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RUNAWAY REACTION ON *tert*-BUTYL PEROXYBENZOATE BY DSC TESTS

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Tert-butyl peroxybenzoate (TBPB) is one of the sensitive and hazardous chemicals which have been popularly employed in petrifaction industries in the past. This study attempted to elucidate its unsafe characteristics and thermally sensitive structure so as to help prevent runaway reactions, fires or explosions in the process environment. We employed differential scanning calorimetry (DSC) to assess the kinetic parameters (such as exothermic onset temperature (T_0), heat of reaction (ΔH), frequency factor (A)), and the other safety parameters using four different scanning rates (1, 2, 4 and 10°C min^{-1}) combined with curve-fitting method.

The results indicated that TBPB becomes very dangerous during decomposition reactions; the onset temperature and reaction heat were about 100°C and 1300 J g^{-1}, respectively. Through this study, TBPB accidents could be reduced to an accepted level with safety parameters under control. According to the findings in the study and the concept of inherent safety, TBPB runaway reactions could be thoroughly prevented in the relevant plants.

Keywords: *curve-fitting method, DSC, kinetic parameters, runaway reactions, tert-butyl peroxybenzoate (TBPB)*

Introduction

Runaway reactions of *tert*-butyl peroxybenzoate (TBPB) often involve a high exothermic peak that could induce a thermal accident and damage the process equipment and the surroundings. Especially, contact should be avoided with acids, alkalis, heavy metals, reducing agent and any rust. Shock, friction, fire or other sources of ignition should be also avoided during a manufacturing process [1]. In general, TBPB is employed as the cross-linker for combining with calcium, unsaturated pitch (UP), and other materials, the ratio being about 1/350 at normal atmosphere. There are about 1500–2000 tons of sheet molding compound (SMC) produced from TBPB annually in Taiwan. Compound materials have been used to produce material that is used in automobiles, architecture, doors, bathtubs, and other envelopes. There are just a few papers that mention its chemical characteristics [2, 3]. The self-accelerating decomposition temperature (SADT) is approximately 65.8°C [4]. Explosion tests have revealed that the deflagration rate lies between 0.35 and 5.0 mm s^{-1} [5]. Reactions of tetraethylgermane with *tert*-butyl, benzoyl peroxides and TBPB are discussed by Swern [6]. Due to hazardous consequences of decomposition of TBPB and its extensive use in the industry, we have made efforts to understand the runaway reaction phenomena by evaluating the kinetic parameters.

Safety parameters must be taken into account for evaluating the degree of hazard based on the kinetic parameters [7, 8], such as exothermic onset temperature (T_0), activation energy (E_a), frequency factor (A), etc. The decomposition of TBPB produces a strong exothermic peak belonging to an n^{th} order reaction. This study has proposed a method to generalize the concept of runaway reaction regarding TBPB by employing DSC as a quantitative measure of reactivity, allowing one to take proper account of kinetic complexity. On the basis of the curve-fitting method and experimental results, we found that a quickly appearing exothermic peak indicated its dangerous features. Therefore, to prevent accidents from occurring in plants, thermal hazard information should be provided to the plant personnel in order to reduce the degree of hazard, and also to the process engineers to design a safe control system, such as the cooling system, alarm system, interlock system, etc. [9].

Utility of safety parameters

During storage or transport of chemicals, the system must emphasize safety. For this to happen, the safety

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parameters must be precisely evaluated. Then one could decide whether a cooling system should be established or not. These chemicals were stored in a container that could be exposed to a thermal source, self-decomposition, or unexpected mixing with contaminants to prompt runaway reactions, such as fire or explosion. In the absence of proper controls, a serious accident could thus be triggered during the upset situations.

Important safety parameters, namely, TMR, T_{NR}, SADT and TCL could be employed to evaluate the degree of hazard to reduce an unacceptable contingency. These parameters are determined according to the methodologies of Townsend [10] and Fisher [11]. The whole results obtained were suitable for the study of the phenomenon of runaway reactions involving pure substances or mixtures. These safety parameters are described below.

Time to maximum rate (TMR)

TBPB has a high seriously exothermic peak during the decomposition reaction; therefore TMR is an adequate indicator to study the variation between time and temperature in four different heating rates (1, 2, 4 and 10°C min^{-1}).

The calculation method by Townsend and Tou is shown in Eqs (1) and (2):

$$\text{TMR} = \frac{RT^2}{AE_a \Delta T_{\text{ad}}} \text{e}^{-\text{E}_\text{a}/\text{RT}} \tag{1}$$

$$\Delta T_{\text{ad}} = \frac{Q}{C_\text{p}} \tag{2}$$

Kinetic parameters via experimental results belong to n^{th} order reaction and only have one exothermic peak for appropriating this method. In an earlier paper, Andreozzi *et al.*, used the TMR for evaluating the runaway hazards of different molar ratios of *tert*-butyl hydroperoxide (TBHP)/*p*-toluenesulphonic acid (R) [12]. Chang *et al.* [13] and Tseng *et al.* [14] have employed curve-fitting to calculate the TMR for comparing the potential runaway hazards of pure MEKPO and mixing contaminants.

Temperature of no return (T_{NR})

To adopt a suitable and deliverable emergency response during an upset situation, T_{NR} is an important index in common use, which could be calculated via the relationship between the rates of heat generation and heat removal [15]. T_{NR} increases with the temperature of runaway reaction. It could be applied to design a cooling system and to tell fire fighters about the remaining time to conduct a rescue operation [16]. T_{NR} could be computed by Eqs (3) and (4) given below:

$$(T_{\text{NR}} + 273.15)^2 = \frac{mE_\text{a} \Delta Hk}{RU(1.8)a} \tag{3}$$

$$= \frac{mE_\text{a} \Delta HA \text{e}^{-\text{E}_\text{a}/\text{R}(\text{T}_\text{NR}+273.15)}}{RU(1.8)a} \tag{4}$$

Self-accelerating decomposition temperature (SADT)

SADT is extensively employed to estimate the decomposition reaction of thermally unstable materials, such as the O–O bond of organic peroxide, which 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 a period of seven days or less [11]. A self-reactive substance must be subject to temperature control, inhibitor, improving the materials and volume for a container during transportation if its SADT is less than or equal to 50°C [17]. In practice, Eq. (5) could be used to calculate this safety parameter:

$$\text{SADT} = T_{\text{NR}} - \frac{R(T_{\text{NR}} + 273.15)^2}{E_\text{a}} \tag{5}$$

Time to conversion limit (TCL)

Assessment of thermal stability (TS) of a substance (stability analysis) lies in evaluating the time when the conversion of a reaction reaches some predefined value – the conversion limit (CL), at a constant set temperature. This time is called TCL. When the TS mode is selected, the forced temperature mode is set in spite of the earlier settings made in the conditions. The constant environment temperature is set equal to the current temperature point.

TS is characterized by the time (TCL) necessary to reach a certain level of conversion at a certain constant temperature. Therefore, for long-term storage, it can be chosen as the maximum permissible time during which the conversion of the product does not have any significant impact on the product quality. If TBPB is used in a synthesis process, TCL indicates the time to an acceptable degree of this reactant consumption due to decomposition, and it does not affect the mass balance of the process [18, 19].

Table 1 Calculated kinetic and safety parameters derived from the kinetic scanning experiments of TBPB 98 mass% by DSC

Sample mass/mg	Scanning rate, r/°C min^{-1}	T_0/°C	T_{max}/°C	E_a/kJ mol^{-1}	ΔH/J g^{-1}	A/s^{-1}	T_{NR}/°C	SADT/°C
2.8	1	86 89*	137	66 106*	1150.1 1133.4*	12.4 24.7*	41	29
2.3	2	88 97*	144	70 110*	1148.8 1126.1*	14.1 26.1*	39	28
2.2	4	98 99*	151	77 108*	1344.4 1332.7*	16.2 25.5*	40	30
2.5	10	100 101*	164	87 107*	1167.1 1162.3*	19.5 25.3*	49	39

*Calculated values based on curve–fitting method, the rest of the data are calculated values based on experimental data, **based on 55 gallon drum with 98 mass% of TBPB

Experimental

Preparation of TBPB 98 mass%

TBPB 98 mass% was purchased directly from Akzo Nobel, and stored in a refrigerator at 4°C. All the experimental results were determined by DSC. Curve-fitting method was, in turn, employed to model the kinetic parameters, as mentioned above.

DSC

Temperature-programmed screening experiments were performed with DSC [20]. The measuring cell is the essential part of the experiment; it was used for carrying out the experiments for withstanding relatively high pressure to approximately 100 bar (DSC 821^e). The scanning rate chosen for the temperature-programmed ramp was 1, 2, 4 and 10°C min^{-1}. The range of temperature rise was chosen from 30 to 300°C for TBPB 98 mass%. DSC was employed to detect the temperature change between the sample and reference for determining the heat flow, time and temperature.

Four types of scanning rates were carried out in the test cells by using DSC [20] for obtaining the experimental data. TBPB (98 mass%, 2–3 mg) was placed in a test cell for detecting the heat flow (mw), time and temperature. At the beginning of an experiment, DSC had to be stabilized for 30 min and then the experiments were started with a scanning rate of 1, 2, 4 and 10°C min^{-1}, respectively. For enhancing the degree of accuracy the samples were weighed again after the experiments were finished, in order to ensure that material had not leaked during the experiment [20].

Results and discussion

Experimental analyses for DSC tests

We carried out experiments of TBPB 98 mass% (about 2.2–2.8 mg samples) with four heating rates (1, 2, 4, 10°C min^{-1}) using DSC, which generated one strongly exothermic peak under runaway conditions due to the sensitive structure of the O–O single bond as depicted in Figs 1 and 2. Our results in Table 1 show for TBPB 98 mass % the kinetic parameters obtained experimentally as well as by curve-fitting for different heating rates. Both methods exhibited similar results, especially for ΔH (J g^{-1}) and T_0 (°C), about 1100–1300 J g^{-1} and 86–100°C, respectively.

The above illustrates that due to a sensitive peroxide structure (O–O), TBPB is more dangerous during storage or transportation than some of the other hazardous materials extensively employed in the chemical industry, such as methyl ethyl ketone peroxide (MEKPO) 31 mass% (951.6 J g^{-1}) [21] and dicumyl peroxide (DCPO) 99.3 mass% (762 J g^{-1}) [22], and so on. Due to its very low T_0, TBPB should be treated with caution during the period of use, storage and transportation in related plants.

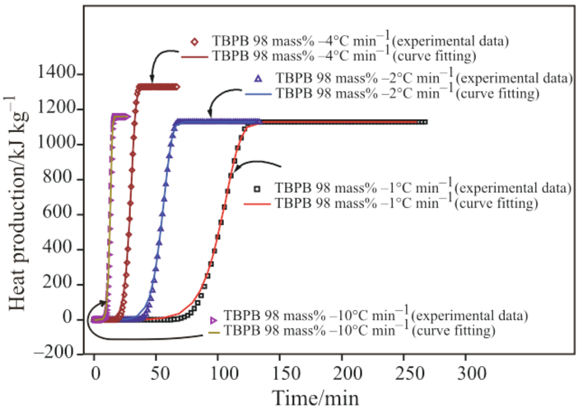

Fig. 1 Heat production *vs.* time for TBPB 98 mass% by DSC for four types of heating rate with kinetics-based curve-fitting results

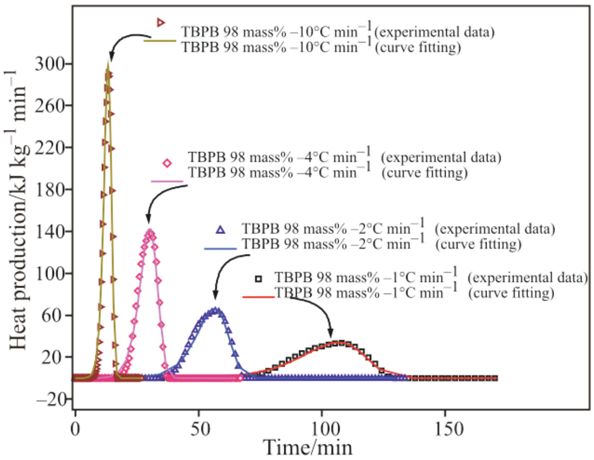

Fig. 2 Heat production rate *vs.* time for TBPB 98 mass% by DSC for four types of heating rate with kinetics-based curve-fitting results

Curve-fitting analyses based upon experimental data

Curve-fitting reflected similar data as the experimental data. We believe that these groups of kinetic parameters can be established by selecting an appropriate kinetic model to identify its basic characteristics as given in Eqs (6) to (10):

The model for decomposition of TBPB 98 mass% has only one stage:

$$A \xrightarrow{\alpha, r} B \tag{6}$$

The following mathematical model describes an n^{th} order reaction:

$$r = \frac{d\alpha}{dt} = k_1(T)f \tag{7}$$

$$f = 1 - \alpha)^n \tag{8}$$

$$\frac{d\alpha}{dt} = Ae^{-E_a/RT}(1-\alpha)^n \quad n^{th}\text{ order reaction} \tag{9}$$

$$\frac{dQ}{dt} = Q_i^\infty r_i \tag{10}$$

where α is the degree of conversion; r and Q_i^∞ denote reaction rate and heat effect of the stage, respectively; dQ/dt is the overall heat generating rate; f denotes kinetic function for the stage that depends on the extent of conversion; $k_i(T)$ obeys the Arrhenius temperature dependency of the rate constant: $k_i(T)$= $A\exp(-E_a/RT)$; A and E_a represent, respectively, the frequency factor and the activation energy of the stage; R is the gas constant (R=8.314 J mol^{-1} K^{-1}).

After the kinetic parameters had been evaluated by curve-fitting in the above model, all the data indicated that the decomposition of TBPB 98 mass% was an n^{th} order reaction, because in the temperature range of about 80–300°C, its activation energy (E_a) was about 106, 110, 108 and 107 kJ mol^{-1}, respectively. All the values of E_a were less than 220 kJ mol–1 [23]. To precisely acquire the kinetic parameters, such as E_a, frequency factor (A), reaction order (n), and heat of reaction (ΔH), having a good baseline to integrate the exothermic peak for each of the thermal curves was very important. For this we performed controlled experiments by employing four heating rates (1, 2, 4 and 10°C min^{-1}), enhancing the degree of accuracy [24].

Safety parameters analyses

Safety parameters have been calculated in this study. Using the above-mentioned model, TMR was between 583–833 h when the temperature was 20°C, while increasing the temperature to 100°C, TMR was reduced to a dangerously low value of 4–5 min in the four heating rate conditions used, as shown in Fig. 4 and Table 2. Therefore, for preventing an accident from occurring, the temperature control system should be initiated every time and the temperature maintained less than 20°C for better control. Another index was TCL, which demonstrated the stability of a product under storage or transportation conditions. If the temperature was about 30°C, TBPB 98 mass% had the highest level of stability (Fig. 3). If the temperature rises to 40°C or above, a thermal accident can occur in the next stage. This phenomenon on runaway reactions was further supported by the results of curve-fitting with various changes of temperature. This can be adopted for preparing a suitable emergency response.

TBPB possesses a sensitive structure and a strong exothermic group. For this reason, the SADT was very low, actually even less than 30°C for the heating rates of 1 and 2°C min^{-1} as listed in Table 1. In contrast, T_{NR} was about 40–50°C During this temperature range, the heat generating rate would be higher than the heat removal rate, leading to a no

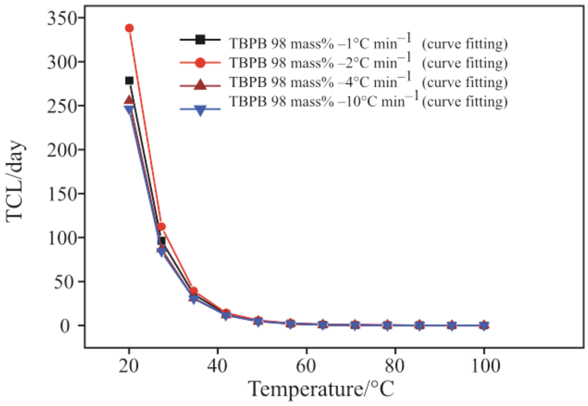

Fig. 3 TCL *vs.* temperature (kinetics-based curve-fitting) for TBPB 98 mass% by DSC for four types of heating rate

Table 2 TMR for TBPB 98 mass% with four heating rates calculated on the basis of kinetics evaluated

1°C min^{-1}		2°C min^{-1}		4°C min^{-1}		10°C min^{-1}	
Temp./°C	Time/min	Temp./°C	Time/min	Temp./°C	Time/min	Temp./°C	Time/min
20	43171	20	53814	20	34070	20	37572
27	15712	27	18839	27	12185	27	13528
34	6005	34	6939	34	4580	34	5118
41	2402	41	2680	41	1803	41	2028
49	1003	49	1081	49	741	49	838
56	435	56	454	56	317	56	361
63	196	63	198	63	141	63	161
70	91	70	90	70	65	70	74
78	44	78	42	78	30	78	35
85	21	85	20	85	15	85	17
92	11	92	10	92	7	92	8
100	5	100	5	100	4	100	4

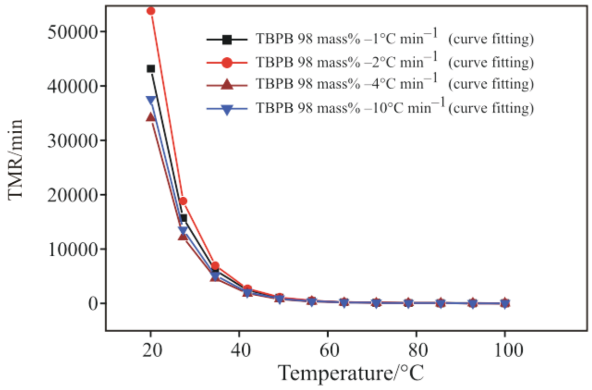

Fig. 4 TMR *vs.* temperature (kinetics-based curve-fitting) for TBPB 98 mass% by DSC for four types of heating rate

return situation and resulting in an explosion or fire. Results from our systematic studies of TBPB 98 mass% clearly indicate that each of the conditions has an influence on the runaway reactions.

Conclusions

The hazardous characteristics–runaway reaction relationship was explored for TBPB 98 mass% with four heating rates by using experimental and curve-fitting methods. We found that TBPB 98 mass% was unstable due to its thermally reactive structure and hence cannot be used without sound safety systems. Further, TBPB decomposition fits an n^{th} order reaction. The degree of hazard increases significantly if the temperature is not well controlled. TBPB was prone to behave exothermically at temperatures as low as 100°C in the test cells, and the heat of reaction (ΔH) may be an important parameter in classification of safety degree. Therefore, for prevention of TBPB accidents, the safety information discussed in this paper must be brought to the notice of all the relevant plants.

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