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Isothermal and non-isothermal kinetic and safety parameter evaluation of tert-butyl(2-ethylhexyl)monoperoxy carbonate by differential scanning calorimetry

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Abstract−Tert-butyl(2-ethylhexyl)monoperoxy carbonate (TBEHC) 95 mass% is intrinsically a very unstable substance that can induce self-decomposition even under normal atmospheric condition. During storage, TBEHC 95 mass% can release an enormous amount of heat if the temperature is higher than the recommended storage temperature, due to the self-accelerating reaction having been ignited. In this study, TBEHC 95 mass% was tested by differential scanning calorimetry (DSC) under five heating rates (1, 2, 4, 6, and 8 °C/min) and four isothermal conditions (120, 125, 130, and 135 °C) to evaluate the basic kinetic and safety parameters of time to maximum rate (TMR), self-accelerating decomposition temperature (SADT), and temperature of no return (TNR). Under runaway reaction TBEHC 95 mass% releases a great quantity of heat. This study establishes an important guiding principle for related manufacturing processes worldwide.

Key words: Tert-butyl(2-ethylhexyl)monoperoxy Carbonate (TBEHC), Differential Scanning Calorimetry (DSC), Kinetic and Safety Parameters, Runaway Reaction

INTRODUCTION

Tert-butyl(2-ethylhexyl)monoperoxy carbonate (TBEHC) 95 mass% is an explosive material that is employed in various types of industries, such as acrylics and PMMA. TBEHC 95 mass% has the potential to induce an accident, due to its unstable structure of O-O bond, which could release an astonishing decomposition heat during upset situations, such as fire, explosion, or other emergency situations [1]. We studied the basic characteristics of TBEHC 95 mass% under isothermal and non-isothermal conditions by differential scanning calorimetry (DSC).

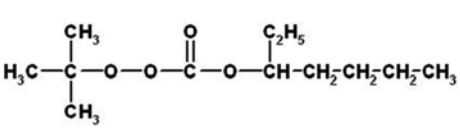
Runaway reactions by sensitive and hazardous materials have been studied via various isothermal, dynamic, and adiabatic calorimetries around the world, such as C80D for testing asphalt salt [2], kinetic parameters of the thermal decomposition of boric acid investigated by using thermogravimetric analyzer (TGA) data [3], and differential scanning calorimetry (DSC) for testing the startling explosive material of nitrocellulose on non-isothermal decomposition [4,5], MEKPO with contaminants [6], the melting points, decomposition temperatures, and electrochemical stabilities of the salts [7]. Vent sizing package 2 (VSP2) is used for testing the temperature or rate of pressure rise for MEKPO [8] or with other contaminants [9], and CHP [10] under various expected conditions. Thermal activity monitor (TAM) is used for testing the hazardous material of dicumyl peroxide [11] under an isothermal system. The reaction calorimeter (RC1) is also used to test high purity (>99 mass%) methanol and acetic anhydride for realizing the kinetic parameters [12], by using adiabatic calorimetry of Phi-Tec II to evaluate the kinetic parameters of MEKPO [13]. If temperature is not properly controlled, the system may become unstable and eventually encounter a runaway reaction, potentially leading to various types of accidents [14-16].

In this study, we determined that TBEHC 95 mass% could release a great quantity of heat under decomposition. Therefore, results from this study could be employed in guiding staff on how to well dictate the manufacturing process, in terms of TBEHC 95 mass%.

EXPERIMENTAL SETUP

1. Materials

TBEHC 95 mass% was purchased directly from ACE Chemical Corp in Taiwan and stored in a refrigerator at 4. Experiments were carried out by five heating rates (1, 2, 4, 6, and 8 min^{-1}) in non-isothermal conditions and 120, 125, 130, and 135 °C in isothermal conditions. The structure is shown as follows:



$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-O-O-\overset{O}{\overset{\|}{C}}-O-\overset{C_2H_5}{CH}-CH_2-CH_2-CH_2-CH_3$$

2. Differential Scanning Calorimetry (DSC)

Temperature-programmed screening experiments were performed

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with DSC (TA Q20). The test cell was used to perform the experiment for withstanding relatively high pressure to approximately 10 MPa. ASTM E698 was used to obtain thermal curves for calculating kinetic parameters. The range of temperature rise was 30 to 300 °C for each experiment. Calorimetric precision was +/− 0.1%, dynamic measurement range was +/− 350 mW, and sensitivity was 1.0 μW.

METHODS OF KINETIC AND SAFETY PARAMETERS

1. Kinetic Parameter Evaluation

1-1. Arrhenius Equation [17]

Based on the Arrhenius equation,

$$-r_A = \frac{-dC_A}{dt} = kC_A^n = A\exp\left(\frac{-E_a}{RT}\right)C_A^n \tag{1}$$

where r_A is the reaction rate; C_A is the sample concentration; k is the reaction rate constant; n is the reaction order; A is the pre-exponential factor; E_a is the activation energy; T is the absolute temperature; R is the gas constant.

1-2. E_a Evaluation of Isothermal Conditions, as Follows

Reaction rate is shown as the following equations:

$$R = -\frac{d[\mathrm{TBEHC}]}{dt} = k[\mathrm{TBEHC}]^m \tag{2}$$

$$\dot{Q} = \frac{dQ}{dt} = \Delta H \cdot \rho \cdot V \cdot A \cdot e^{-E_a/RT} \cdot [\mathrm{TBEHC}]^m \cdot (1-\alpha)^m \tag{3}$$

$$\ln Q \alpha \ln k = \ln C - E_a/RT \tag{4}$$

where Q is the heat power; ΔH is the heat of reaction; v is volume; α is the conversion rate; A is the pre-exponential factor; m is the reaction order.

1-3. Determination of E_a by Kissinger Method [18]

$$\ln\left(\frac{\beta}{T_P^2}\right) = \ln\frac{AR}{E} - \frac{E_a}{RT_P}, \tag{5}$$

where β is the heating rate; T_P is the peak temperature; A is the pre-exponential factor; E_a is the activation energy; R is the gas constant. At the different heating rates, Kissinger's kinetic equation can be derived:

$$\ln\frac{\beta_1}{T_{P_1}^2} + \frac{E_a}{RT_{P_1}} = \ln\frac{\beta_2}{T_{P_2}^2} + \frac{E_a}{RT_{P_2}} = \ln\frac{\beta_3}{T_{P_3}^2} + \frac{E_a}{RT_{P_3}} = \cdots \tag{6}$$

where, β_1, β_2, and β_3 are the different heating rates; T_{P_1}, T_{P_2}, and T_{P_3} are the peak temperature of different heating rates.

1-4. Determination of E_a by Ozawa Method [19]

$$\ln(\beta) = -1.0516\frac{E_a}{RT_P} + \mathrm{const.} \tag{7}$$

where β is the heating rate; T_P is the peak temperature; A is the pre-exponential factor; E_a is the activation energy; R is the gas constant.

At the different heating rates, Ozawa's kinetic equation can be derived:

$$\ln\beta_1 + 1.0516\frac{E_a}{RT_{P_1}} = \ln\beta_2 + 1.0516\frac{E_a}{RT_{P_2}} = \ln\beta_3 + 1.0516\frac{E_a}{RT_{P_3}} = \cdots \tag{8}$$

where β_1, β_2, and β_3 are the different heating rates; T_{P_1}, T_{P_2}, and T_{P_3} are the peak temperature of different heating rates.

2. Safety Parameter Evaluation

2-1. Temperature of No Return (T_{NR})

T_{NR} is an important index employed to plan a suitable and deliverable emergency response measure, via evaluating the heat release rate and heat removal rate [20] and also extensively used to design a cooling system and to evaluate the remaining time for conducting a rescue operation [21].

$$(T_{NR} + 273.15)^2 = \frac{m \cdot E_a \Delta H \cdot k}{R \cdot U \cdot (1.8) \cdot a} \tag{9}$$

$$= \frac{m \cdot E_a \cdot \Delta H \cdot A \cdot e^{-E_a/R \cdot (T_{NR}+273.15)}}{R \cdot U \cdot (1.8) \cdot a} \tag{10}$$

2-2. Self-accelerating Decomposition Temperature (SADT)

SADT is defined as the lowest ambient air temperature at which a self-reactive substance of specified stability (contaminant level, inhibitor concentration, vessel volume filled ratio, etc.) undergoes an exothermic reaction in a specified commercial package in seven days or less [20]. A self-reactive substance [3,5] must be well temperature controlled, inhibited, and other ways found for a container during transportation under SADT to be less than or equal to 50 °C [22].

$$\mathrm{SADT} = T_{NR} - \frac{R(T_{NR} + 273.15)^2}{E_a} \tag{11}$$

2-3. Time to Maximum Rate (TMR)

TMR is applied to obtain the variation between time and temperature. We used four different isothermal conditions-120, 125, 130, and 135 °C-to compare each condition.

Table 1. Results of kinetic parameters for TBEHC 95 mass% with scanning rates of 1, 2, 4, 6, and 8 °C/min

Sample	TBEHC 95 mass%				
Scanning rate (°C/min)	1	2	4	6	8
Sample mass (mg)	3.0	2.9	3.0	2.9	3.2
Onset temperature, T_o (°C)	111.11	116.91	121.72	127.57	131.66
Peak temperature, T_p (°C)	135.13	141.75	148.48	154.26	156.79
Frequency factor, A (ln1/s)	36.69	29.23	29.89	33.38	32.03
Activation energy, E_a (kJ/mol)	145.92	121.11	122.89	135.22	130.58
Reaction order (n)	1.04	0.80	0.84	0.97	0.89
Reaction heat, ΔH (kJ/kg)	817.4	891.1	878.8	918.6	937.1

Table 2. Calculation of E_a for TBEHC 95 mass% with scanning rates of 1, 2, 4, 6, and 8 °C/min by Kissinger and Ozawa equation

Kinetic model	E_a (kJ/mol)	R	SD
Kissinger equation	130.89	0.99819	0.0556
Ozawa equation	131.09	0.99838	0.0554

Table 3. ΔH, TMR, E_a, and n of TBEHC 95 mass% in isothermal conditions of 120, 125, 130, and 135 °C

Sample	TBEHC 95 mass%			
Isothermal conditions (°C)	120	125	130	135
Sample mass (mg)	2.9	3.3	3.2	3.0
ΔH (J/g)	652.1	697.8	750.6	622.0
TMR (min)	4.34	3.99	3.99	2.92
E_a (kJ/mole) by lnQ vs. T	115.16 (R=0.99597; SD=0.0615)			

Table 4. Results of safety parameters for TBEHC 95 mass% with scanning rates of 1, 2, 4, 6, and 8 °C/min

Sample	TBEHC 95 mass%				
Scanning rate (°C/min)	1	2	4	6	8
TNR (°C)	79	70	69	74	73
SADT (°C)	71	61	61	66	65

$$\mathrm{TMR}=\frac{RT^2}{AE_a\Delta T_{ad}}e^{-E_a/RT} \tag{12}$$

$$\Delta T_{ad}=\frac{Q}{C_p} \tag{13}$$

RESULTS AND DISCUSSION

Results by DSC tests are arranged in Tables 1-4 and Figs. 1-8. All of the results were detected under five heating rates (1, 2, 4, 6,

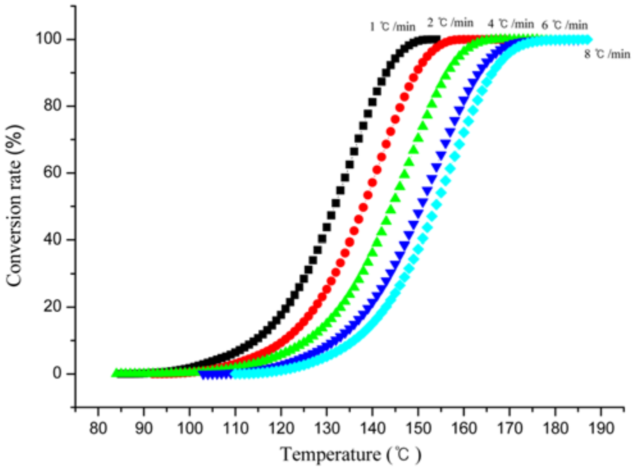

Fig. 2. Conversion rates of TBEHC 95 mass% by DSC in non-isothermal conditions of 1, 2, 4, 6, and 8 °C/min.

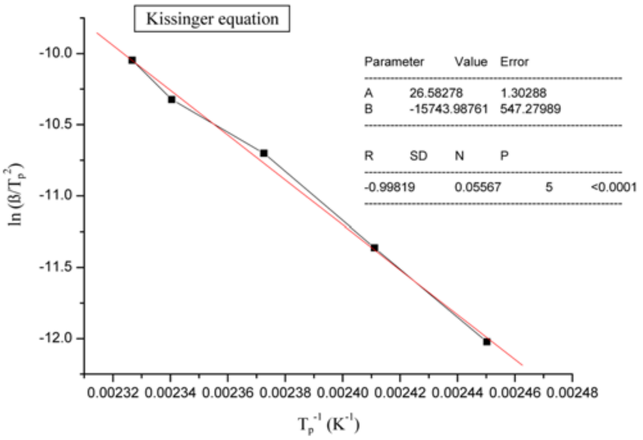

Fig. 3. Activation energy analysis graph for TBEHC 95 mass% with different scanning rates of 1, 2, 4, 6, and 8 °C/min by Kissinger equation.

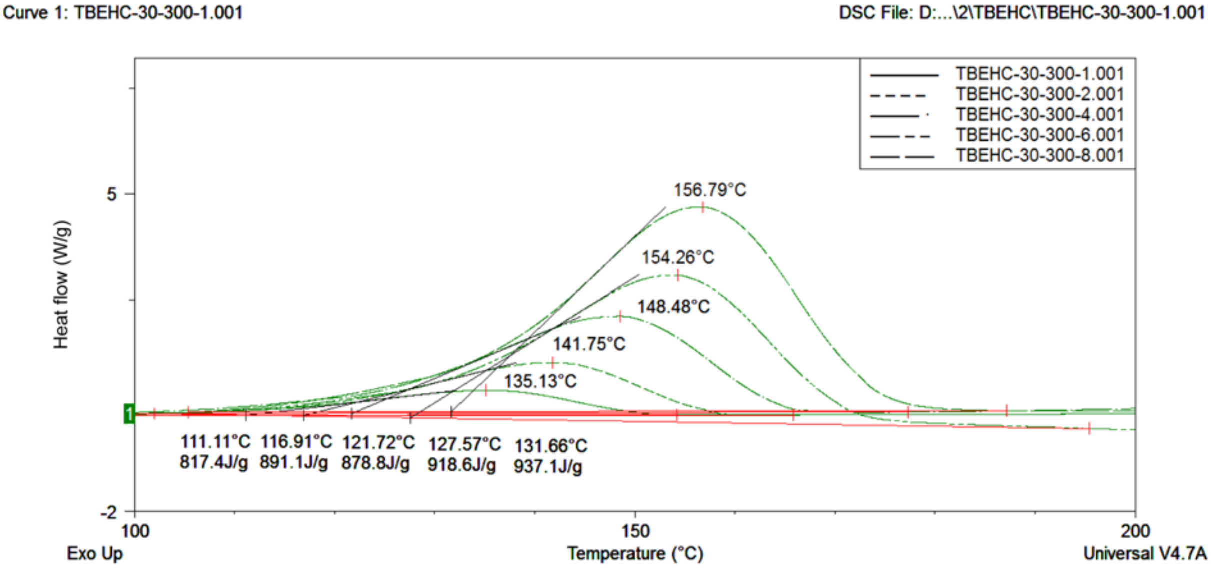

Fig. 1. Thermal analysis of TBEHC 95 mass% by DSC in non-isothermal conditions of 1, 2, 4, 6, and 8 °C/min.

and 8 °C/min) and four isothermal conditions (120, 125, 130, and 135 °C), which showed that the TBEHC 95 mass% could release considerable quantities of heat under decomposition, even more than 900 J/g. All of the sample masses were controlled very closely at about 3.0 mg. Figs. 1-2 and 5-7 demonstrate the results of the measurements on TBEHC 95 mass% under isothermal and non-isothermal conditions.

Tables 1-3 contain the results of calculating E_a by the above-mentioned equations. In Figs. 3 and 4, the E_a were 130.89 and 131.09 kJ mol^{-1}, separately by Kissinger and Ozawa equations for pure TBEHC 95 mass% in non-isothermal conditions, with higher R values of 0.99819 and 0.99838. Table 3 and Figs. 5-6 indicate that all of the reaction rates were increased, while isothermal conditions were increased from 120 to 135 °C in isothermal conditions. TBEHC 95 mass% released a great quantity of heat under decomposition reaction. We demonstrated that TBEHC 95 mass% has a low E_a, due to its unstable structure of -O-O-, which facilitates reactions to the

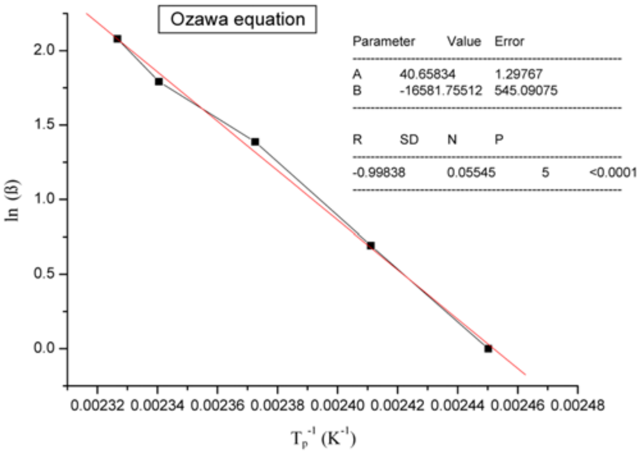

Fig. 4. Activation energy analysis graph for TBEHC 95 mass% with different scanning rates of 1, 2, 4, 6, and 8 °C/min by Ozawa equation.

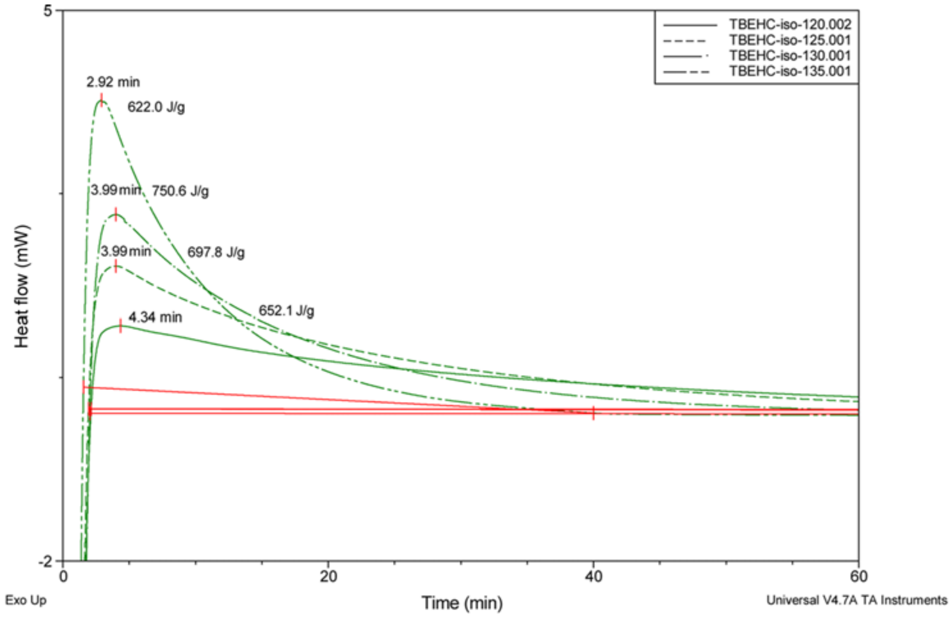

Fig. 5. Thermal analysis of TBEHC 95 mass% in isothermal conditions of 120, 125, 130, and 135 °C by DSC.

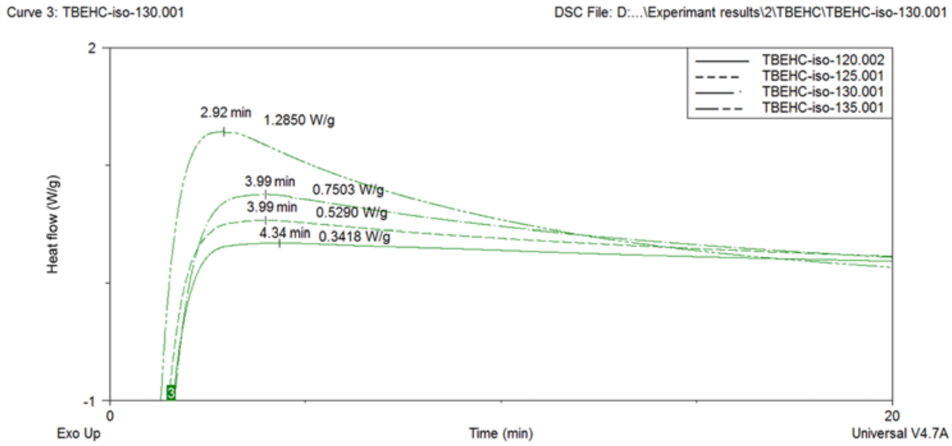

Fig. 6. TMR of TBEHC 95 mass% in isothermal conditions of 120, 125, 130, and 135 °C.

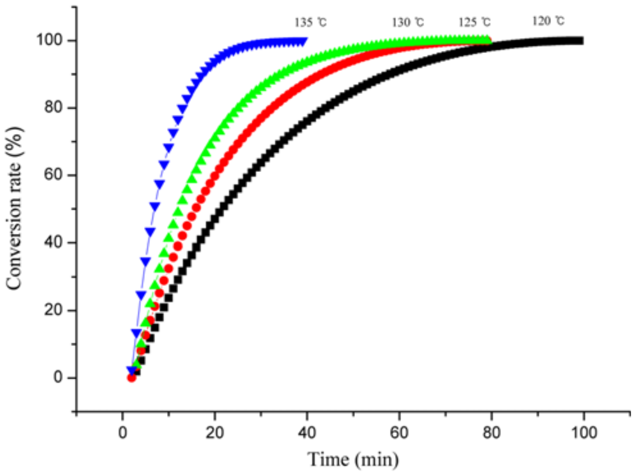

Fig. 7. Conversion rate vs. Time of TBEHC 95 mass% in isothermal conditions of 120, 125, 130, and 135 °C.

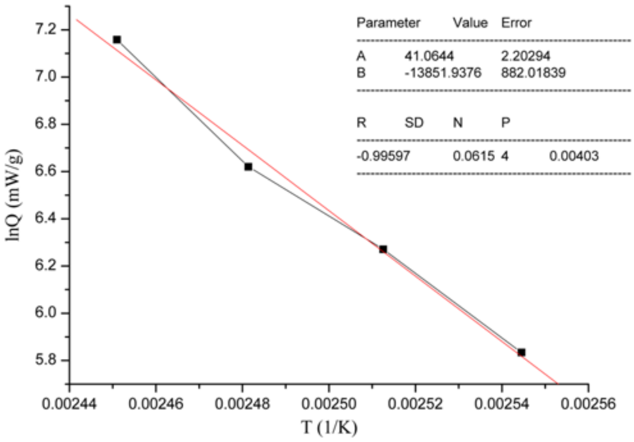

Fig. 8. E_a calculation of TBEHC 95 mass% in isothermal conditions of 120, 125, 130, and 135 °C.

upset situations, such as fire or explosion. As for the safety parameters, TMR was about 2.92-4.34 min during the isothermal conditions of 120-135 °C, which indicated that a temperature-controlled system must be well started to lessen the reaction rate for preventing the normal reactions from reaching the uncontrolled stage; the SADT also was applied to calculate the TBEHC 95 mass% for deep understanding of the self decomposition phenomenon. Results were obtained at about 61-71 °C in non-isothermal conditions; therefore, TBEHC 95 mass% must be well controlled during usage, storage, and transportation for preventing the released heat from destroying the unstable structure of -O-O-. Even increasing the self decomposition rate to reach the TNR, if the temperature is higher than the TNR, the onset temperature (T_0) could be reached fairly quickly. Evaluation results of T_0 and TNR were about 111.11-131.66 °C and 69-79 °C, separately. And, T_0 and T_p were increased while the heating rates increased from 1-8 °C/min. As for safety, normal conditions could be broken faster as the temperature increases. According to the above-mentioned descriptions, TBEHC 95 mass% had the explosive characteristics while temperature reached the TNR or T_0, or even the SADT. To prevent accidents, a temperature control system must be well designed for effective control reaction to deal with the upset situations. This study is the first discussion on evaluating the kinetic and safety parameters of TBEHC 95 mass% by DSC.

CONCLUSIONS

Isothermal and non-isothermal kinetic parameters of TBEHC 95 mass% were determined by DSC. TBEHC 95 mass% was demonstrated to have an unstable structure of O-O, which could release a huge amount of heat during decomposition reaction, especially under higher temperature conditions. Such an unstable structure of O-O in TBEHC 95 mass% content plays an important role in runaway reactions. DSC is a precise tool for testing basic characteristics for a runaway reaction under isothermal and non-isothermal conditions. Our results provide a deeper understanding of the runaway reactions of TBEHC 95 mass% so that accidents in the manufacturing process can be prevented or at least mitigated.

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