to the k.

In Fig. 4, the plot of ln[MWNTs] *vs*. time with different composition was a straight line; the k could be calculated by the slope and n determined by the highest R-square value. The k at 470°C was about $1.67\cdot10^{-5}$ s^{-1}.

$$k=A\mathrm{e}^{\frac{-E_a}{RT}} \qquad (2)$$

where T, A and R are absolute temperature, frequency factor and universal gas constant, respectively.

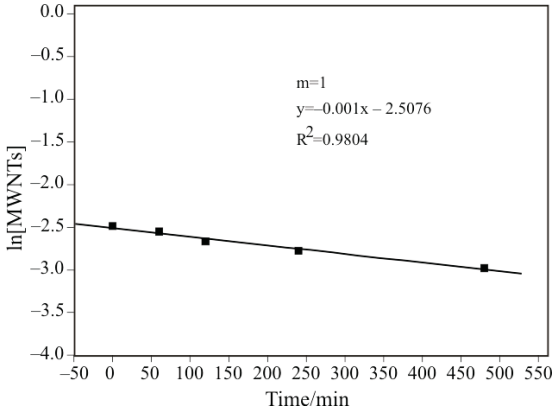

Fig. 4 Natural logarithm of MWNTs composition *vs*. time for various MWNTs composition with reaction order calculation

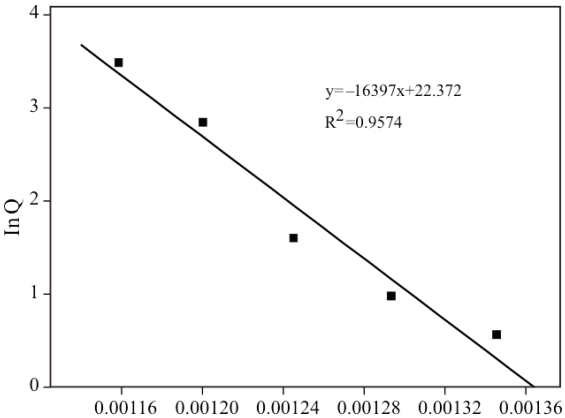

Fig. 5 ln$Q$ *vs*. T^{-1} for MWNTs by DSC

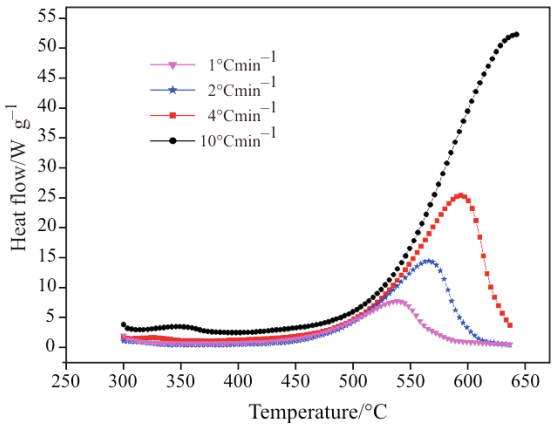

Fig. 6 Comparison of DSC thermal curves of MWNTs at heating rates of 1, 2, 4 and 10°C min^{-1}

Table 3 Experimental data of MWNTs conducted by DSC with four scanning rates

M/mg	Heating rate/°C min^{-1}	T_0/°C	T_p/°C	ΔH_d/J g^{-1}	n	E_a/kJ mol^{-1}	ln(k_0)/s^{-1}
0.57	1	360	539	31723	0.7	161.1	16.26
0.81	2	364	566	31170	0.6	156	15.33
0.80	4	391	593	25107	0.6	162.6	16.24
0.80	10	457	>640.00	Out-of-range	0.4	142.5	13.56

Table 4 Parameters for the decomposition of various materials by DSC [17, 18]

Sample	T_0/°C	ΔH_d/J g^{-1}
Cumene hydroperoxide (CHP)	95	618.6
Lauroyl peroxide (LPO)	70	808
Dicumyl peroxide (DCPO)	110	993
Benzoyl peroxide (BPO)	104	1034
di-*tert*-Butyl peroxide (DTBP)	115	1202
Methyl ethyl ketone peroxide (MEKPO)	80	1479
Cumene hydroperoxide (CHP)	110	1487
tert-Butyl hydroperoxide (TBHP)	65	2300
Nitrobenzene	380	2756
1,3,5-trinitro-1,3,5-triazacyclohexane (RDX)	NA	4222
1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX)	NA	4226
2-methyl-1,3,5-trinitrobenzene (TNT)	NA	4686
Nitromethane	315	5292
MWNTs	360	31723

NA: not applicable

Based on the measurement results of isothermal calorimetric, which was delineated in Fig. 3, the plot of ln$Q$ *vs*. T^{-1} with different temperatures was a straight line, the slope provided the activation energy (E_a) for MWNTs, as demonstrated in Fig. 5. The E_a and k were verified to be about 136.32 kJ mol^{-1} and $6.38 \cdot 10^4$ s^{-1} exp(–136,320/8.314T), respectively. The comparison of the DSC thermal curves for MWNTs measured at a heating rate of 1, 2, 4 and 10°C min^{-1} was shown in Fig. 6 and Table 3. In Fig. 6 and Table 3, for four corresponding DSC curves appear exothermic peaks at about 539, 566, 593.6 and exceeding 640°C, respectively. In addition, the DSC exothermic peak moved toward higher temperature and heat flow was enhanced with increasing heating rate.

Comparison of various materials

From Table 4, the parameters for the decomposition of various materials were tested by DSC. We aimed at a comparison between various materials and MWNTs. We obtained MWNTs that had much higher heat of decomposition than other materials [17, 18].

Conclusions

The test results indicated that much attention should be paid when using H_2SO_4 with MWNTs in a process. The purification reactions were strongly influenced for MWNTs. Especially, H_2SO_4 raised the T_0 and reduced the value for the heat of decomposition (ΔH_d). Thermal curves possessed an n^{th} order phenomenon during the period of decomposition, which was a novel discovery between 470–590°C. At initial reaction, MWNTs induced the n^{th} order decomposition and was then catalyzed during the isothermal stage. In summary, the results revealed that the n^{th} order reaction phenomenon can be determined to be 1.0. The E_a, A, and k were about 136.32 kJ mol^{-1}, $6.38 \cdot 10^4$ s^{-1} and $6.38 \cdot 10^4$exp(–136,320/8.314T) by the Arrhenius equation for MWNTs, respectively.

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References

1 S. Iijima, Nature, 354 (1991) 56.
2 K. A. Dean, T. P. Burgin and B. R. Chalamala, Appl. Phys. Lett., 79 (2001) 121.
3 H. Yu, C. Yu, T. Xi, L. Luo, J. Ning and C. Xiang, J. Therm. Anal. Cal., 82 (2005) 97.
4 T. Kashiwagi, E. Grulke, J. Hilding, K. Groth, R. Harris, K. Butler, J. Shields, S. Kharchenko and J. Douglas, Polymer, 45 (2004) 4227.
5 M. S. Dresselhaus, G. Dresselhaus and R. Satio, Carbon, 33 (1995) 883.
6 T. W. Ebbesen, Annu. Rev. Mater. Sci., 24 (1994) 235.
7 W. A. de Heer, Science, 270 (1995) 1179.
8 D. K. Pritchard, Literature Review–Explosion Hazards Associated with Nanopowders, HSL/2004/12,, 2004.
9 J. Jin, M. Song and F. Pan, Thermochim. Acta, 2007, DOI:10. 1016/j. tca. 02. 003.
10 S. Chervin and G. T. Bodman, Process Saf. Prog., 16 (1997) 94.
11 Y. W. Wang, C. M. Shu, Y. S. Duh and C. S. Kao, Ind. Eng. Chem. Res., 40 (2001) 1125.
12 C. M. Shu and Y. J. Yang, Thermochim. Acta, 392 (2002) 257.
13 M. K. Seo, J. R. Lee and S. J. Park, Mater. Sci. Eng., A, 404 (2005) 79.
14 Mettler Toledo, STAR^e Thermal Analysis, Sweden 2005.
15 W. Jang, Chemistry Department, Drexel University.
16 Mettler Toledo Company, TA8000 Operation Instructions, Switzerland 2003.
17 Y. S. Duh, C. S. Kao, C. Lee, C. C. Hsu and S. W. Yu, The 2nd International Conference and Exhibition on Loss Prevention in the Oil, Chemical and Process Industries, Singapore 1995.
18 Y. S. Duh, C. S. Kao, C. Lee, M. L. Chen and S. W. Yu, International Symposium on Runaway Reactions and Pressure Relief Design, 237, Boston, MA, USA 1995.

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